Synthetic Studies of Dehydroannulenes.

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CONTENTS

ABSTRACT

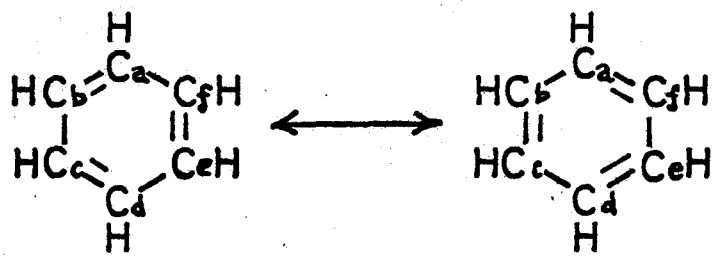
Synthesis of aromatic tetra-t-butyltetradehydro[22]annulene (50) by the dehydroxylative aromatization of the polyenyne-glycol was described. The identity of the diacetylene and hexapentaene units incorporated in this dehydroannulene system has been proved. Tetrasubstituted-didehydro[18]- (71 and 74), didehydro[22]- (83), didehydro[26]- (84) and didehydro[30]annulene (91) have been prepared by reductive dehydroxylation of cyclic glycols obtained by the cyclic dimerization of polyene-ketones under the conditions of the Favorskii reaction. The aromaticity and conformational stability of these didehydroannulenes have been shown by their n.m.r. spectra. It is stated that a diatropic thia[13]annulene derivative (120) was synthesized.

Substituted-2,8-decadien-4,6-diyndials (121, 122 and 123) were synthesized by the oxidative coupling of corresponding substituted pentenynals (127 and 41b) or acetals (44a and 44b). It was found that these dialdehydes give readily dihydrofuranylidene derivatives (140, 141, 129 and 131) by the addition of methanol followed by intramolecular cyclization. The thermal reaction of the dialdehydes afforded difuranylacetylene derivatives (139, 128 and 136).

Dimerization by Favorskii reaction of ethynylnaphthalene-ketone (176) yielded the cyclic glycol (177). The glycol was converted into dinaphtho-di-t-butyldidehydro[14]annulene (178) by dehydroxylative aromatization at -20~-30 °C. The formation of the annulene could be confirmed on the basis of electronic and n.m.r. spectroscopy. The annulene showed an apparent diatropic ring current. This is a first example of aromatic non-bridged neutral annulene annelated with benzenoid nuclei.

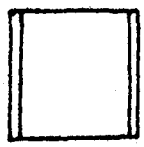
I. INTRODUCTION

Through the thermal decomposition of whale oil, benzene was first obtained in 1825 by Faraday, and recognized that the molecular formula is C_6H_6. Thereafter there had been much argument about the structure of benzene. In 1865 Kekulé published a paper entitled Sur la constitution des substances aromatiques[1] in which he suggested that the six atoms of carbon form a closed chain. In another paper[2] published in the same year he used a regular hexagon formula in which the six carbon atoms were labelled by the letters a-f. The familiar hexagon formula with alternate single and double bonds was first used in a paper published in 1869[3].



(1) (1')

Benzene is considered to be an "aromatic" compound because its cyclic conjugation leads to great stability. "Aromaticity" in this sense of word thus means special stability due to cyclic conjugation. As early as 1925, Armit and Robinson[4] suggested an idea of aromatic sextet since the fact that all of the aromatic systems contain six π-electrons. This idea would also explain why cyclobutadiene (2) and cyclooctatetraene (3) are not aromatic. Cyclobutadiene (2)



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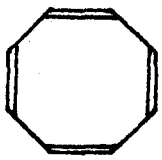
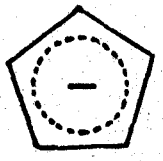


(3)

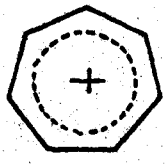
and cyclooctatetraene (3) are not aromatic. (2) and (3) contain four and eight π-electrons respectively, so according to the sextet postulation it would not be expected to be aromatic.

The requirement of the sextet of electrons for aromaticity cannot be explained by valence bond theory. However, several decades ago, Hückel formulated his famous (4n + 2) rule[5], which states that monocyclic coplanar systems of trigonally hybridised atoms which contain (4n + 2) π-electrons will possess relative electronic stability. His molecular orbital treatment yielded the conclusion that, if a molecule has occupied antibonding or nonbonding π-orbitals, its stability should considerably reduced; on the other hand, if the electrons fill all of the bonding orbitals, stability should be gained. As has been pointed out by several authors, the great stability shown by benzene (1), cyclopentadienide anion (4) and cycloheptatrienium (tropylium) cation (5) are consistent with Hückel's prediction being n=1 (six π-electron system). The physical evidences such as electron diffraction[6] and X-ray diffraction[7] indicate that benzene has a regular planar hexagonal structure of side 1.39 Å.



Cyclopentadienide anion

(4)

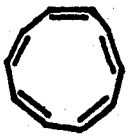


Cycloheptatrienium cation

(5)

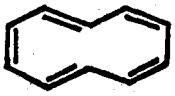
II. TEN π-ELECTRON SYSTEMS

Considering the case where n=2, i.e., ten π electron systems, it seems that one obvious possibility would be cyclodecapentaenes (6, 7, and 8). Recently two cyclodecapentaenes (6, 7) have been synthesized by Masamune[8]. His challenging experiments showed that π electrons in the compound (6)(a ten-membered ring with five cis double bonds) do not delocalize to form an aromatic system.



(6)

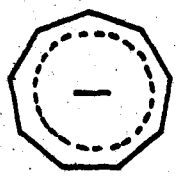
(7)



(8)

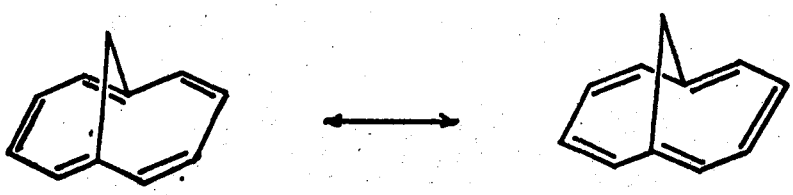
The internal angles in (6) would be 144° compared with the sp^2 optimal angle of 120°; this involves too much strain to be planar. If one trans double bond is involved the angle strain disappears, but at the expense of severe hindrance at hydrogen atom inside of the ring. Therefore (7) is incapable of taking a planar conformation, and not aromatic. The third cyclodecapentaene (8) having two trans double bonds would seem to be most unstable, and the system has not yet (1974) been synthesized. On the other hand, two anionic ten π electron compounds are known (cyclooctatetraene dianion (9)[9] and cyclononatetraenyl anion (10)[10]). Both compounds are apparently aromatic.

(9)

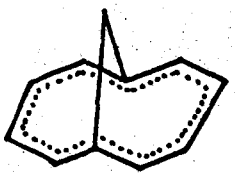


(10)

Two "internal" hydrogen atoms in (8) would prevent the molecule from assuming a planar configuration. If these two hydrogen atoms are replaced by a methano- or hetero-bridge, very unique systems result. Several such compounds have been synthesized by Vogel. While these are not monocyclic, the π electrons are restricted to the periphery of the system, and the compounds are aromatic by spectroscopic and chemical criteria. 1,6-Methanocyclodecapentaene (11), for example, has been first prepared and investigated[11]. This compound was found to be stable and showed the presence of an induced diamagnetic ring current. Aromatic substitution reactions, e.g., bromination, acetylation and nitration, have been found to give mono- and disubstituted products. The n.m.r. spectrum shows the resonance of the ring protons at very low field and the strong shielding of the CH_2 protons, which can be considered as evidence for the presence of a ring current.



(11a) (11b)



(11c)

III. THE ANNULENES

It was pointed out very early by Mislow[12] that all the cyclic polyenes from $C_{10}H_{10}$ to $C_{88}H_{88}$ presumably cannot be planar in view of the steric interactions of the internal hydrogen atoms in the planar molecules as is shown in the rough scale drawings of Fig. 1. Finally the cyclic polyene with 30-membered ring (17) can adopt a planar conformation and was expected to be aromatic.

Many advances in recent acetylenic chemistry haveenabled the synthesis of macrocyclic conjugated polyenes and polyenynes (i.e., compounds with both double and triple bonds). Almost all of the work on the synthesis of higher cyclic polyenes ($C_{14}H_{14}$[13], $C_{16}H_{16}$[14], $C_{18}H_{18}$[15], $C_{20}H_{20}$[16], $C_{22}H_{22}$[17], $C_{24}H_{24}$[18] and $C_{30}H_{30}$[19]) has been

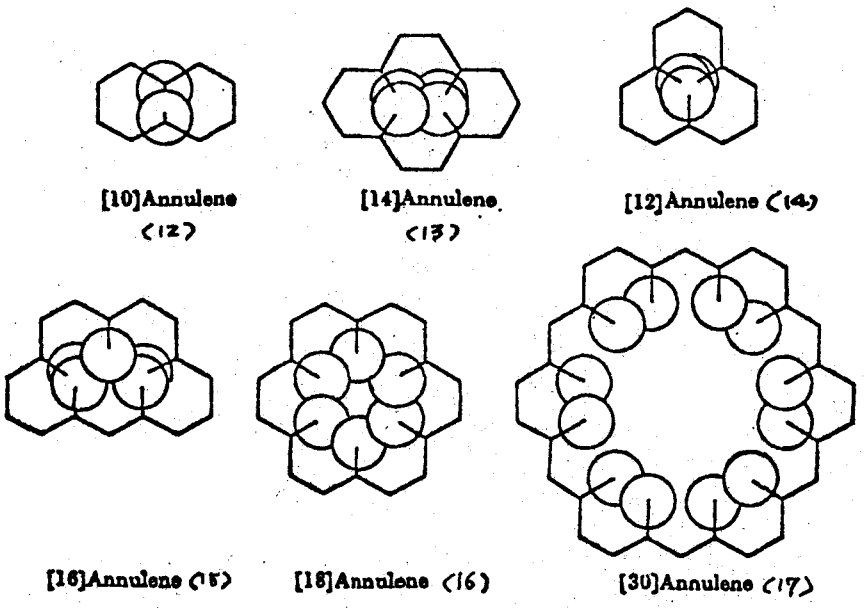
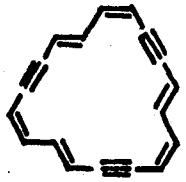


Fig. 1. Scale drawing of some annulenes (bond length: R_{CC} = 1.40 Å all equal; R_{CH} = 1.10 Å; all valence angles 120°; hydrogen radii = 1.00 Å)[12].

done by Sondheimer and his co-workers. These cyclic polyenes are called annulenes according to the proposal by Sondheimer[20]. The annulenes are the completely conjugated monocyclic polyenes, the ring size being indicated by a number in brackets. For instance, benzene is [6]annulene, and (16) is [18]annulene. The completely conjugated monocyclic polyenynes are similarly called dehydroannulenes. (18)[21] and (19)[22] are called tridehydro-[18]annulene and hexadehydro[18]annulene, respectively*.



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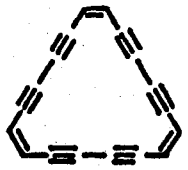

(19)

As shown in Fig. 1, molecular models and scale drawings indicate that the van der Waals radii of the six internal hydrogen atoms overlap each other but that this overlap is not so extreme as to exclude a reasonably plannar carbon skeleton. [18]Annulene (16) synthesized has been found to display relatively little

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* In the trivial nomenclature originally proposed by Sondheimer, (18) is named tridehydro[18]annulene, since it contains three acetylenic bonds. In another trivial nomenclature system, occasionally used subsequently by other workers[23], (18) is named hexadehydro[18]annulene, since it contains six fewer protons than [18]annulene. We use original nomenclature by Sondheimer to avoid confusion in the literature.

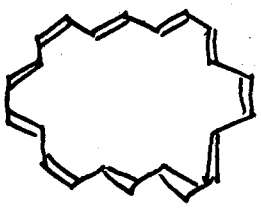
aromatic character in the classical sence. On the other hand, the physical evidence clearly indicates that [18]annulene (16) is aromatic. X-ray analysis has established the fact that [18]annulene (16) possesses a center of symmetry, and an essentially planar molecule[24].

The n.m.r. spectrum shows two broad bands at room temperature, one at very low field (τ 1.1) due to the outer protons and one at very high field (τ 11.8) due to the six internal protons[24]. The areas under the two bands were found to be in the ratio 2 : 1. These peaks become progressively sharper and exhibit fine structure as the solution is cooled. Heating a solution of [18]annulene causes the bands at τ 1.1 and τ 11.8 to broaden, and at 40°C these bands can no longer be recognized (e.g. coalescence). At 110°C the spectrum consists of a relatively sharp singlet at τ 4.55. It is thought that the protons change position at such a rate that an average value results for the bond locations. The mobility of [18]annulene is caused by overlapping of its internal hydrogen atoms. Similar behavior was found at the n.m.r. spectra of [14]-annulene (13) and [22]annulene (20). Recently Oth showed that in general the annulene indicates conformational and configurational mobilities if the internal hydrogen atoms overlap each other to some extent[26].

Insertion of acetylenic linkage in an annulene system increases the conformational stability of the resulting dehydroannulene system owing to the linear feature of acetylenic bond. This situation is reflected in the n.m.r. spectrum of dehydroannulenes, ie., the coalescence temperature of n.m.r. spectrum of a dehydro annulene has been found to be much higher than that of corresponding

annulene itself[27]. Consequently, dehydroannulenes may be regarded as suitable compounds for studies of aromaticity of macrocyclic conjugated system. However, contribution of nondelocalized alternate bond structure should increase in dehydroannulene as compared with that in annulene itself due to the perturbation of acetylenic linkage. The fact that tridehydro[26]annulene (21) shows no diamagnetic ring current[28], whereas monodehydro[26]annulene (22) is found to be diatropic[29], indicates the effect of the perturbation of acetylenic linkages.

We have been interested in a dehydroannulene system which contains cumulenic and acetylenic linkages in the cyclic systems. It can overcome the disadvantage of dehydroannulene (the increase in contribution of nondelocalized alternate bond structure), and possesses the conformational stability. We will discuss it at the next chapters.



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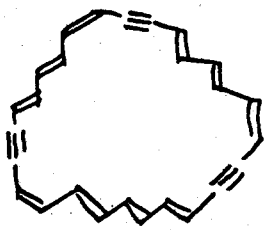

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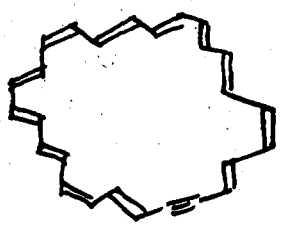
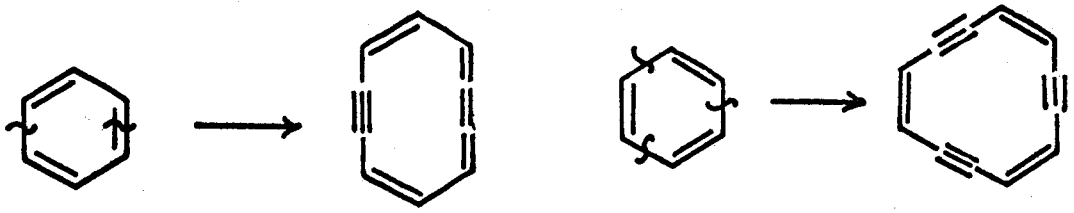


(22)

IV. DEHYDROANNULENES CONTAINING ACETYLENIC AND CUMULENIC LINKAGES IN THE CYCLIC SYSTEM.

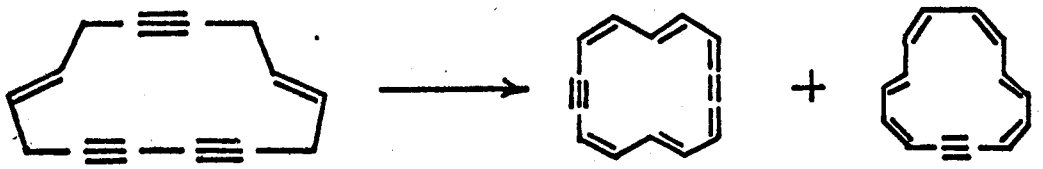
Ignoring the Hückel's $(4n+2)$ π electron rule[5], Sworskij[30] has suggested that the compound (23) and (24) which may arise inserting two or three acetylenic linkages into benzene nucleus should possess a great stability and aromaticity. However, according to the Hückel's rule tridehydro [12]annulene (24) is nonaromatic (or antiaromatic[31]) and in fact, recent synthesis of (24) has shown its nonaromaticity[32].



(23) (24)

Scheme I

Sondheimer obtained didehydro[14]annulene (26) as by-product through base treatment of the unconjugated 14-membered ring precursor shown[33][34] in scheme II.



(26)

poor yield major product

Scheme II

1,8-Didehydro[14]annulene (26) has been proved to be highly aromatic on the basis of n.m.r. spectroscopy[34] and electrophilic substitution reactions[35]. The n.m.r. spectrum and X-ray crystal structure analysis of the didehydro[14]annulene (26)[36] have shown the symmetrical structure of the molecule indicating the dehydroannulene (26) is the resonance hybrid of the two Kekulé-type structures (26a and 26b). In other words, the structure can be expressed more adequately by the symmetrical formula (26c). The aromaticity found in 1,8-didehydro[14]annulene (26) revealed that the sp-hybridized carbon atoms of cumulenic linkage can participate in the formation of aromatic system equivalent to the acetylenic carbon atoms, and the symmetrical structure of (26) seems to render a particuler situation to the dehydroannulene (26) different from usual dehydroannulene in which any equivalent Kekulé-type resonance structure cannot be drawn.

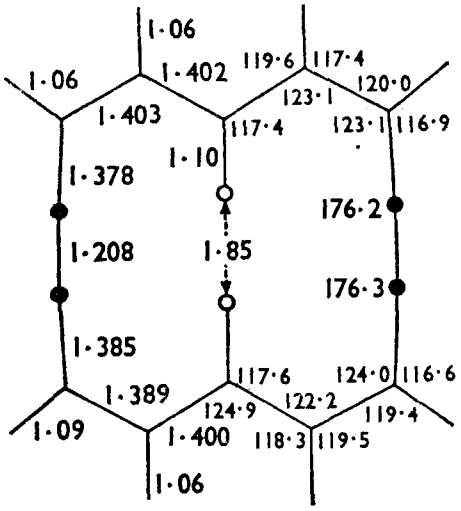
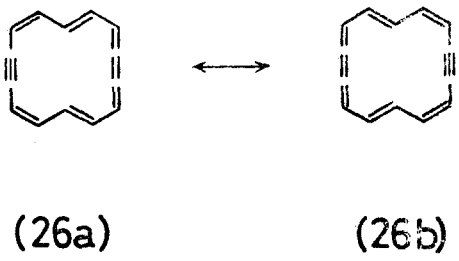
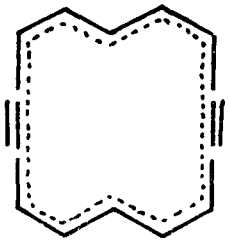


Fig. 1

X-ray structure of 1,8-bisdehydro[14]annulene

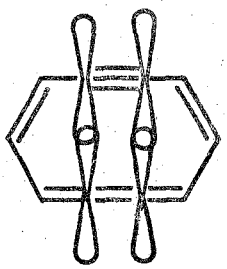


(26a) (26b)



(26c)

We have attempted a synthesis of dehydroannulenes (27[37] and 28[38]) proposed by Sworskii[30]. However, all atempts to prepare 1,6-didehydro[10]annulene (27)[37] and 1,5,8,10-tetradehydro[14]annulene (28)[38] have been unsuccessful. This fact seems to be attributable to a π-π interaction of p-electrons in the orbitals coplanar with the moleculer plane[39]



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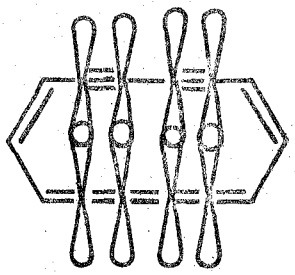
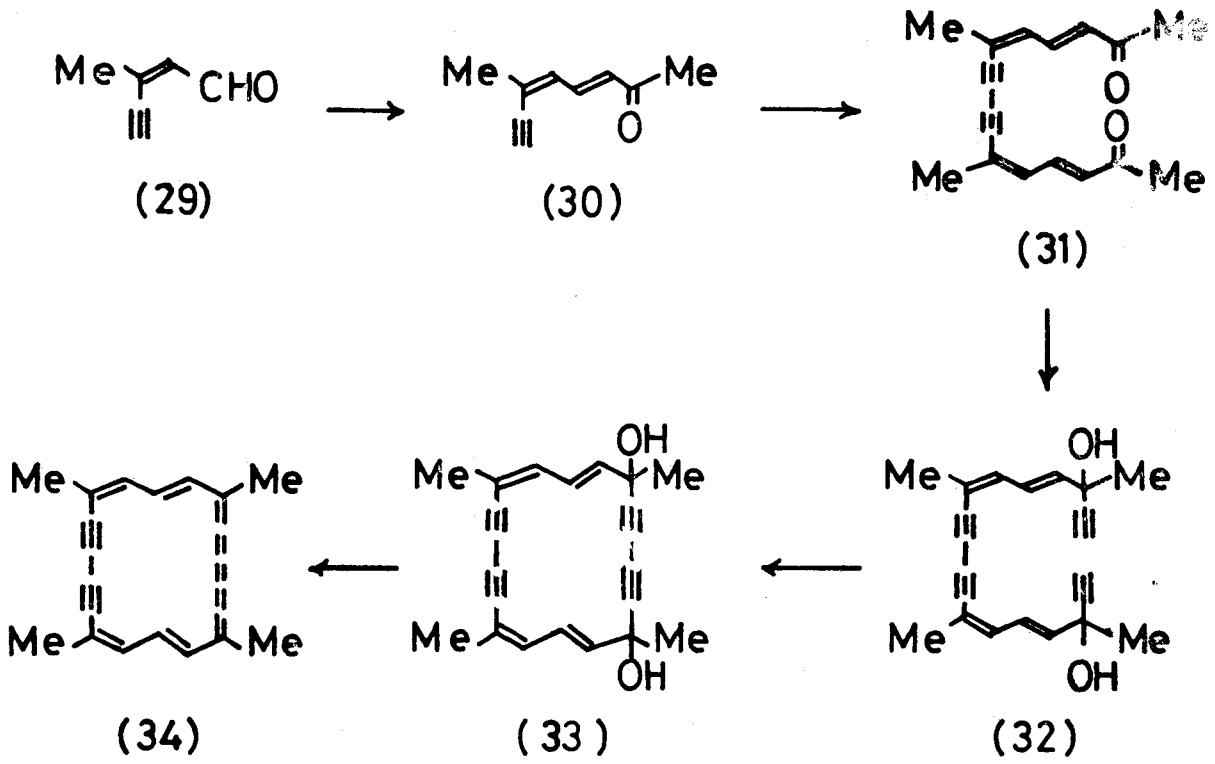


(28)

The problem of π-π interaction was overcome by inserting a double bond to tetradehydro[14]annulene (28). Tetramethyl-tetradehydro[18]annulene (34) was first synthesized by Ojima and Nakagawa through stepwise route shown in Scheme III[40].

5,9,14,18-Tetramethyl-1,3,10,12-tetradehydro[18]annulene (34) thus prepared was found to be rather unstable compound. Exposure of the crystals of (34) to air and a diffused day light at room temperature caused a complete decomposition within a few hours. Because of its low solubility, the n.m.r. spectrum was measured using time-average computer. The fact that the outer protons resonate at a low field and the inner protons exhibit signal at fairly high field clearly indicates the aromatic nature of the tetradehydro[18]annulene (34).



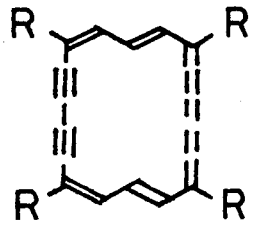
Scheme III

The framework of the tetradehydro[18]annulene ring is expected to hold a high conformational stability owing to the presence of a pair of straight rods of six carbon atoms in the cyclic system. In fact, the n.m.r. spectra of (34) exhibited essentially no tempra-ture dependency in the region of -60°C to +64°C. The measurement at higher than 64°C could not be performed owing to the decomposition of (34).

In this molecule, the outer protons appear at τ 0.34 ppm and the inner protons at τ 15.23 ppm, thus suggesting a much more important ring current than in (26). This has been shown to be due to a much more effective quenching of the π-diamagnetic anisotropy by bond-alternation in (26) than in (34)[41].

Tetramethyltetradehydro[18]annulene (34) is unexpectedly unstable and hardly soluble in all organic solvents. Therefore,

we tried to synthesize more stable and soluble tetradehydro[18]-annulene than (34). Tetraphenyltetradehydro[18]annulene (35) synthesized by Fukui and Nakagawa[42] found to be more stable, but unfortunately it is extremely insoluble in organic solvents. The synthesis of tetra-t-butyltetradehydro[18]annulene (36) performed by Tomita and Nakagawa[43] gave a solution of this problem, i.e., (36) was found to be very stable and more soluble than the other tetra-substituted-tetradehydro[18]annulenes making easier the measurement of n.m.r. spectra*. Thus we found t-butyl group is the best substituent, and we began to attempt the synthesis of the different ring-size dehydroannulenes.



(34), R = Me
(35), R = Ph
(36), R = t-Bu

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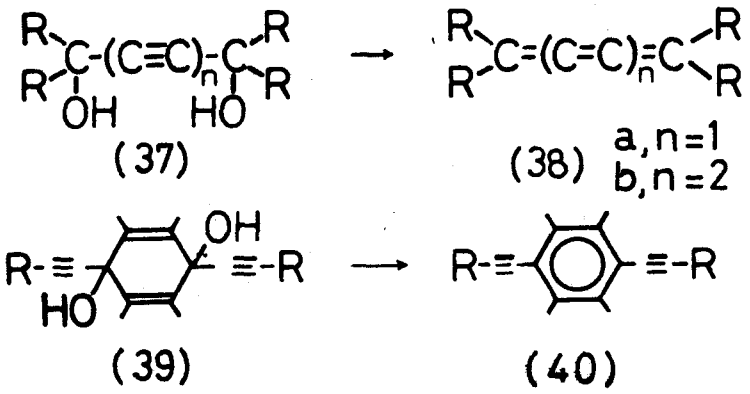
* In early investigation the measurement of n.m.r. spectra needs good solubility. But quite recently, owing to the advance in the technique of n.m.r. spectroscopy, it is possible to measure n.m.r. spectra of the compounds which have very poor solubility.

V. SYNTHETIC STUDIES OF TETRADEHYDROANNULENES

V-1. SYNTHESIS OF TETRA-t-BUTYL-TETRADEHYDRO[22]ANNULENE*[44].

In view of the conformational stability and the highly delocalized π-electron system of the above-mentioned 5,9,14,18-tetrasubstituted-1,3,10,12-tetradehydro[18]annulenes (34, 35 and 36), it was of interest to synthesize higher members of tetradehydroannulenes having analogous rigid molecular framework.

The synthesis of tetramethyltetradehydro[18]annulene (34) has been mentioned previous chapter (Scheme III). The last step of this synthesis was reductive dehydroxylation of 18-membered cyclic glycol (33). Reductive dehydroxylation of 2-butyn-1,4-diols (37a) or hexa-2,4-diyn-1,6-diols (37b) to form butatrienes (38a) or hexapentaenes (38b) is a well-known reaction[45].

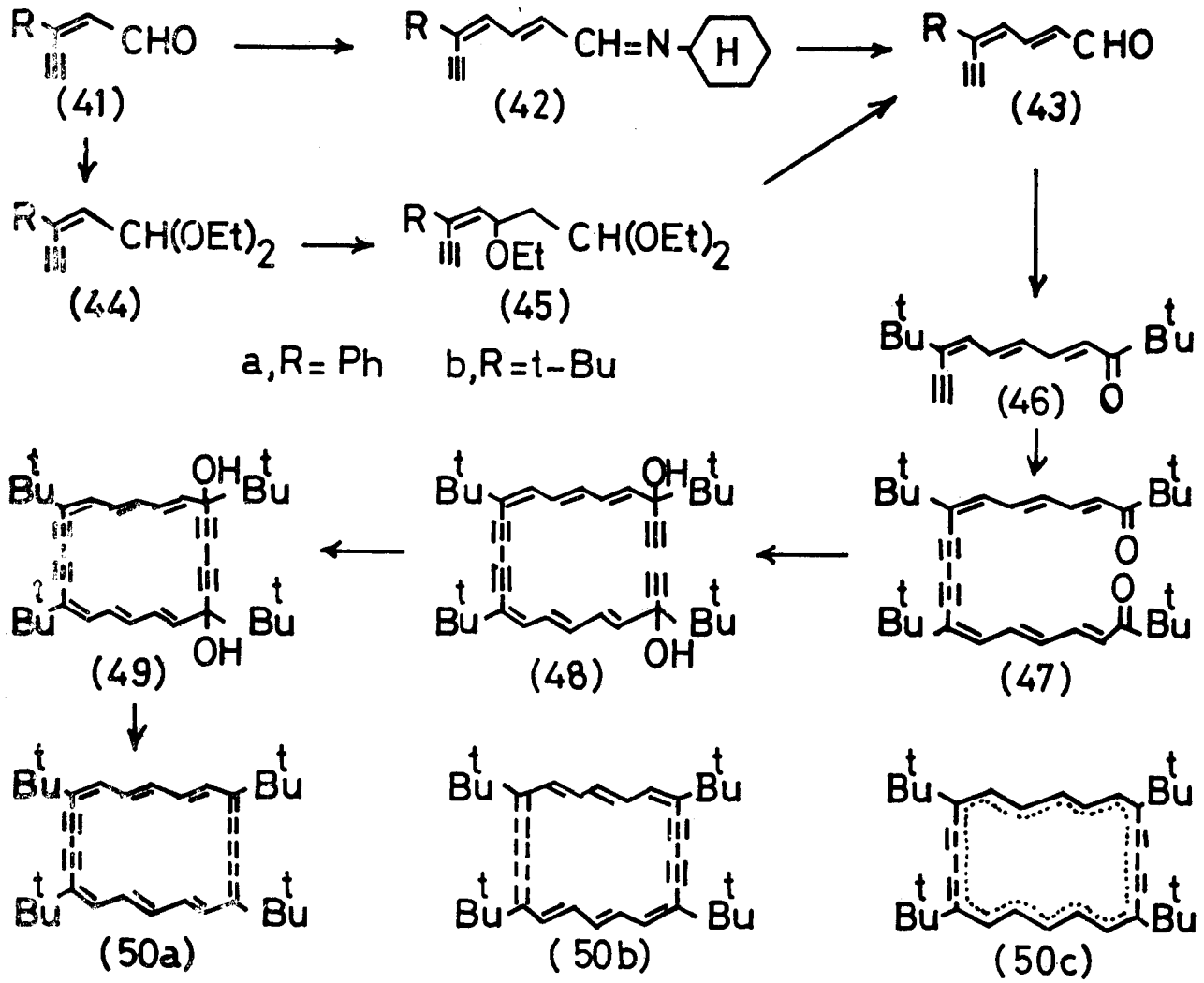


Scheme IV.

* These experiments were carried out in collabolation with Hideaki Miyazaki.

Also reductive aromatization of cyclohexadiendiols (39) to give disubstituted benzenoid compounds (40) has been reported in several cases[46].

We expected that the reductive aromatization of cyclic polyenyne-glycols should result in the formation of the dehydroannulenes containing acetylenic and cumulenic linkages shown in Scheme IV. The present investigation started from the synthesis of 22-membered cyclic glycol (49), a key intermediate. In general, cyclic glycols are good precursors for their stability and ease of purification compared with corresponding annulenes.



Scheme V

Firstly, we attempted the conversions of pentenynal (41) into heptadienynal (43). Phenylheptadienynal (43a) was prepared by different two routes. Phenylpentenynal (41a)[42] was treated with diethyl 2-(cyclohexylimino)ethylphosphonate carbanion[47] and the product (42a) was hydrolyzed to yield (43a) in a yield of 51%. Condensation of ethyl vinyl ether in the presence of borontrifluoride[48] with acetal (44a) derived from (41a) afforded ethoxy acetal (45) which gave (43a) of treatment with hydrochrolic acid in tetrahydrofuran (61% based on (44a)).

Similarly, t-butylpentenynal (41b) was converted into diethyl acetal (44b). The condensation of ethyl vinyl ether with (44b) in the presence of borontrifluoride[48] afforded ethoxyacetal (45b) in a 90% yield which gave dienyne-aldehyde (43b) in a yield of 70% on treatment with 3N hydrochrolic acid in dioxane.

According to the fact that tetradehydro[18]annulene is endowed with higher stability and solubility by the introduction of t-butyl groups, the synthesis of tetra-t-butyltetradehydro[22]annulene (50) has been carried out in the first place.

The aldol condensation of pinacolone with (43b) afforded trienyne-ketone (46) as pale yellow crystals which was oxidatively coupled with cupric acetate-pyridine-methanol to yield hexaendiyne-diketone (47) as yellow crystals in a yield of 83%. The reaction of the diketone (47) in tetrahydrofuran with lithium acetylide-ethylenediamine complex[49] gave diethynyl glycol (48) as colorless crystals in a 97% yield. Intramolecular cyclization of (48) was performed under a high dilution condition by means of cupric acetate-pyridine-methanol using ether as an entraining agent. Cyclic glycol (49) was obtained as yellow crystals, m.p. 240°C (decom.), mass

spectrum M^+ 536 (Calcd. for $C_{38}H_{48}O_2$=536.8) in a yield of 78%. This 22-memberd cyclic glycol (49) is stable and can be stored without decomposition at 0°C for a year.

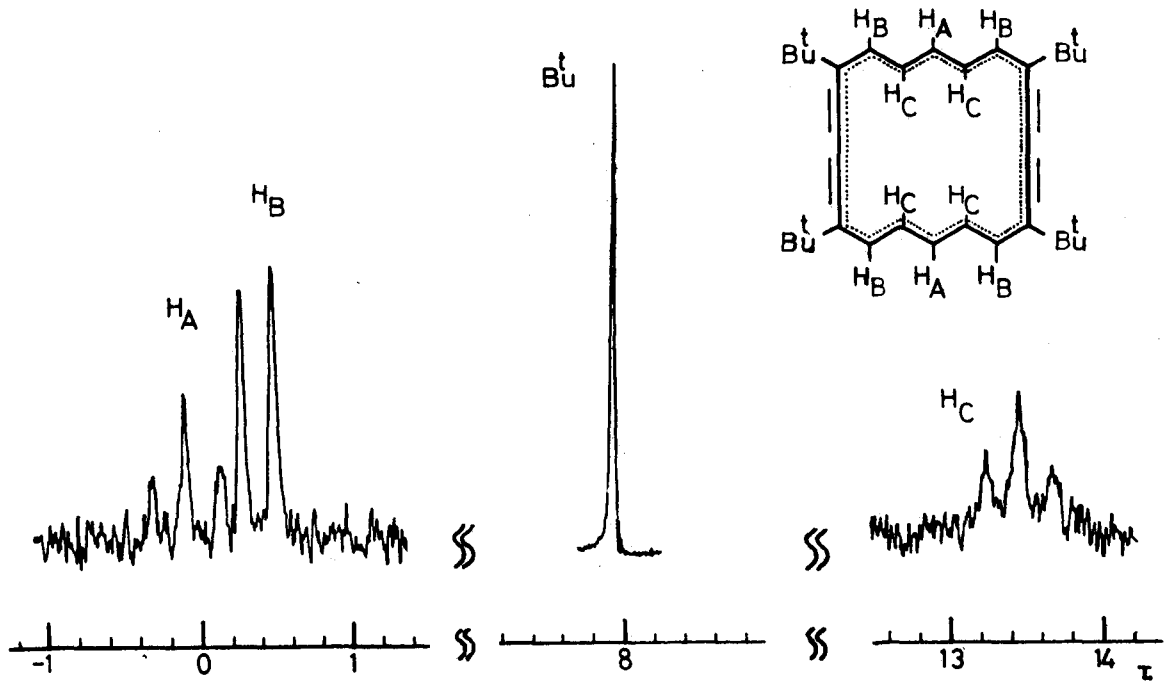
Dehydroxylative aromatization of cyclic glycol (49) was accomplished at very low temperature[50]. Finely powdered stannous chlolide dihydrate was added to a stirred solution of the cyclic glycol (49) in ether saturated with hydrogen chloride at -60°C under nitrogen atmosphere, resulting in a deep blue violet solution. Chromatography on alumina at -20°C gave tetra-t-butyltetradehydro-[22]annulene (50) as dark violet crystals in a 85% yield. The tetradehydro[22]annulene (50) was found to be rather unstable and decomposed quickly at ca. 100°C to form colorless solid on attempted melting point determination. (50) gave unsatisfactory elemental analysis owing to the unstable nature, but was satisfactorily stored at -78°C for several days. Hydrogenation of (50) in ethyl acetate-acetic acid (1:1) over platinum catalyst followed by chromatography on alumina afforded tetra-t-butylcyclodocosane (mass spectrum, M^+ 532, Calcd. for $C_{38}H_{76}$=532.9) as colorless crystals in a 86% yield. The n.m.r. spectra of (50) are summarized in Table 1, and the spectrum measured at 30°C is illustrated in Fig. 3. The fact that the outer protons (H^A and H^B) resonate at unusually low-field and the inner protons (H^C) exhibit signals at fairly high-field clearly demonstrates the existence of induced diamagnetic ring current, indicating the aromatic nature of the tetradehydro[22]-annulene (50), which can be expressed more suitably by the symmetrical formula (50c). Because the coalescence temperature of [22]-annulene (20) has been reported to be ca. 20°C[51], the fact that the n.m.r. spectra of the tetradehydro[22]annulene (50) measured

at 30 °C and -40 °C exhibit no essential change reflects the conformational stability of the 22-membered ring containing diacetylene and hexapentaene linkages. The coalescence could not be determined owing to the thermal decomposition of (50) at 30 °C.

Table 1. The 60 MHz N.m.r. Spectra of Tetra-t-butyl-tetradehydro-[22]annulene (50) in $CDCl_3$

Temp.	H^A	H^B	t-Bu	H^C
-40 °C	-0.43, t	0.09, d	7.88, s	13.71, t
	J=13 Hz	J=13 Hz		J=13 Hz
+30 °C	-0.16, t	0.33, d	7.93, s	13.44, t
	J=13 Hz	J=13 Hz		J=13 Hz

Fig. 3. The 60 MHz N.m.r. Spectra of (50) in $CDCl_3$ at 30 °C.



The electronic spectrum of (50) is illustrated in Fig. 4 together with that of tetra-t-butyltetradehydro[18]annulene (36).

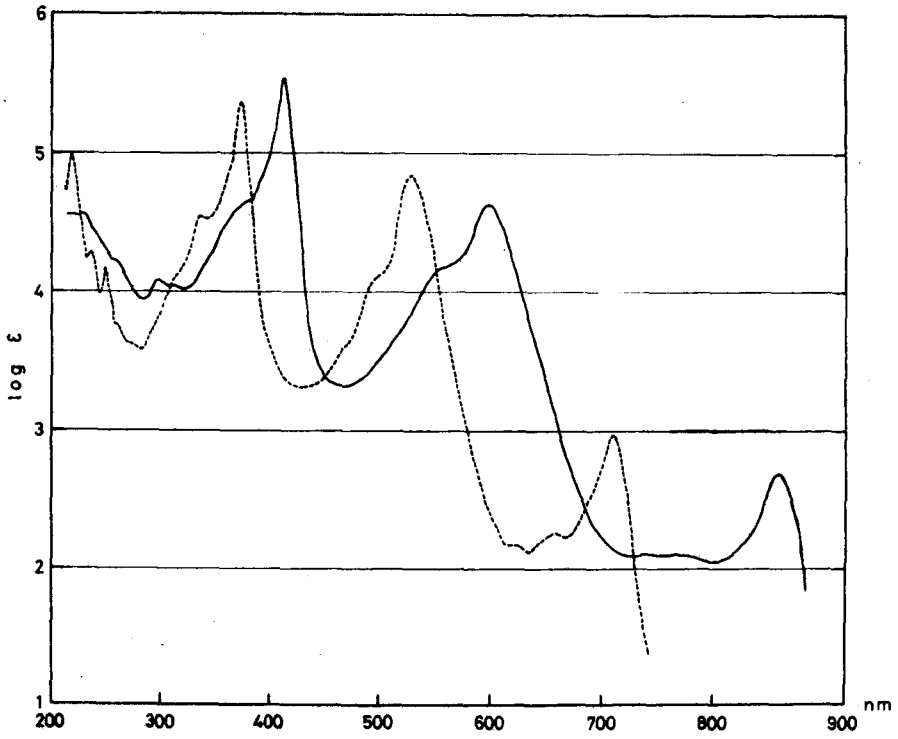


Fig. 4. Electronic Spectra of tetradehydroannulenes

------ Tetra-t-butyl-tetradehydro[18]annulene. (36)

——— Tetra-t-butyl-tetradehydro[22]annulene. (50)

The synthesis of 5,11,16,22-tetraphenyl-1,3,12,14-tetradehydro-[22]annulene (51) was carried out at the same time when (50) was synthesized. The annulene synthesized was very unstable as well as (50). Additionally, it was extremely insoluble in all organic solvents. Although tetraphenyl-tetradehydro[22]annulene was expected to be aromatic, n.m.r. spectrum could not measured because of its insolubility. Quite recently, n.m.r. spectrum was measured by means of Fourier-Transform n.m.r. Technique, and indicated a large induced diamagnetic ring current in the annulene[52].

V-2. SYNTHETIC STUDIES OF DISUBSTITUTED TETRADEHYDRO[18]ANNULENES*

Mention has already been made of the synthesis of 3,7,10,14-tetrasubstituted tetradehydroannulenes. Sondheimer reported that 1,8-didehydro[14]annulene was relatively stable and underwent electrophilic substitution reactions at 3,7,10 and 14-carbons neighboring acetylenic and cumulenic linkage. We have been interested in 3,7-disubstituted-1,3,8,10-tetradehydro[18]annulenes (55 and 60) in order to examine the properties and reactivities at 5,9,14,18-positions. Therefore, we first attempted the synthesis of 3,7-diphenyltetradehydro[18]annulene (55) shown in Scheme VI.

Oxidative coupling of phenylheptadienynal (43a) by Eglinton's method (cupric acetate-pyridine-methanol) yielded (51) in a high yield. Ethynylation of (51) with ethynyl-monogrignard bromide in tetrahydrofuran gave mono-adduct (52) but di-adduct (53) could

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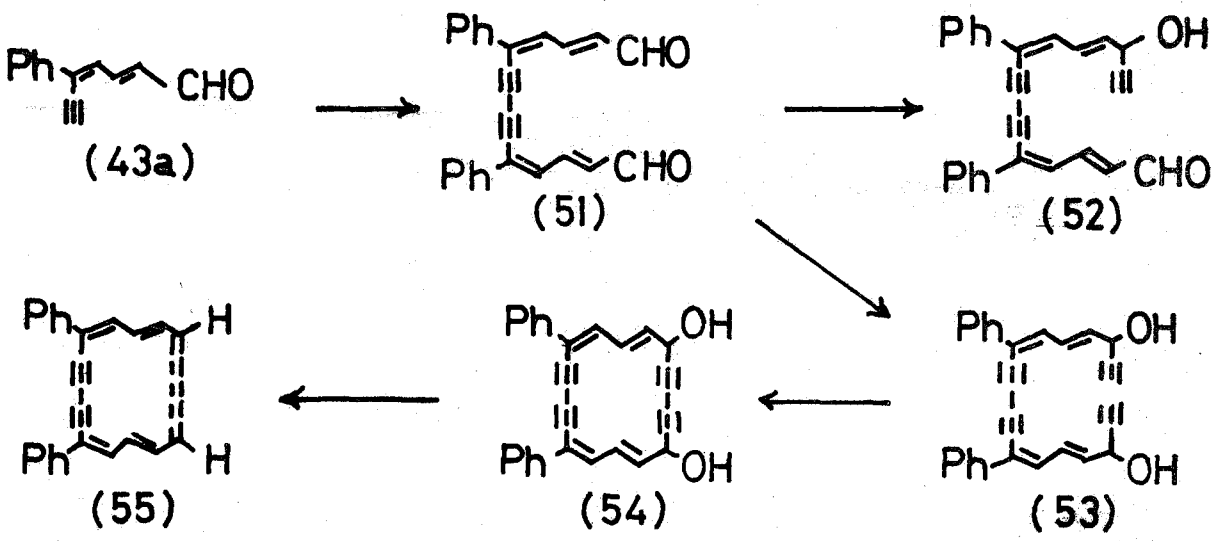
* These experiments were carried out in collaboration with Hideaki Miyazaki.

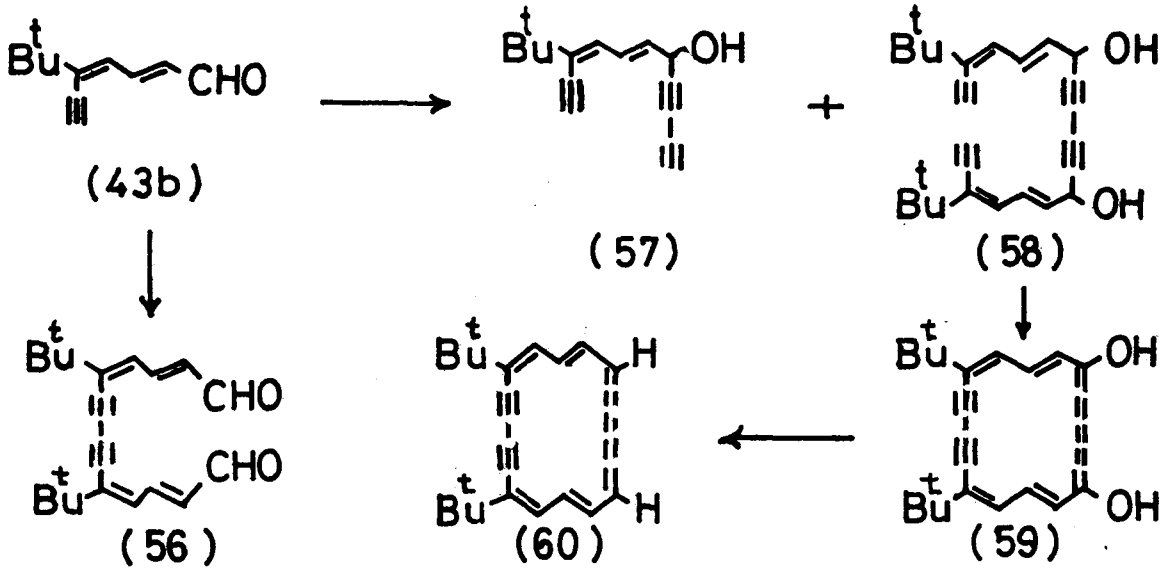
not be obtained. The desired di-adduct (53) was obtained in a low yield by ethynylation using lithium acetylide in liquid ammonia. Oxidative coupling of (53) by means of cupric acetate-pyridine-methanol afforded a small amount of products.



Scheme VI

A solution of the products without purification in benzene was treated with stannous chloride in concentrated hydrochloric acid to result in a green solution. The u.v. spectrum of the solution ($\lambda_{max}^{benzene}$ 344, 416sh, 622, 778 nm) was found to be similar with that of (35), except for a slight bathochromic shift. Unfortunately, the coupling products was obtained in a very low yield under every reaction conditions[53]. For the green solution generated by the dehydroxylative aromatization contained very small amounts of materials, we could not further examine the annulene-like material.

Introduction of the phenyl group to the annulene rings results in disadvantage of solubility but that of the t-butyl group leads to



Scheme VII

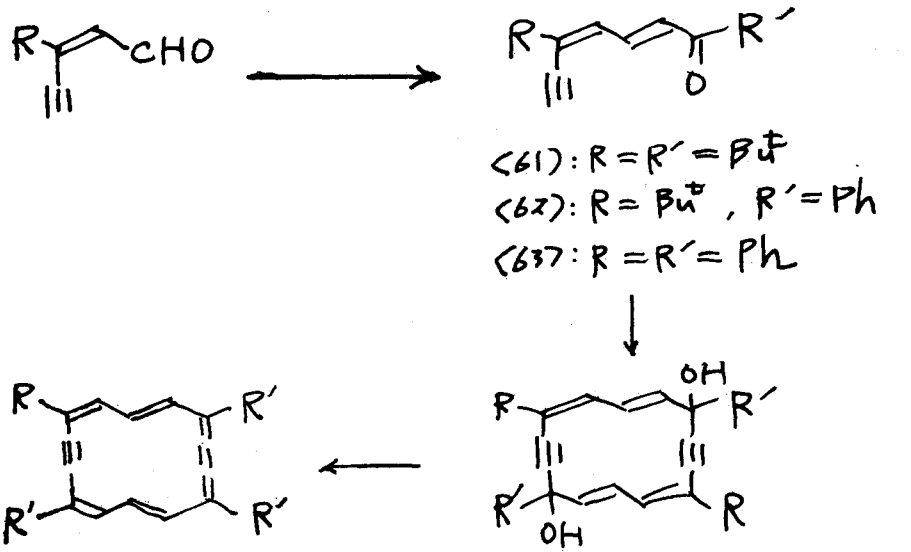
good solubility and relatively high stability. Therefore we attempted the synthesis of 3,7-di-t-butyl-1,3,8,10-tetradehydro[18]-annulene (60) shown in Scheme VII. Oxydative coupling of t-butyl-heptadienynal (43b) by Eglinton's method gave dialdehyde (56). In the case of (56) it was thought difficult to carry out the reactions (56)→(59)→(60). We attempted another route (43b) →(58)→(59)→(60) to synthesize di-t-butyletetradehydro[18]-annulene (60). The reaction of (43b) with diacetylene bis-Grignard reagent[54] afforded mono-adduct (57) and di-adduct (58). After separation of (57) and (58) by chromatography, (58) was oxidatively coupled by Eglinton's method and followed by treatment with stannous chloride in concentrated hydrochloric acid. A red solution obtained showed u.v. spectrum ($\lambda_{max}^{benzene}$ 372, 400sh, 505, 520, 713 nm) which was closely related to tetrasubstituted tetradehydro-[18]annulenes.

We could not decide whether the annulene-like products were the desired dehydroannulenes (55 and 60) or not. Considering that u.v. spectra showed more bathochromic shift than expected in both cases, the obtained compounds might be conjugated linear polymer.

VI. SYNTHETIC STUDIES OF DIDEHYDROANNULENES

VI-1. 1,8-DIDEHYDRO[14]ANNULENES

We have stated 1,8-didehydro[14]annulene (26) synthesized by Sondheimer. The dehydroannulene (26) bears the same molecular geometry as our tetradehydroannulenes. The dienyne-ketones (61 and 63), key intermediates in the synthesis of tetrasubstituted-tetradehydro-[18]annulenes (36 and 35) appeared to be potential precursors of the synthesis of tetrasubstituted-didehydro[14]annulenes provided they can be transformed in 14-membered cyclic glycols. The cyclic dimerization of the dienyne-ketones (61 and 63) was an unknown reaction and the most difficult problem in view of the facile conjugate addition to α,β-unsaturated ketone and the labile nature of carbonyl group to strong base such as sodium amide and sodium hydride.



Scheme VIII

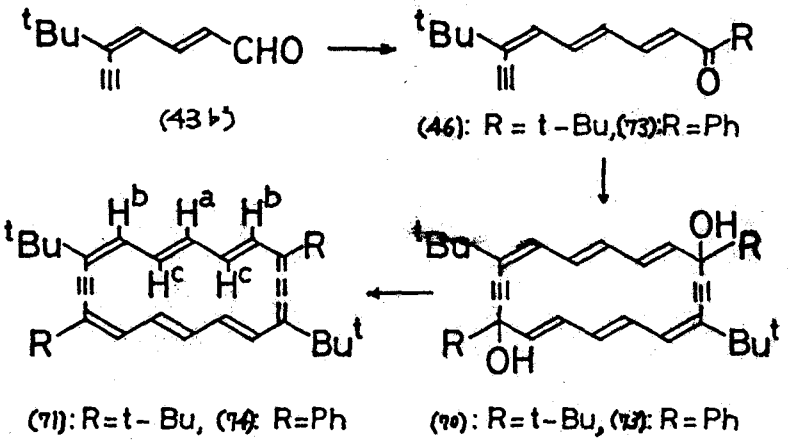
After several experimentations, cyclic dimerization of the dienyn-ketone (61, 62 and 63) could be realized under conditions of the Favorskii reaction[55] by Fukui, Nomoto, Nakatsuji and Nakagawa[56]. A diluted solution of dienyne-ketone (61, 62 and 63) in tetrahydrofuran was added dropwise to a stirred suspension of finely powdered potassium hydroxide in liquid ammonia and stirring was continued for several hours. The reaction mixture was worked up by the usual manner. For example, di-t-butyldienyne-ketone (61) afforded besides an unidentified by-product, the cyclic glycol (64) in crystalline state in a 69% yield which could be separated on chromatography on silica gel in diastereomeric (64a), m.p. 220.0 ~ 222.2°C (dec.) and (64b), m.p. 230.9~232.4°C (dec.). The cyclic glycol (64, 65 and 66) in benzene or ether was treated with stannous chloride in concentrated hydrochloric acid. Chromatographic purification of the reaction product afforded tetrasubstituted-didehydro-[14]annulenes (67, 68 and 69). The didehydro[14]annulenes thus prepared decomposed at over 200°C accompanying color change on attempted melting point determination.

Tetrasubstituted-didehydro[14]annulenes (67, 68 and 69) were found to be stable and strongly aromatic. The dehydroannulenes proved to be one of the most aromatic monocyclic nonbenzenoid systems known. We can now prepare the didehydro[14]annulenes readily because of a qantitative conversion of ketones to 14-membered cyclic glycols in the Favorskii reaction.

VI-2. DIDEHYDRO[18]ANNULENES[57)]

The cyclic dimerization of ethynyl-ketones under the conditions of the Favorskii reaction appeared to open a new route leading to various unknown tetrasubstituted-didehydroannulenes.

The di-t-butyltrienyne-ketone (46) which has been prepared as a key intermediate in the synthesis of tetra-t-butyltetradehydro[22]-annulene (50)[44)] was dissolved in tetrahydrofuran and added slowly to a stirred suspension of finely powdered potassium hydroxide in liquid ammonia at -34°C. After stirring for several hours, the reaction mixture was worked up to give 18-membered cyclic glycol (70) as colorless crystals in a 66% yield. The cyclic glycol (70) was found to be a 1:1 mixture of diastereomers and could be separated on chromatography on silica gel, yielding (70a), m.p. 230.5~231.5°C, M^+ 488 and (70b), m.p. 170.0~171.0°C, M^+ 488 (Calcd. for $C_{34}H_{48}O_2$ =448.7). The diastereomers (70a and 70b) gave identical electronic



Scheme IX

and n.m.r. spectra but slight difference was observed in their i.r. spectra. A mixtrue of (70a) and (70b) was suspended in ether saturated with hydrogen chloride, and finely powdered stannous chloride dihydrate was added to the mixture at -60 °C under stirring in nitrogen atmosphere to afford a reddish brown solution. Chromatographic purification of the product on alumina gave 3,9,12,18-tetra-t-butyl-1,10-didehydro[18]annulene (71) as dark reddish violet crystals, m.p. ca. 260 °C (dec.), M^+ 454 (Calcd. for $C_{34}H_{46}$= 454.6) in a yield of 93%. The didehydro[18]-annulene (71) forms 1:1 π-complex with 2,4,7-trinitrofluorenone; the complex crystallized as deep violet needles, m.p. ca. 260 °C (dec.). Full hydrogenation of the didehydro[18]-annulene (71) in acetic acid-ethyl acetate using platinum oxide as a catalyst resulted in tetra-t-butylcyclooctadecane, m.p. 151.0~154.0 °C, M^+ 476 (Calcd. $C_{34}H_{68}$=476.9).

Condensation of acetophenone with dienyne-aldehyde (43b)[44] yielded trienyne-ketone (72) as yellow crystals in a 76% yield. The Favorskii reaction of (72) performed under the above-stated reaction conditions afforded cyclic glycol (73) as a yellow solid. The crude glycol (73) was subjected to the dehydroxylative aromatization without further purification to give a violet solution. After purification di-t-butyldiphenyldidehydro[18]annulene (74) was obtained as deep violet crystals, m.p. 235 °C (dec.) in a 33% yield based on the trienyne-ketone (72), M^+ 494 (Calcd. for $C_{38}H_{38}$=494.7). (74) gave 1:1 π-complex with trinitrofluorenone as deep violet needles, m.p. 250 °C (dec.).

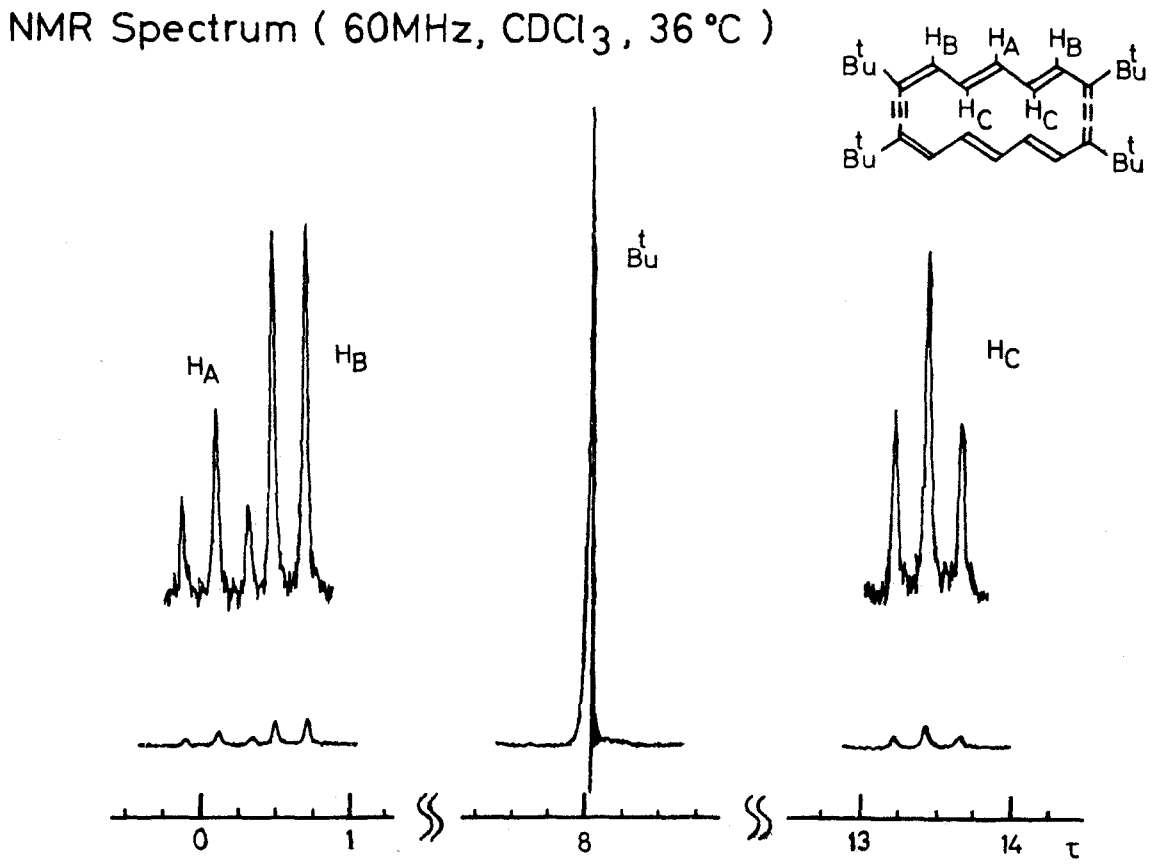


Fig. 5. The 60 MHz n.m.r spectrum of (71) in $CDCl_3$.

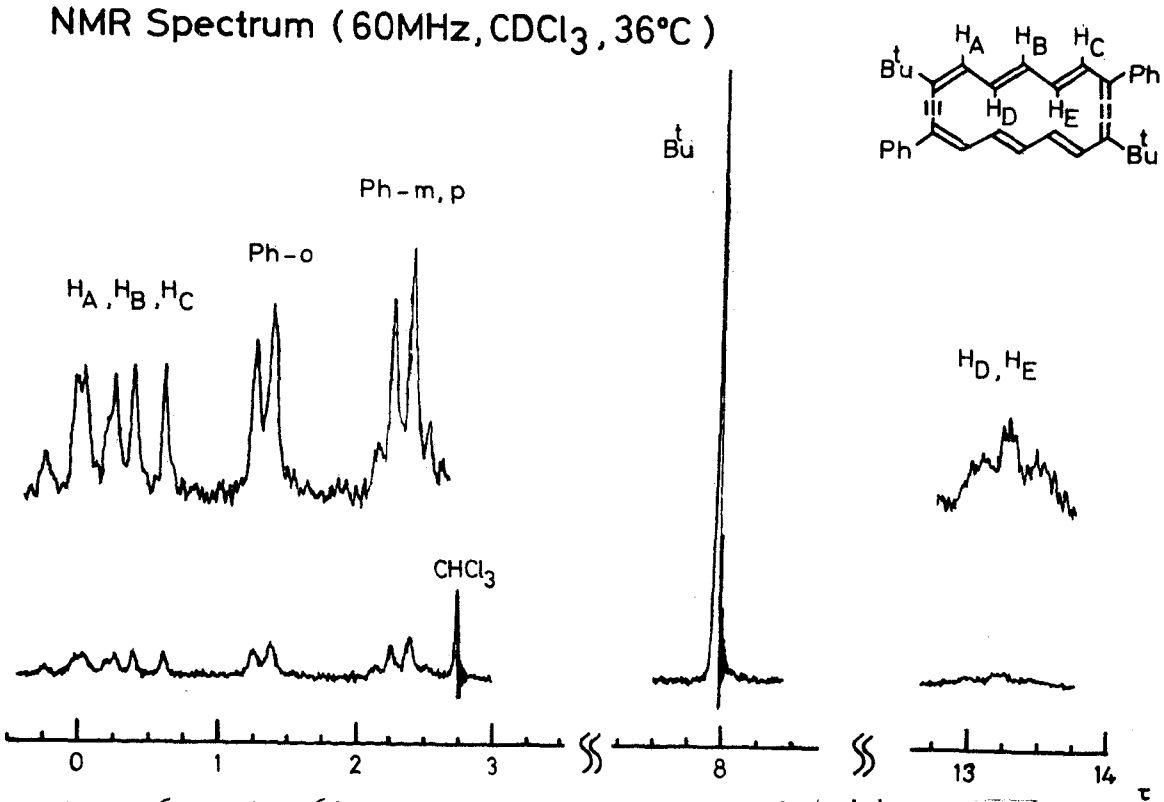


Fig. 6. The 60 NHz n.m.r. spectrum of (74) in $CDCl_3$.

The didehydro[18]annulenes (71 and 74) were found to be fairly stable compounds and as illustrated in Fig. 5 and Fig. 6, they exhibit "aromatic" n.m.r. spectra indicating the presence of diamagnetic ring current. As recorded in Table 2, the n.m.r. spectra of (71) were found to be temperature-independent being essentially unchanged up to 110°C. This fact reveals the high confomational stability of 1,10-didehydro[18]annulene system. An attempted measurement of the n.m.r. spectrum at 150°C in $CDBr_3$ resulted in a rapid decomposition of (71).

Table 2. The 60 MHz N.m.r. Spectra of Tetra-t-butyl-didehydro[18]annulene in $CDBr_3$.

Temp.	H_A	H_B	t-Bu	H_C
36°C	0.18, t J=13 Hz	0.68, d J=13 Hz	8.09, s	13.64, t J=13 Hz
70°C	0.30, t J=13 Hz	0.78, d J=13 Hz	8.10, s	13.46, t J=13 Hz
110°C	0.44, t J=13 Hz	0.81, d J=13 Hz	8.10, s	13.28, t J=13 Hz

Table 3. The 60MHz N.m.r. Spectra of Tetra-t-butyl-didehydro[18]annulene in $CDCl_3$

Temp.	H_A	H_B	t-Bu	H_C
36°C	0.13, t J=13 Hz	0.62, d J=13 Hz	8.03, s	13.42, t J=13 Hz
70°C	0.14, t J=13 Hz	0.63, d J=13 Hz	8.06, s	13.23, t J=13 Hz

Electronic spectra of the didehydro[18]annulenes (71 and 74) are shown in Fig. 7. The spectra exhibit regular bathochromic shift according to the phenyl substitution in the same ways in didehydro-[14]annulenes (67, 68 and 69).

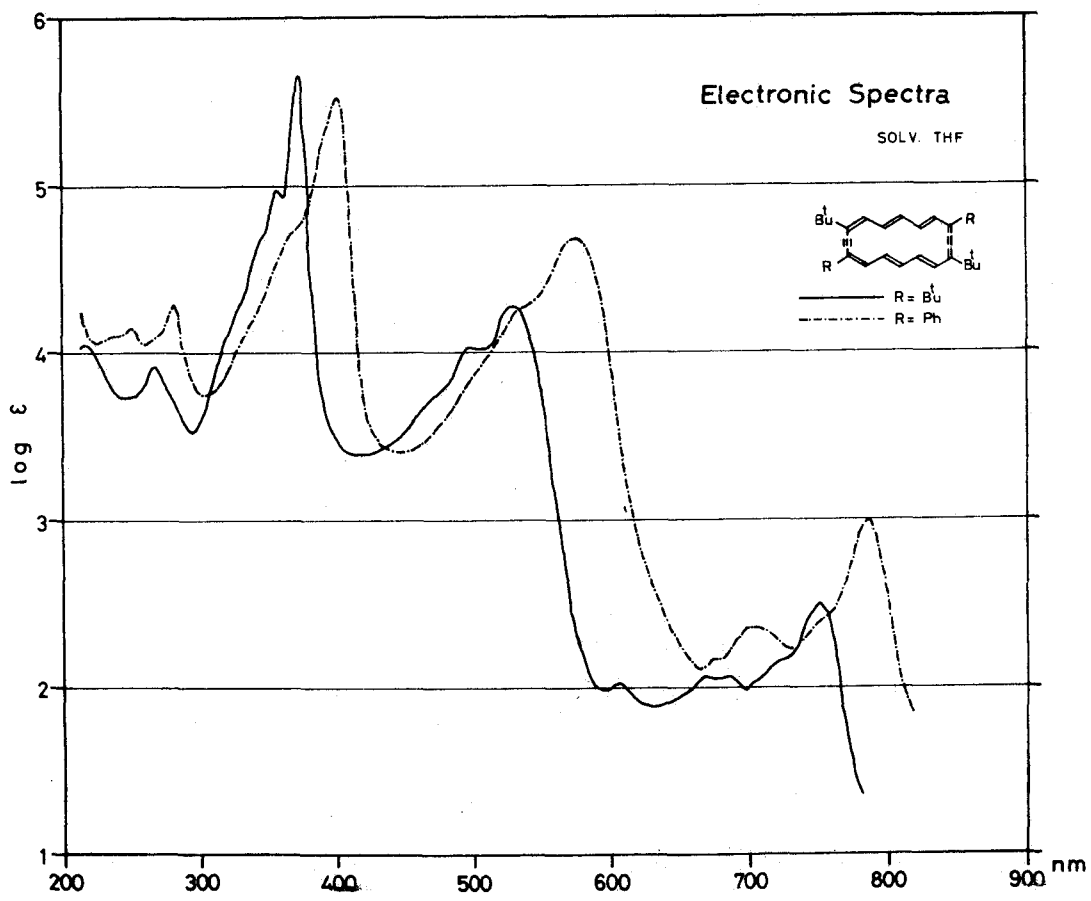
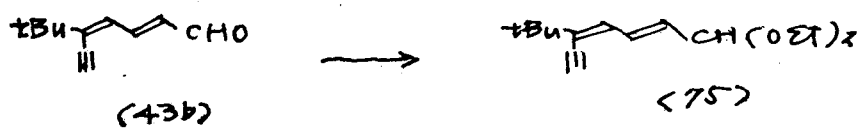


Fig. 7. Electronic Spectra of the Didehydro[18]-annulenes(71 and 74) in tetrahydrofuran.

VI-3. DIDEHYDRO[22]ANNULENE[58)]

The fairly stable nature and induction of strong diamagnetic ring current observed in 1,10-didehydro[18]annulenes (71 and 74) provide a stimulus to further efforts to synthesize higher members of analogous dehydroannulenes.

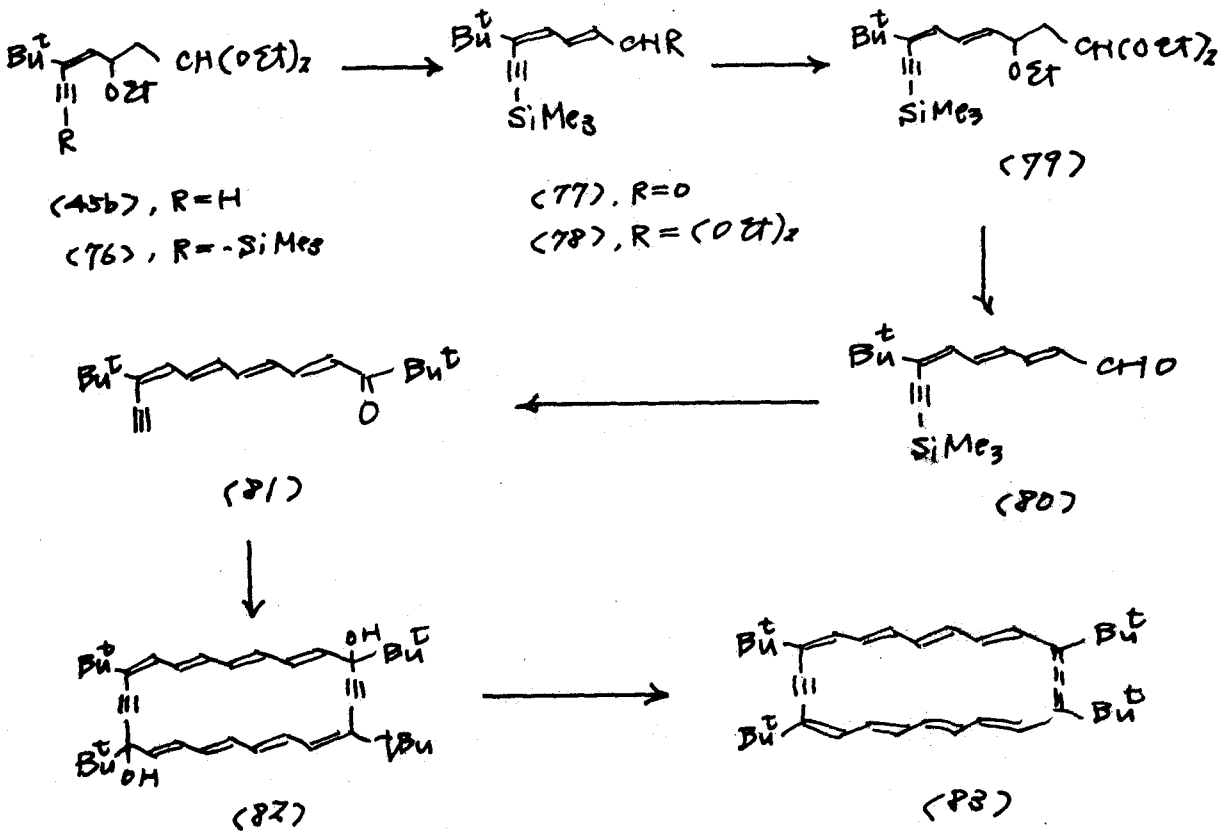
For the purpose of the further extension of double bond by means of Isler's method (ethyl vinyl ether-borontrifluoride etherate), first we converted t-butylheptadienyne-aldehyde (43b) into the corresponding diethyl acetal (75). Contrary to our expectation, acetal (75) was not sufficiently stable. The comparison of (41b) and (43b) indicates that the stability of t-butylpolyene-aldehyde decreases with the increase of the length of conjugate system. Taking this into consideration, dieneyne-aldehyde (43b) was converted into trimethyl silyl derivative (78) to increase the stability.



(43b) (75)

5-t-Butyl-3-ethoxy-4-hepten-6-ynal diethyl acetal (45b) used as an intermediate in the synthesis of tetra-t-butyltetradehydro-[22]annulene (50) was treated with ethylmagnesium bromide in tetrahydrofuran and then with chlorotrimethylsilane. Distillation of the reaction product afforded trimethylsilyl derivative (76) as a pale yellow liquid in a 92% yield. Hydrolysis of (76) with an aqueous acetic acid containing sodium acetate gave trimethylsilyldienyne-aldehyde (77) as a yellow liquid in a 89% yield. The aldehyde (77) was converted into diethyl acetal (78) by the usual method. The reaction of ethyl vinyl ether with (78) in benzene in the presence

of borontrifluoride etherate[48] yielded ethoxy-acetal (79), pale yellow liquid, in a 86% yield. Trimethylsilyltrienyne-aldehyde (80)



Scheme X

was obtained as viscous yellow liquid in a 87% yield from (79) on treatment with an aqueous acetic acid-sodium acetate. In general, trienyne-aldehyde seems to be unstable but trimethylsilyltrienyne-aldehyde (80) was found to be relatively stable and could be isolated by rapid distillation under nitrogen. Condensation of pinacolone with the aldehyde (80) under an alkaline condition resulted in tetraenyne-ketone (81) as yellow crystals in a 60% yield accompanying with the hydrolysis of trimethylsilyl group. A diluted solution of

the tetraenyne-ketone (81) in tetrahydrofuran was added slowly to a stirred suspension of finely powdered potassium hydroxide in liquid ammonia. The 22-membered cyclic glycol (82) was obtained as a mixture of diastereomers which could be separated on alumina chromatography in (82a), colorless crystals, m.p. 252°C (dec.), 31% yield, M^+ 540 and (82b), colorless crystals, m.p. 220～221°C, 58% yield, M^+ 540 (Calcd. for $C_{38}H_{52}O_2$=540.8). The diastereomers (82a and 82b) gave identical electronic and n.m.r. spectra, but slight difference was observed in their i.r. spectra. Finely powdered stannous chloride dihydrate was added to a stirred suspension of the cyclic glycol (82_{a-b}) in ether containing hydrogen chloride at -60°C under nitrogen atmosphere. After chromatography on alumina, 3,11,14, 22-tetra-t-butyl-1,12-didehydro[22]annulene (83) was obtained as dark violet crystals, m.p. ca. 230°C (dec.), M^+ 506 (Calcd. for $C_{38}H_{50}$=506.8) in a 94% yield. Hydrogenation of (83) in ethyl acetate-acetic acid over platinum catalyst at -15～-20°C afforded crystalline tetra-t-butylcyclodocosane (84), colorless crystals, 92% yield, as a mixture of stereoisomers. Recrystallization of the hydrocarbon from ethyl acetate-methanol resulted in a crude separation of isomers; (84a), 104～112°C, M^+ 532 and (84b), mp 91～95°C, M^+ 532(Calcd. for $C_{38}H_{76}$ = 532.9).

The didehydro[22]annulene (83) and 2,4,7-trinitrofluorenone form 1:1 π-complex, dark violet crystals with metallic lustre, m.p. 260°C (dec.). As recorded in Fig. 8, the electronic spectrum of (83) was found to be closely related with that of 1,6,12,17-tetra-t-butyl-2,4,13,15-tetradehydro[22]annulene (50)[44].

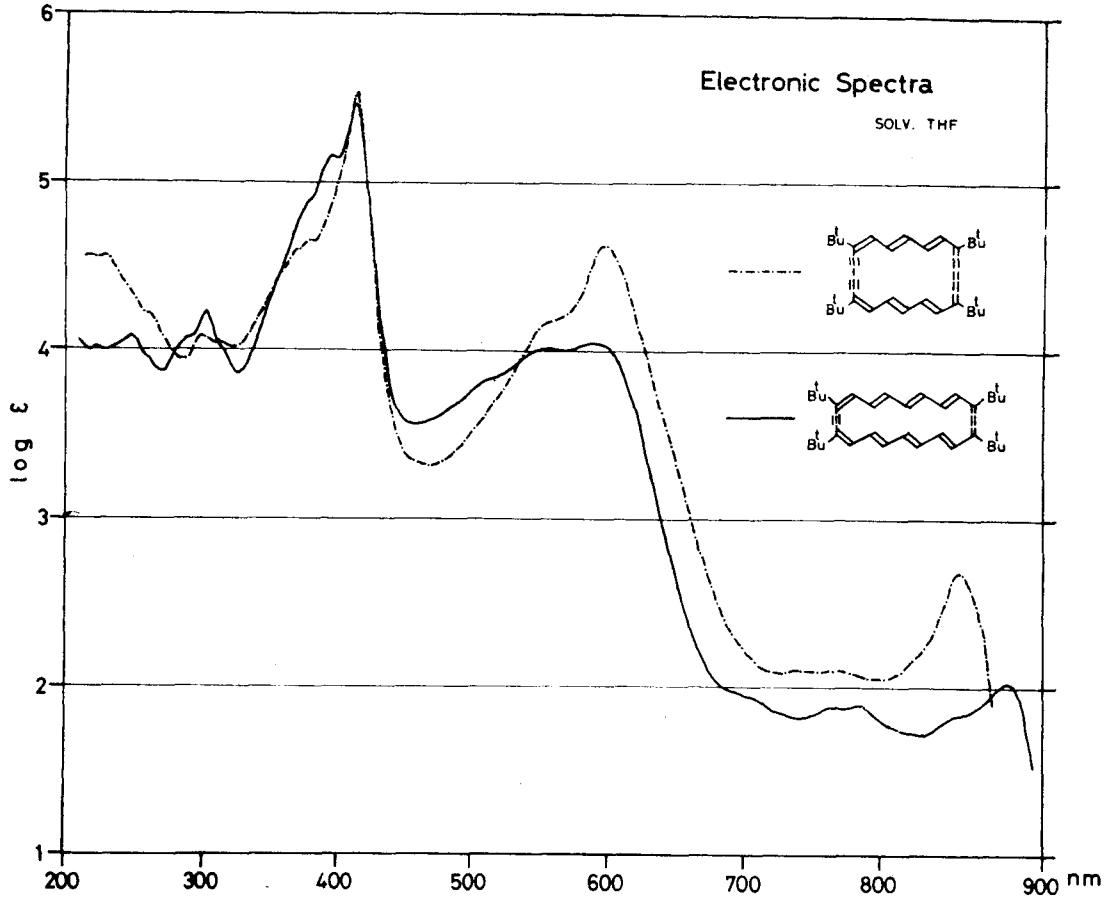


Fig. 8. The Electronic Spectra of Tetra-t-butyl-tetradehydro[22]annulene(50)- · -, and Tetra-t-butyl-didehydro-[22]annulene(83) —— in Tetrahydrofuran.

The n.m.r. spectra of the didehydro[22]annulene (83), as summarized in Table 3, clearly indicate

Table 4. The 60 MHz N.m.r. Spectra of Tetra-t-butyldidehydro[22]annulene (83) in $CDCl_3$.

Temp.	H_A	H_B	t-Bu	H_C , H_D
36°C	0.79, t J=13 Hz	1.24, d J=13 Hz	8.18, s	10.82, m
70°C	0.81, t J=13 Hz	1.26, d J=13 Hz	8.21, s	10.68, m

the aromatic nature and conformational stability of 1,12-didehydro-[22]annulene system.

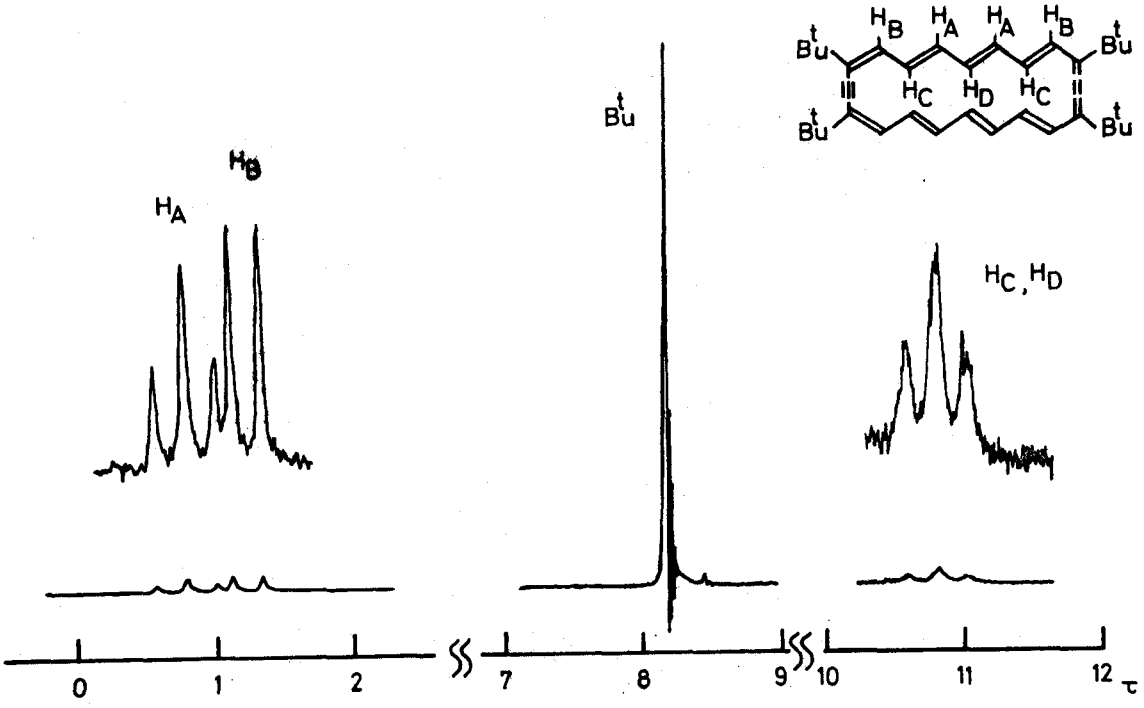
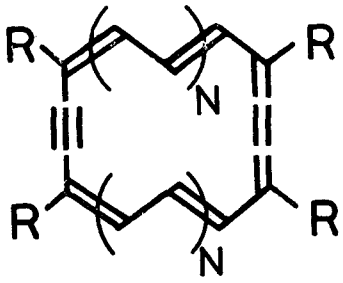


Fig. 9. The 60 MHz N.m.r. Spectrum of (83) in $CDCl_3$.

The n.m.r. spectrum measured in $CDBr_3$ (36°C and 70°C) showed the same tendency as in $CDCl_3$. An attempted measurement of the n.m.r. spectrum at 80°C in $CDBr_3$ resulted in a rapid decomposition of (83).

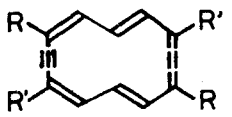
VI-4. DIDEHYDRO[26]ANNULENE[59]

Didehydroannulenes described above, may be represented by the following general formula shown in Scheme XI. Didehydro[14]annulene (N=1), didehydro[18]annulene (N=2) and didehydro[22]annulene (N=3) have essentially the same molecular geometry. These didehydroannulenes show a strong diamagnetic ring current in the n.m.r. spectra.



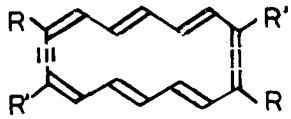
Didehydro-
(4n+2)annulene

N=1, (14)annulene



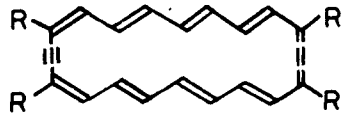
a: R=R'=^{t}Bu
b: R=^{t}Bu, R'=Ph
c: R=R'=Ph

N=2, (18)annulene



a: R=R'=^{t}Bu
b: R=^{t}Bu, R'=Ph

N=3, (22)annulene



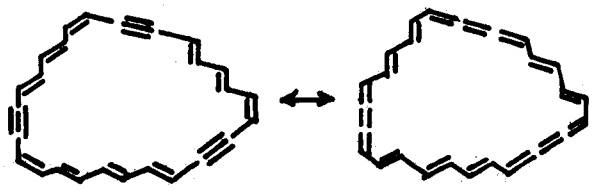
R=R'=^{t}Bu

Scheme XI

The question of the exact limit for "aromaticity" in [4n+2]-annulenes is an interesting one. It has been calculated that the limit lies between the 22- and the 26-membered rings[60)61)62)]. In agreement with this presumption [22]annulene and monodehydro[22]-annulene synthesized by Sondheimer show a diamagnetic ring current in the n.m.r. spectra, but tridehydro[26]annulene (21) synthesized

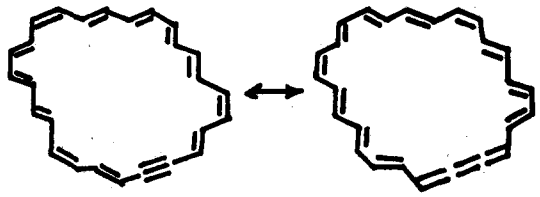
by Sondheimer[28] shows no ring current. However, the fact that monodehydro[26]annulene (22) prepared recently by Sondheimer[29] was found to be diatropic indicates the limit for "aromaticity" in [4n+2]annulene ought to lie above 26-membered ring. It is thought that the lack of a diamagnetic ring current in tridehydro[26]annulene (21) is due to the perturbation of the three acetylenic linkages, which causes the nondelocalized alternate bond structure to be energetically preferred to the delocalized system. This perturbation is likely to become of less importance in rings of monodehydro[26]-annulene (22), since the difference in energy between the two forms (22 ↔ 22') is predicted to be small.

This result has spurred us up to synthesize didehydro[26]-annulene (84), which can be written in the two equivalent Kekulé-type structures (84 ↔ 84'). Because the difference in energy between the two forms (84 ↔ 84') is nothing, it is contemplated that didehydro[26]annulene shows more definite induction of diamagnetic ring current in n.m.r. spectrum.



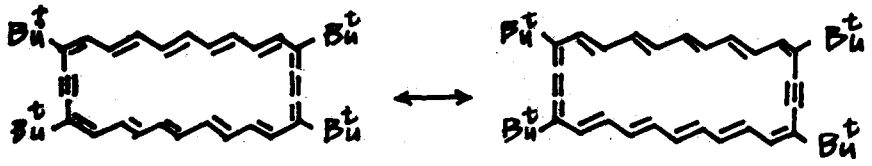
(21) (21')

Tridehydro [26] annulene



(22) (22')

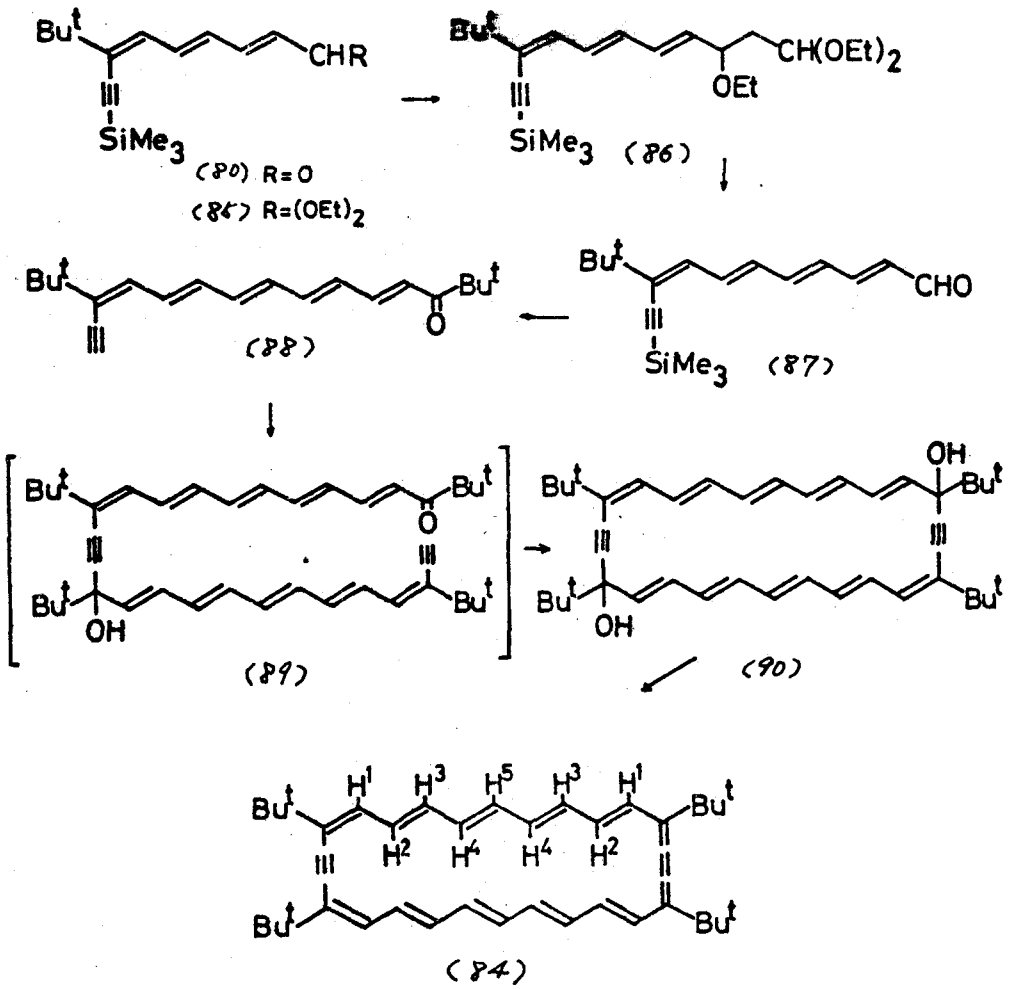
Monodehydro [26] annulene



(84) (84')

Didehydro [26] annulene

Trimethylsilyltrienyne-aldehyde (80), the key intermediate in the synthesis of didehydro[22]annulene (83), was converted into diethyl acetal (85). The diethyl acetal (85) obtained as a viscous yellow liquid was treated with ethyl vinyl ether in the presence of boron trifluoride etherate[48] in benzene to afford ethoxy trienyne-acetal (86) as a viscous yellow liquid. Trimethylsilyl tetraenyne-aldehyde (87), a viscous orange yellow liquid, was prepared on treatment of (86) with an aqueous acetic acid containing sodium acetate. Condensation of pinacolone with (87) under an alkaline



(84)

Scheme XII

condition afforded pentaenyne-ketone (88) as orange crystals, m.p. 92-94°C in a yield of 41% based on (85). A solution of the pentaenyne-ketone(88) in tetrahydrofuran was added over a period of 12 hours to a stirred suspension of powdered potassium hydroxide in liquid ammonia at the boiling point of ammonia and stirring was continued for further 8 hours. Crude 26-membered cyclic glycol (90) obtained as yellow crystals was chromatographed on alumina to result in a separation of diastereomers, (90a), pale yellow crystals, m.p. 277°C (decom.), 33% yield and (90b), lemon yellow crystals, m.p. 236.0-236.5°C, 60% yield. The mass spectra of (90a) and (90b) gave molecular ion peaks at 592 (Calcd. for $C_{42}H_{56}O_2$=592.9). It was found that a slow addition of a diluted solution of pentaenyne-ketone (88) is essential to obtain the cyclic glycol in a high yield (93%). This fact seems to indicate that the cyclic dimerization of (88) under the condition of the Favorskii reaction proceeds through two steps. As the chain length of the ethynyl ketone (88) increases, more diluted conditions may be required to predominate the intramolecular ring closure of the initially formed ketoalcohol (89). Ether saturated with hydrogen chloride was added to a suspension of 26-membered cyclic glycol (90a) in ether maintained at -75°C, and then finely powdered stannous chloride dihydrate was added at the same temperature to result in a deep green solution. The reaction product was chromatographed on alumina at -15°C. Elution with methylene chloride-n-pentane yielded 3,13,16,26-tetra-t-butyl-1,14-didehydro[26]annulene (84) as black violet crystals in a 89% yield. Similar treatment of (90b) afforded (84) in a yield of 86%. The mass spectrum of the tetra-t-butyldidehydro[26]annulene (84) showed molecular ion peak (M^+) at 558 along with a strong peak at 501 (M - 57)

being 57 ($t\text{-}Bu^+$) as base peak (Calcd. for $C_{42}H_{54}$=558.9). The didehydro[26]annulene (84) was found to be rather unstable and decomposed on attempted melting point determination. Full hydrogenation of (84) in ethyl acetate-acetic acid over platinum catalyst afforded tetra-t-butylcyclohexacosane, m.p. 111-113°C, M^+ 588 (Calcd. for $C_{42}H_{84}$=589.1) in a 91% yield. As illustrated in Fig. 10, the electronic spectra of didehydroannulenes show a striking difference of the

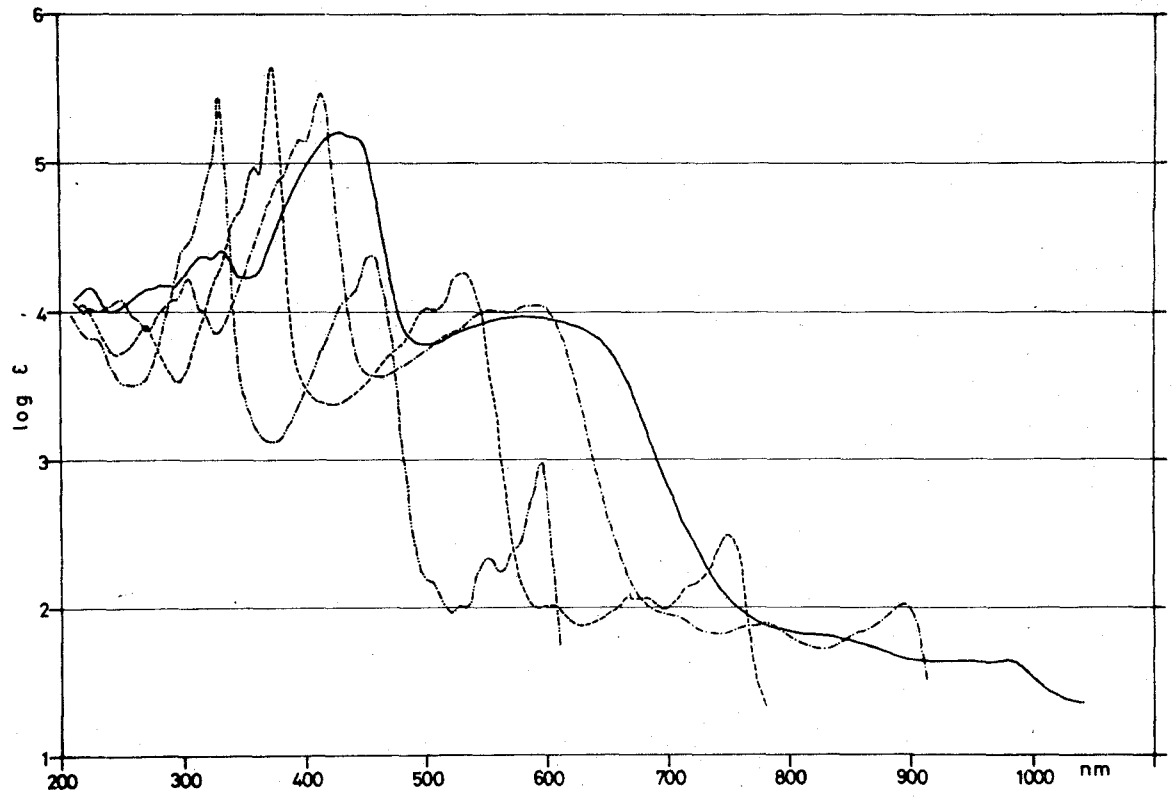


Fig. 10. The Electronic Spectra of Tetra-t-butyldidehydro[4n + 2]annulenes in Tetrahydrofuran.
-·-·- (67), ----- (71), -·-·- (83), —— (84).

absorption curves between didehydro[22]annulene (83) and didehydro[26]annulene (84). The electronic spectrum of (84) exhibits a broad absorption curve, but in contrast with it the spectra of the lower members of didehydroannulenes (67, 71 and 83) display sharp curves.

The difference may be due to an increase in flexibility of the didehydroannulenes, even though the conformation is maintained in the didehydro[26]annulene. However, the possibility of presence of some sort of discontinuous change between (84) and (83) cannot be ruled out in view of the marked difference of electronic spectra between (84) and (83), because the difference of electronic spectra between [18]annulene and [30]annulene[63] can be attributed undoubtedly to the difference of degree of delocarization of π-electrons.

Fig. 11 shows the n.m.r. spectrum of the didehydro[26]annulene (84). The spectrum gave signals of outer protons at τ 1.75 (poorly resolved double triplets, H^3, H^5) and τ2.05 (d, J=13 Hz, H^1). Un-

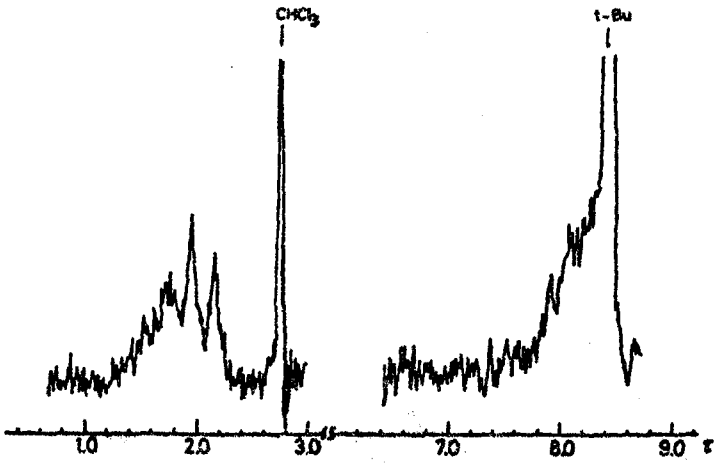


Fig. 11. The 60 MHz n.m.r. spectrum of tetra-t-butyldidehydro[26]annulene(84) in $CDCl_3$.

fortunately, the signals of inner protons (H^2 and H^4) seemed to be submerged in the low-field tail of the signal of t-butyl protons (τ 8.39). This difficulty could be overcome by the double resonance

technique of n.m.r. spectrum measurment. As shown in Fig. 12, marked change of the shape of signals of outer protons on irradiation at τ 8.20~8.16 region indicates that the signals of inner protons may exist in this region*. The fact that the signals of outer protons was observed at fairly low-field indicates the presence of diamagnetic ring current in the didehydro[26]annulene (84).

The difference of chemical shifts between inner protons and outer protons of didehydro[26]annulene (84) was found to be Δ=6.45, whereas no diamagnetic ring current could be detected in tridehydro-[26]annulene (21) and the difference of monodehydro[26]annulene (22) is estimated Δ=3.9~0.7 (inner protons τ 5.0~6.0), outer protons τ 2.1~4.5), being much smaller than that of (84). Comparison of n.m.r. spectra of three dehydro[26]annulenes (21,22 and 84) indicates that the delocalization of π-electrons in the dehydroannulenes is suppressed by the introduction of acetylenic linkage and enhanced by the presence of both of acetylenic and cumulenic linkages reflecting the contribution of equivalent-Kekulé-type resonance structures.

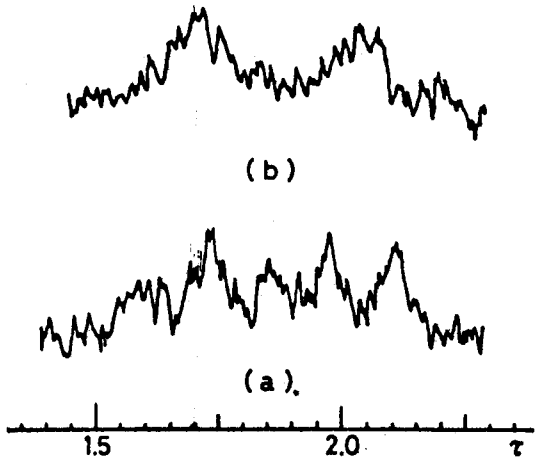


Fig. 12. The 100 MHz n.m.r. spectra of outer protons of didehydro[26]annulene(84) in $CDCl_3$.
(a): normal spectrum. (b): irradiated at τ8.20.

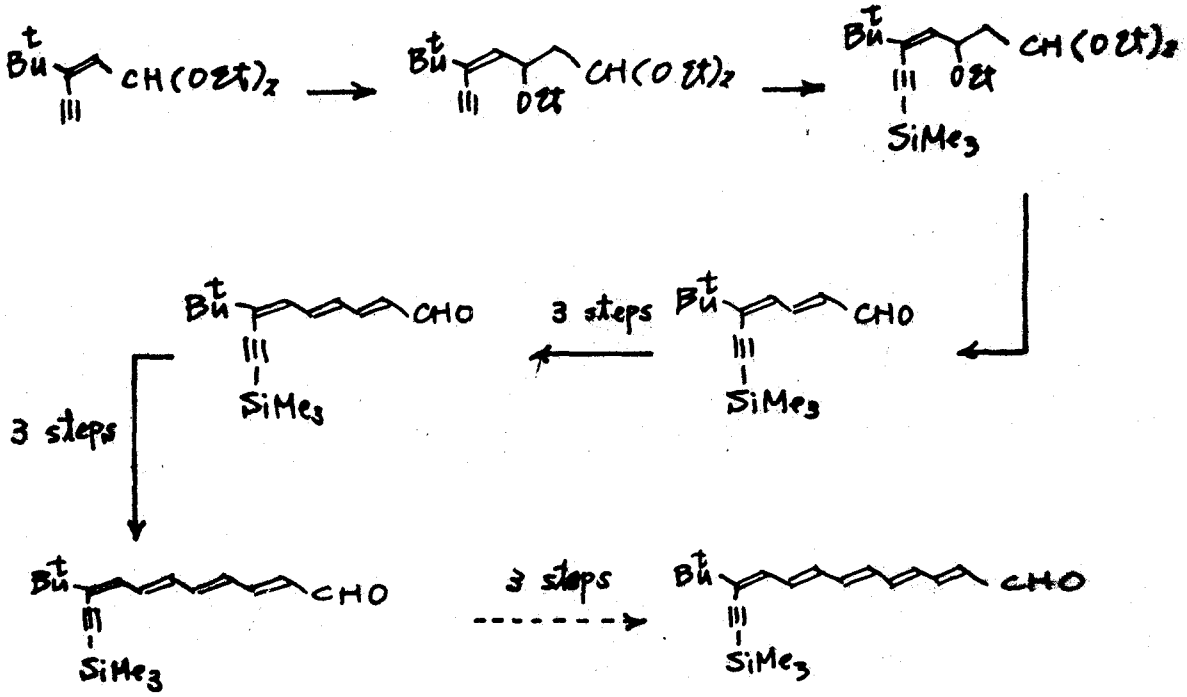
* The author is grateful to Dr. Kazuo Tori of Shionogi Research Laboratory, Shionogi & Co., Ltd. for the double resonance measurement.

VI-5. DIEHYDRO[30]ANNULENE[64]

Unlike the various annulenes, the didehydroannulenes expressed by the general formula (p.30) have essentially the same geometry owing to the presence of acetylene and butatriene linkages in the cyclic systems having high conformational stability. The dehydroannulenes have been shown to sustain a fairly large diamagnetic ring current. The geometrical similarity of the dehydroannulenes makes it possible to study the effect of increasing the value of n in aromatic [4n + 2] π-electron systems, keeping the geometry largely unchanged. The n.m.r. spectral data indicate that the diamagnetic ring current becomes progressively less as the value of n is increased, although the ring current is still evident in the 26-membered compound. In view of this fact, the higher member of this series of didehydroannulenes can be regarded as an adequate model compound to test the validity limit of Hückel's rule for aromaticity. Therefore, we attempted the synthesis of 3,15,18,30-tetra-t-butyl-1,16-didehydro[30]annulene (91).

When we began to synthesize the dehydroannulene, three 30-membered annulenes had been known, i.e., pentadehydro[30]annulene (92)[65], tridehydro[30]annulene (93)[66] and [30]annulene (17).[19] These annulenes have not shown an induction of the diamagnetic ring current in the n.m.r. spectra, and was found to be nonaromatic (or atropic*)[25].

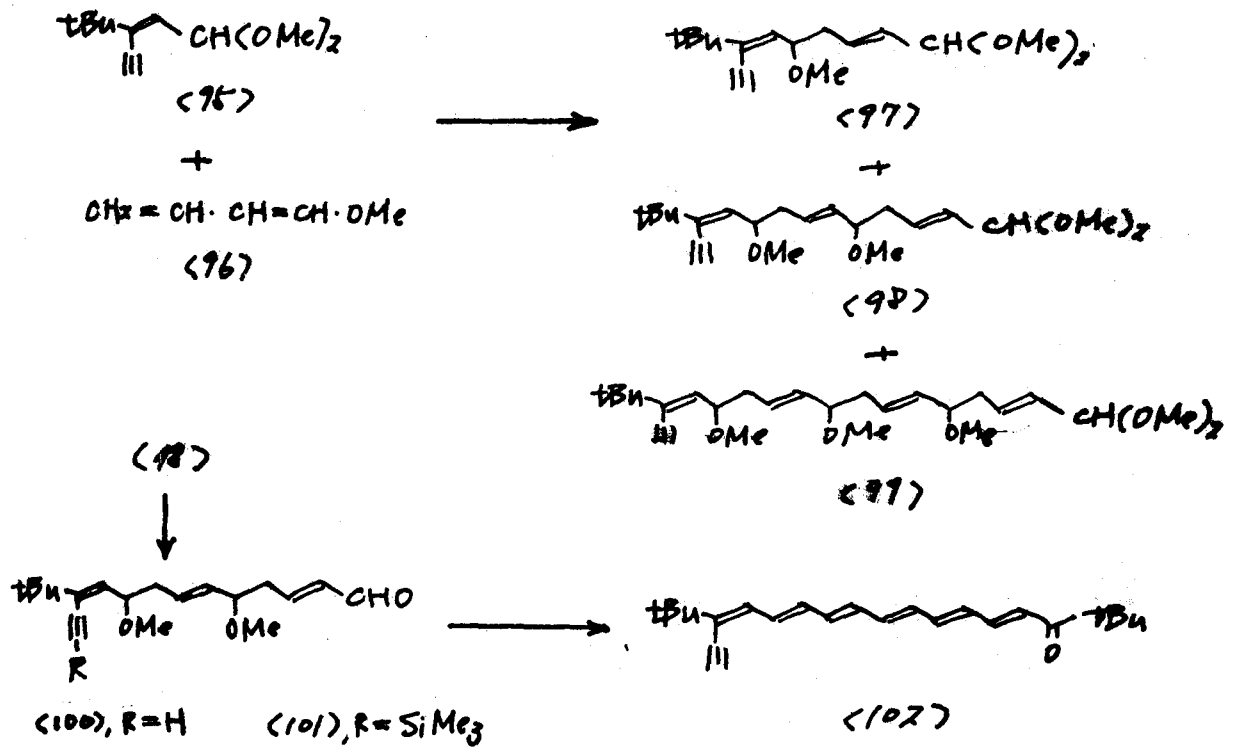
* Annulenes and Dehydroannulenes showing no ring current were named atropic by Sondheimer[68].



Scheme XIII

We have so far synthesized didehydro[4n+2]annulenes stepwise extension of double bonds so as to put one bilding-block on another by means of Isler's method [ethyl vinyl ether / boron trifluoride etherate]. Because this method proceeded readily and in a good yield, stepwise extension of double bonds could be performed without too great difficulty. However, if didehydro[30]annulene (91) is planned to synthesize step by step using this method, we should carry out to prepare the key intermediate, pentaenyne-aldehyde (94) by the use of a very long path shown in Scheme XIII. In addition to the disadvantage, intermediates containing long chain conjugated groups are unstable and indistillable liquids, and it may be difficult to deal with these compounds. We, therefore, attempted to convert the starting aldehyde or acetal into a potential pentaenyne-aldehyde in one step.

First, we employed the methyoxybutadiene (96)[67)68)] to extend the double bonds. Dimethylacetal (95) derived from aldehyde (41b) was allowed to react with methoxybutadiene (96) (0.4 eq.) in the presence of borontrifluoride etherate as catalyst[69)70)]. The reaction mixture was separated by fractional distillation to give mono-adduct (97), di-adduct (98) and tri-adduct (99). The di-adduct (98) was

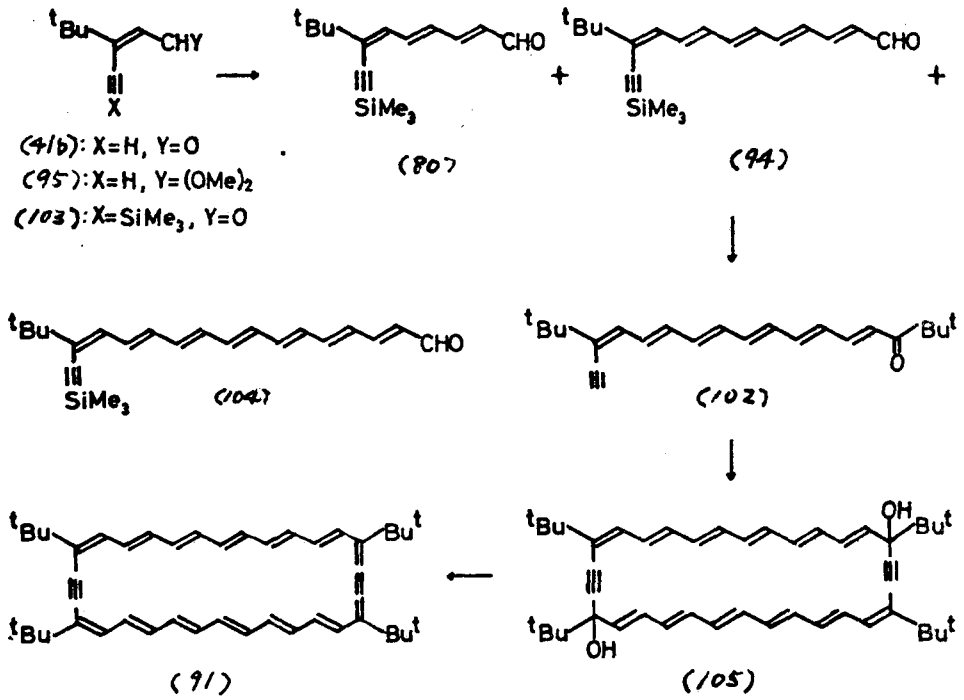


Scheme XIV

considered to be a potential pentaenyne-aldehyde, hydrolyzed with aqueous acetic acid to give dimethoxyaldehyde (100). Condensation of the aldehyde (100) with pinacolone afforded hexaenyne-ketone (102) in a very poor yield together with un-identified oily compounds. Trimethylsilylation of the acetal (98) followed the hydrolysis with aqueous acetic acid gave trimethylsilylaldehyde (101). The trimethylsilylaldehyde (101) reacted with pinacolone to afford the hexaenyne-ketone (102) also in a very low yield. One of the major

problems might be active methylene group of the aldehydes (100 and 101), which could cause the self-condensation of the aldehyde. We attempted to convert the methoxyaldehyde (101) into pentaeryne-aldehyde (94). This reaction was carried out by means of sodium acetate in acetic acid-H_2O at 60 °C for 2 hours, but the starting material was recovered. Taking into account the instability of the pentaen yne- aldehyde (94), the plan has been suspended.

This difficulty could be removed by the use of the following route (Scheme XV). Dimethylacetal (95) was converted into Grignard derivative and treated with trimethylchlorosilane. The prodı was hydrolyzed with aqueous acetic acid to give trimethylsilylated aldehyde (103) in a yield of 92.9%. To a mixture of (103), acetic acid, ethanol and piperidine was added gradually a solution of freshly distilled crotonaldehyde (0.5 eq.) in ethanol under carbon dioxide atmosphere[71]. The reaction products were chromatographed on silica gel to give mainly trienyne-aldehyde (80) except for the recovered starting material (41b). However, using excess croton-



Scheme XV

aldehyde (2.5 eq.) in the same reaction followed the chromatographic separation on silica gel (eluted with n-hexane-benzene) afforded the desired pentaenyne-aldehyde (94) in a yield of 25% together with trienyne-aldehyde (80) in a 11% yield and heptaenyne-aldehyde (104) in a 3.4% yield. Condensation of (94) with pinacolone gave ethynylhexaene-ketone (102) as unstable orange yellow crystals (38%). Elemental analyses indicate that (102) is gradually oxidized by atmospheric oxygen. A solution of (102) in tetrahydrofuran was added over a period of 10 hours to a suspension of finely powdered potassium hydroxide in liquid ammonia at -34°C, and the mixture was stirred for further 6 hours. Crude crystals obtained by working up the reaction mixture by the usual manner were chromatographed on alumina. Elution with tetrahydrofuran-benzene (1:9-2:8) afforded a diastereomer of 30-membered glycol (105a, yellow crystals, m.p. ca. 270°C (dec.), M^+ 644) in a 34% yield. Another diastereomer (105b, yellow crystals, m.p. 260.0-260.5°C (dec.), M^+ 644) (Calcd. $C_{46}H_{60}O_2$=644.9) could be obtained by elution with tetrahydrofuran-benzene (1:1). Both stereoisomers (105a and 105b) showed almost superimposable electronic spectra. However, difference was observed in the region of OH streching vibration in their i.r. spectra.

A suspension of stannous chloride dihydrate in ether saturated with hydrogen chloride was slowly added to a solution of (105a) in ether-tetrahydrofuran (1:1) at -78°C resulting in a deep green solution. After being worked up rapidly at a low temperature, the product was chromatographed on alumina and eluted with n-pentane-dichloromethane (1:1) at -20°C. Tetra-t-butyldidehydro[30]annulene (91) was obtained as unstable black violet crystals, M^+ 610 (Calcd. for $C_{46}H_{58}$=610.97). The mass spectral pattern of (91) was found to

be closely related with those of lower members of tetra-t-butyl-annulenes of this series. It is difficult to rule out a possibility that the mass spectrum may not show that of the dehydroannulene (91) itself. Taking into consideration that mass spectrum was measured at 200°C in a vacuum system, the spectrum may show the secondary product which thermally arised from (91). The other stereoisomer (105b) also gave (91) under analogous reaction conditions. No satisfactory elemental analyses could be obtained owing to the unstable nature of (91). Full hydrogenation of (91) in ethyl acetate-acetic acid over platinum oxide catalyst at -15 ~ -20°C (6 hours) and then at room temperature (2 hours) followed chromatography on alumina gave colorless crystals (57% based on (105a)), m.p. 77 ~ 87°C, M^+ 644 (Calcd. for $C_{46}H_{98}$=645.24). The electronic spectrum of (91) shown in Fig. 13 was obtained using a solution prepared by dissolving fresh (91) which was derived from (105b). The ε-value were estimated assuming quantitative conversion of (105b) into (91) without decomposition or formation of by-products. In contrast to the absorption curves of the lower members of this series of dehydroannulenes, which show distinct vibrational fine structures in the electronic spectra, (91) displays a broad and structureless feature of the absorption curves like that of didehydro[26]annulene(84). It seems to reflect an increasing flexibility of dehydroannulene skeleton along with an increase in ring size.

Owing to the poor solubility and instability of didehydro[30]-annulene(91), n.m.r. spectral measurement was difficult to accomplish.(about 5 mg of the dehydroannulene could be dissolved in 5ml

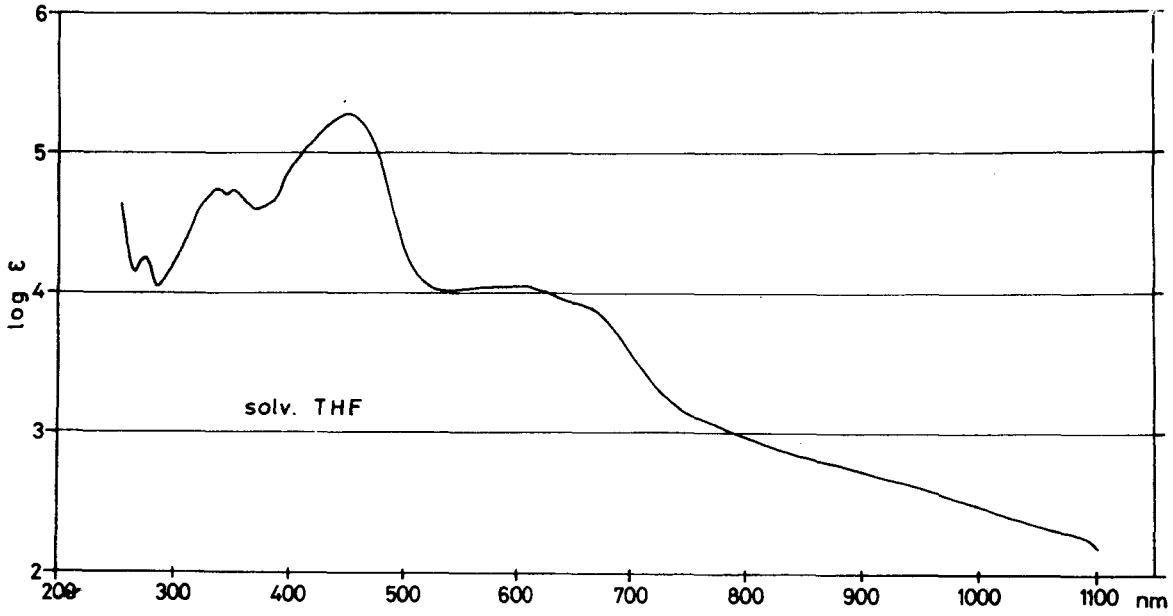


Fig. 13. Electronic Spectrum of Tetra-t-butyldidehydro-[30]annulene(91) in Tetrahydrofuran at -78°C.

of deuteriochloroform). The compound was less soluble in methylene-chloride, benzene and ether. Tetrahydrofuran was dissolved the dehydroannulene(91) better, but could not be used as n.m.r. solvent since it shows the signal near τ 6.50 in n.m.r. spectrum. Consequently, the n.m.r. spectrum of (91) was measured in deuteriochloroform at -60°C using Fourier Transform technique (Fig. 14). The signals at τ 2.10~2.90 (center, τ 2.50 ca. 12H), τ 6.10~7.00 (center, τ 6.50, ca. 10H) and τ 8.56 could be assigned to outer protons, inner protons and t-butyl protons, respectively. No essential change was observed in n.m.r. spectra measured at -40°C and -20°C, but (91) was

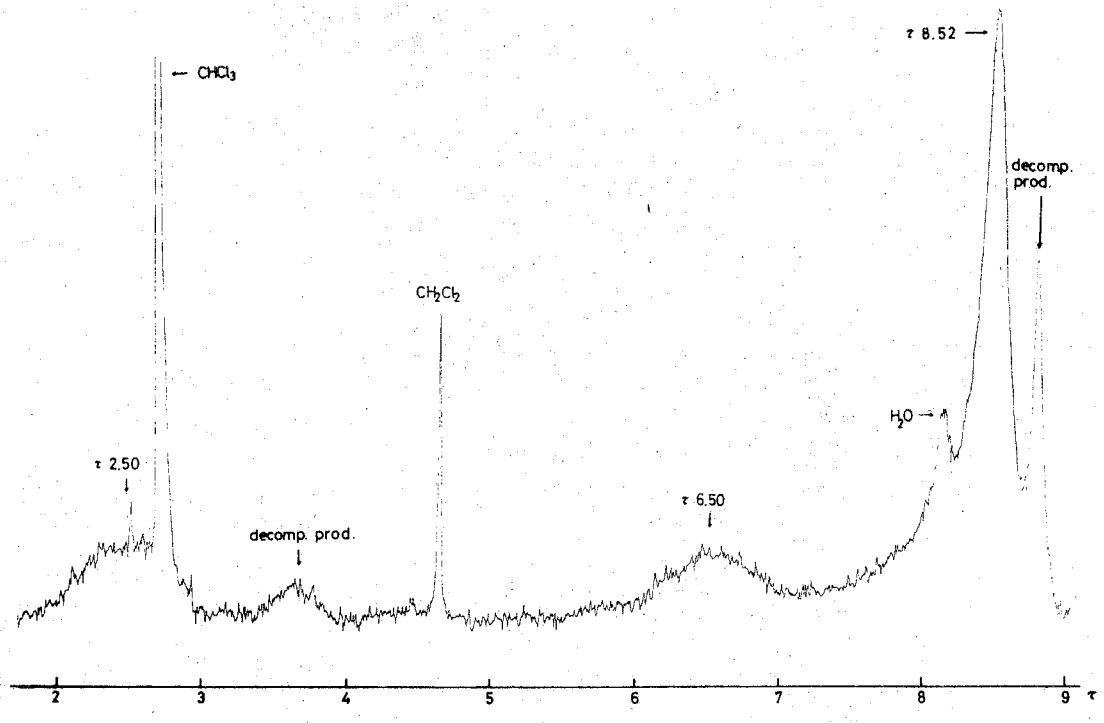


Fig. 14. 100 MHz FT-n.m.r. spectrum of tetra-t-butyl-didehydro [30] annulene (91).

decomposed relatively fast at -20 °C. The fact that inner protons exhibit signal at higher field than that of outer protons demonstrates the existence of a diamagnetic ring current. To our knowledge, this is the first instance of diatropic 30 π-electron system. This result indicates that the upper limit of aromaticity of [4n + 2] annulene should lie above 30-membered ring[72].

Broadening of the signals of outer and inner protons of the dehydroannulene (91) seems to be attributable to a decrease of rigidity of perimeter of the didehydro [30] annulene (91) as is reflected in the electronic spectrum.

The didehydro[4n+2]annulenes possess the same symmetry and approximately the same degree of planality. If we assume the difference of chemical shifts between inner and outer protons is an index of the magnitude of the ring current[73], the series of tetra-t-butyldidehydro[4n+2]annulenes (67, 71, 83, 84 and 91) furnishes a pertinent data on the effect of ring size on the magnitude of diamagnetic ring current (Table 5).

Table. 5. The Magnitude of Ring Current of Tetra-t- butyldidehydro[4n+2]annulenes

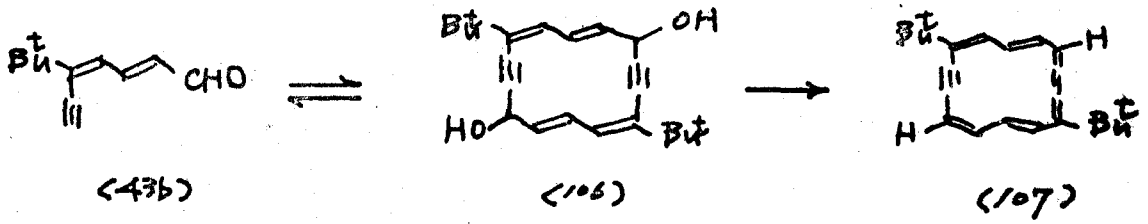
	[4n+2]	Inner protons (τ_i)	Outer protons (τ_o)	Ring Current ($\tau_i - \tau_o$)
(67)	[14]	14.44	0.68	13.76
(71)	[18]	13.42	0.62	12.80
(83)	[22]	10.82	1.24	9.58
(84)	[26]	8.2	2.05	6.15
(91)	[30]	6.5	2.5	4.0

A saturated solution of (91) in deuteriochloroform decomposed fairly rapidly even at -40°C resulting a black violet solid with less solubility. The rate of decomposition is decreased markedly on dilution of the solution suggesting an intermolecular mode of decomposition reaction. The n.m.r. spectrum of decomposition product exhibits signals at τ 3.40 ~ 4.00(m) and τ 4.05 ~ 4.60(m). The electronic spectrum of decomposition product showed hypsochromic shift and hypochromism as compared with that of (91). The nature of decomposition product is not clear.

VI-6. ATTEMTED SYNTHESIS OF DISUBSTITUTED DIDEHYDRO-[14]ANNULENE* AND DICARBOXYDIDEHYDRO[14]ANNULENE**.

We have synthesized a series of didehydro[4n+2]annulenes using dimerization of ketones by Favorskii reaction followed by dehydroxylative aromatization. Favorskii reaction is scarcely employed in acetylenic chemistry, and application of the reaction has been often faced with the problem achieving the dimerization in a good yield. It is said that "the method is of limited application for the conversion of aldehydes and not at all for α,β-unsaturated carbonyl compounds"[74]. However, our dimerization reaction of α,β-unsaturated ketones have developed the new utility of Favorskii reaction. In this chapter, we will state some attempts applying Favorskii reaction to various carbonyl compounds.

We have interested in 3,10-disubstituted-1,8-didehydro[14]-annulene in order to examine the properties and reactivities at 7, 14-positions. Attempted synthesis of (107) was done by the route shown in Scheme XVI. We expected that Favorskii reaction should proceed more readily, but against our expectation the starting material (43b) was recovered in many reactions, in which corresponding



(43b) (106) (107)

Scheme XVI

*These experiments were carried out in colaboration with Hideaki Miyazaki.

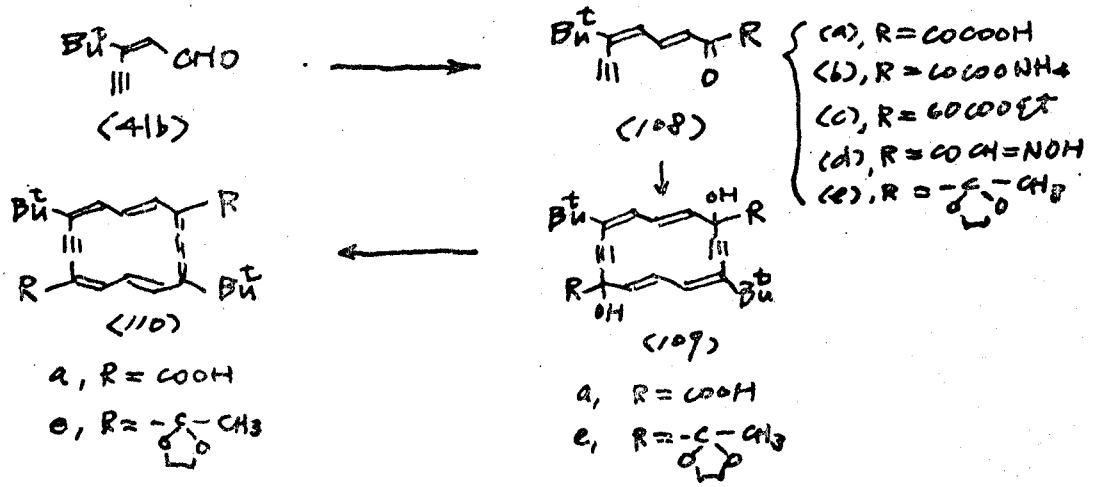
*These experiments were done in colaboration with Sin'ichi Nakatsuji.

ketones was converted into glycols.

This result may be attributed to the reversibility of Favorskii reaction[75].

Electronic properties and reactivities of benzene and substituted benzenes have been intensively investigated in the field of benzenoid aromatic chemistry. Phenyl group acts both as electron with-drawing and as electron attracting group, and σ-value of Hammett's equation is plus. In order to examine a resemblance or a difference between benzene and didehydro[14]annulene system. We have attempted the synthesis of didehydro[14]annulene carboxylic acid (110a). It may be possible to determine the properties by detecting the difference of pKa-value between annulene-carboxylic acid (110a) and its precursor, glycol (109a).

First, we prepared ketocarboxylic acid derivatives (108a-c) by the condensation of the aldehyde (41b) with pyruvic acid. Ketocarboxylic acid (indistillable liquid, 108a), its ammonium salt (108b) and its ethyl ester (108c) were attempted to converted into glycol (109a-c). All these attempts were unsuccessful under conditions of

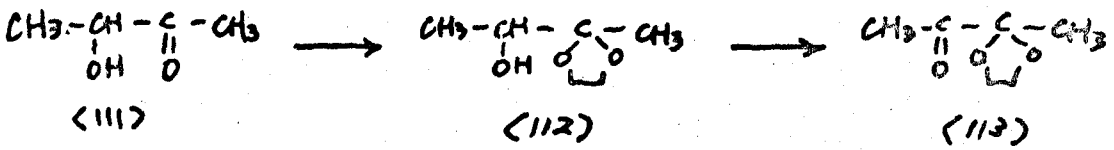


Scheme XVII

Favorskii reaction because of the lability of ketone (108a-c) and glycol (109a-c) in basic media. In almost all cases, the reactions afforded nothing without decomposition products which did not show the signal in n.m.r. spectra.

Secondly, ketoxime derivative (108d) prepared from the condensation of the aldehyde (41b) with isonitrosoacetone[76] was subjected to dimerization under Favorskii reaction condition. In this case, the ketoxime (108d) was completely recovered.

Thirdly, we planned the synthesis of diacetyldidehydro[14]-annulene diethyleneketal (110e), which might be transformed to (110a). Biacethyl monoethyleneketal (113) was prepared by following reaction.



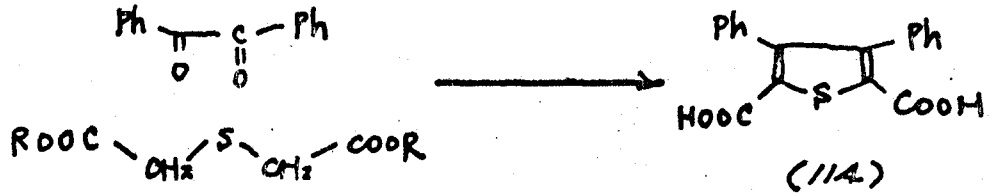
(111) (112) (113)

Condensation of aldehyde (41b) with (113) yielded dienyne-ketone (108e). Favorskii reaction of the ketone (108e) was very slow and needed a long time and an extreme dilution. The obtained mixtrue of glycols containing (109e) and polymers was treated with stannous chloride dihydrate in ether containing hydrogen chloride to give a yellow solution. The solution showed u.v. spectrum ($\lambda_{max}^{benzene}$ 343, 454sh, 480, 616 and 646 nm) like that of didehydro[14]annulenes. Although the desired dehydro[14]annulene (110e) might be presented in this solution, the solution obtained was too little to measure n.m.r. spectrum.

Recently the electronic properties are investigated based on other compounds, and will become more apparent through these researches.

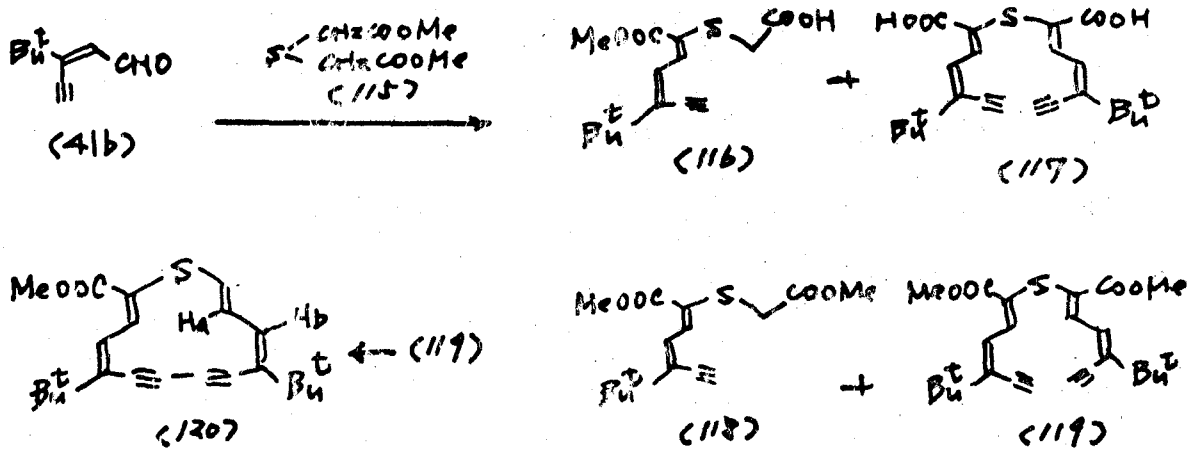
VII. SYNTHESIS OF DIDEHYDROTHIA[13]ANNULENE

All the nonbenzenoid aromatic systems discussed hitherto have been carbocyclic. I would now like to mention didehidrothia[13]-annulene(120) only briefly. Condensation of benzil with thiodiglycolate gave thiophene derivative(114)[77].



(114)

In a similar manner as above we synthesized didehydrothia-[13]annulene(120) shown in Scheme XVIII. Stobbe condensation of enyne-aldehyde(41b) with dimethyl diglycolate(115)[78] yielded mono-adduct(116) and di-adduct(117). Mixture of (116) and (117) was converted to esters by means of methanol-hydrogen chloride, which was chromatographed on silica gel to give (118) and (119). Oxidative coupling of the desired di-adduct diester(119) by Eglinton's



Scheme XVIII

method(cupric acetate-pyridine) gave brown solid. Didehydrothia-[13]annulene(120) was isolated by short column chromatography on silica gel. The dehydrothia[13]annulene was found to be rather unstable, and decomposed on standing at room temperature for several days. Didehydrothia[13]annulene(120) began to decompose by adsorption on T.L.C. plates prepared from silica gel.

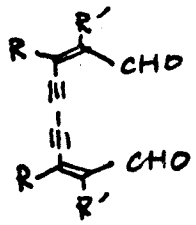
Table. 6. shows the n.m.r. data of (119) and (120). Didehydrothia[13]annulene(120) thus synthsized is diatropic, (according to the nomenclature proposed by Sondheimer), but only shows very small ring current compared with other annulenes described above. In this case we cannot say anything definite about its "aromaticity", since delocalization of π-electrons is considered too small to detect. Taking into account the aromaticity and the stability of thiophene, it seems strange that the annulene(120) shows very small ring current, even though the effect may be due the steric hinderance between inner hydrogens.

Table. 6. The N.m.r. Data of (119) and (120) in $CDCl_3$ at 36°C.

	Ha	Hb	-OMe	C≡CH	t-Bu
(119)	2.00, d 2H J= 13Hz	2.93, d 2H J= 13Hz	6.28, s 3H	6.45, s 2H	8.84, s 18H
(120)	2.02, d 2H J= 13Hz	2.81, d 2H J= 13Hz	6.23, s 3H	——	8.74, s 18H

VIII. SYNTHESES OF DECADIENDIYNDIALS AND FACILE INTRAMOLECULAR CYCLIZATION OF THE ALDEHYDES*80).

During the course of studies on the syntheses of dehydro[4n+2]annulenes containing acetylenic and cumulenic linkage, we have investigated the syntheses of substituted decadiendiyndials(121, 122 and 123). These diendiyne-dialdehydes seemed to be potential precursors of tetradehydro[14]annulene system. It was found that the dialdehydes(121, 122 and 123) gave readily difuranylacetylene derivatives(137, 128 and 136) by thermal reaction, and dihydrofuranilidene derivatives(140, 141, 129 and 131) by nucleophilic addition of methanol followed by intramolecular cyclization.

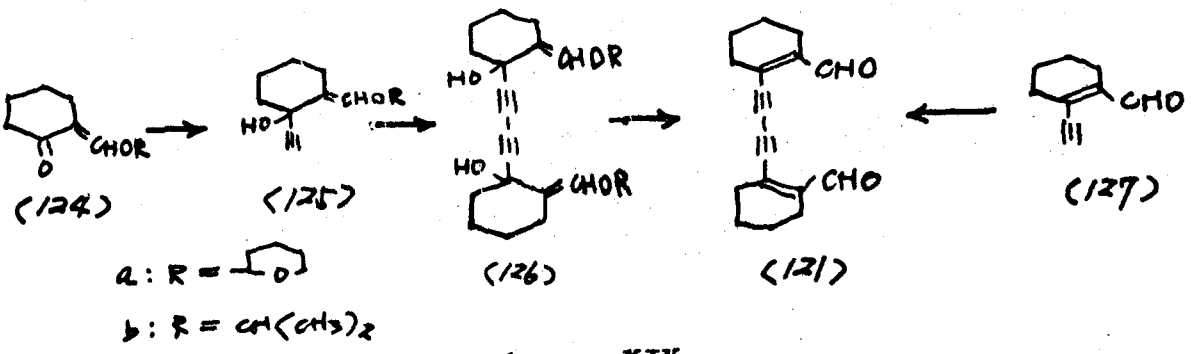


(121) : $R = R' = -(CH_2)_4-$

(122) : $R = Ph$, $R' = H$

(123) : $R = Bu^t$, $R' = H$

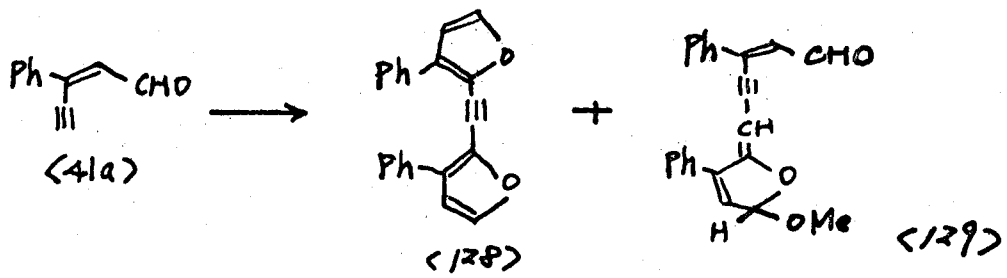
Synthesis Bis-tetramethylene derivative(121) could be obtained by two routes outlined in Scheme XIX. One route was performed by



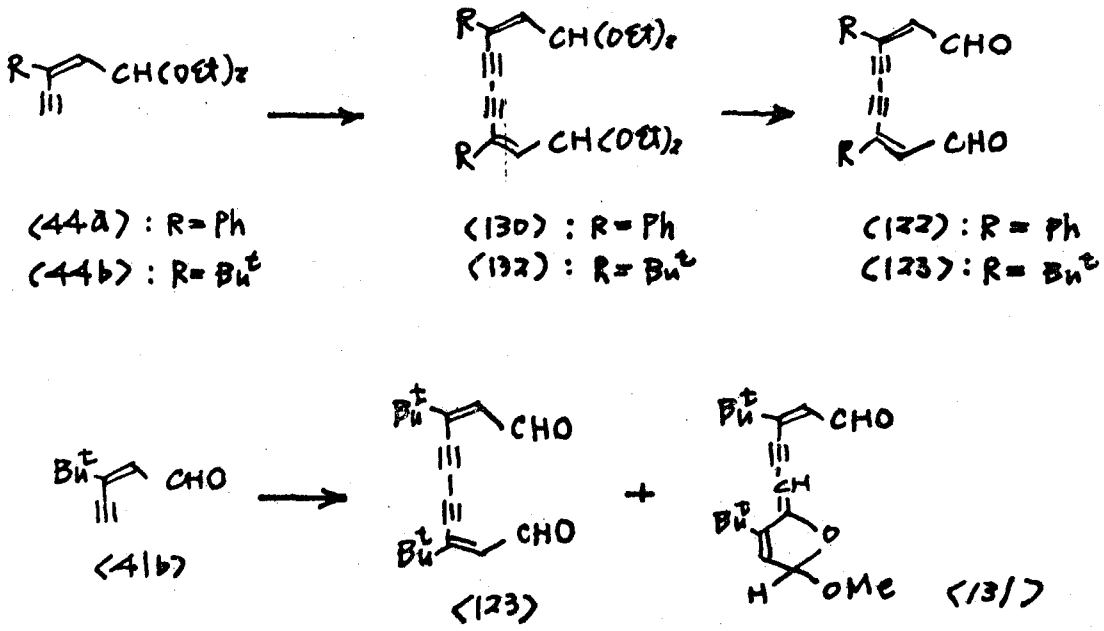
Scheme XIX

*These experiments were carried out in colabolation with Takayoshi Kashitani.

Muneyuki, Morimoto and Tanaka in our group. Acetylenic alcohol (125) obtained by ethynylation of 2-alkoxymethylenecyclohexanone (124)[81] was treated with cupric acetate in pyridine(the Eglinton's method) to yield hexadiyndiol(126). Hydrolysis of (126) afforded dialdehyde(121). Another route was carried out to obtain (121) more conveniently and in better yield. (121) could be also prepared by the Eglinton's oxidative coupling of 1-ethynyl-2-formylcyclohexene(127)[82] in the presence and absence of methanol. However, the oxidative coupling of 3-phenyl-2-pentene-4-ynal(41a) in the presence of methanol resulted in the formation of bis(3-phenyl-2-

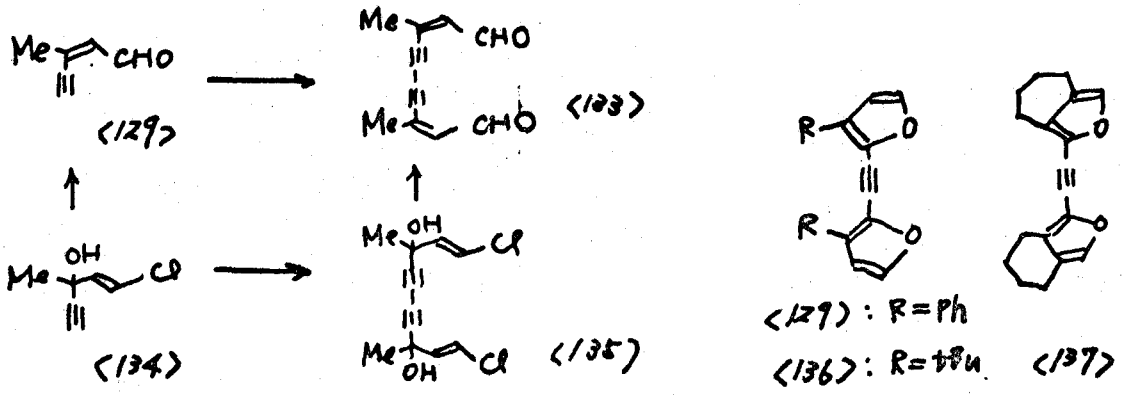


furanyl)acetylene(128, 13%) and dihydrofuranylidene derivative(129, 41%). In the absence of methanol, (128) was obtained in a yield of 30.5%. Phenylpentenynal(41a) was converted into diethyl acetal (44a). Hydrolysis of bis-diethyl acetal(130) obtained by the oxidative coupling of (41a) yielded extremely unstable dialdehyde(122) in a yield of 74%. Formation of appreciable amount of (128) was observed when (122) was allowed to stand for 2 days at room temperature. The Eglinton's reaction of t-butylpentenynal(41b) in the absence of methanol at a low temperature(15°-20°C) afforded dialdehyde in a 80% yield. However, the reaction performed in the presence of methanol gave a mixture of (123) and dihydrofuranylidene deriv-



ative(131). N.m.r. spectroscopy reveal that the mixture consist of 50% of (123) and 10-15% of (131). Di-t-butyldialdehyde(123) could be obtained by the hydrolysis of bis-diethyl acetal(132) which was prepared by the oxidative coupling of the diethyl acetal(44b).

Dialdehyde(133) could not be obtained by the Eglinton's reaction of methylpentenynal(129) in the presence of methanol, but the u.v. spectrum of the product(λ_{max}^{EtOH} 247, 285, 357 nm) was found to be similar with that of (141 and 142). Attempts to prepare (133) from



Scheme XX

diacetylenic glycol(135) obtained by the Glaser reaction of (134)[83] gave fruitless results owing to sluggish acid-catalyzed allylic rearrangement[84].

Thermal Cyclization of Dialdehydes(121, 122 and 123). Formation of bis(2-furanyl)acetylene derivatives(128, 136 and 167) was observed on heating solutions of the dialdehydes(122, 123 and 121) in organic solvents. The results are summarized in Table 7. This results indicate that the formation of (128) in the oxidative coupling of phenylpentenynal(41a) is attributable to a secondary reaction of initially formed dialdehyde(132). The possibility of catalytic action of cupric acetate in pyridine for cyclization reaction could be excluded by the experiments performed in benzene or ether containing cupric acetate and pyridine(see Experimental). Intramolecular cyclization of acetylenic compounds contaning the oxygen functions has been well known[85]. However, the formation of difuranylacetylene derivatives(128, 136 and 137) from dialdehydes (122, 123 and 121) seems to be symmetry-allowed thermal process.

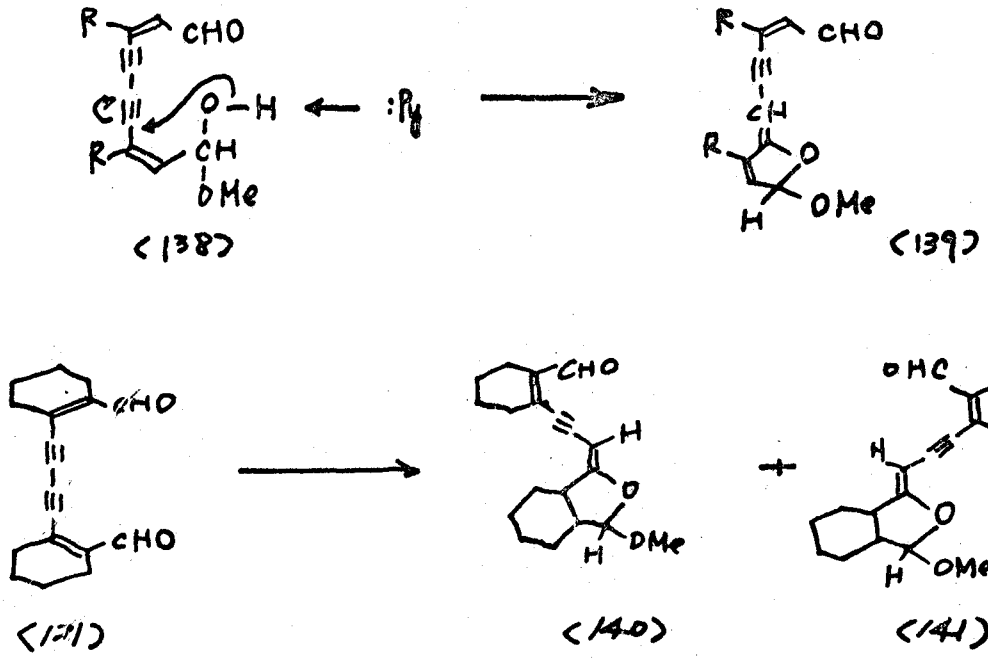
Table 7. Formation of Difuranylacetylenes

Dialdehyde	Solvent	Temparature (°C)	Reaction period (hr)	Yield (%)
(121)	xylene	120	5	(137) 57
(122)	benzene	50	8	(128) 86
(123)	benzene	60	20	(136) 82
(123)	pyridine	60	6.5	(136) 56[a]

a) Low yield of (136) can be attributed to gradual decomposition of (123) in pyridine.

It is to be noted that the mass spectral patterns of (121), (122) and (123) were found to be similar to those of (137), (128) and (136) respectively, indicating facile formation of difuranyl-acetylene derivatives from (121), (122) and (123) prior to the fragmentations.

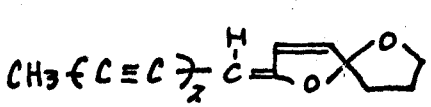
Formation of Dihydrofuranylidene Derivatives(129, 131, 140 and 141). The formation of dihydrofuranylidene derivatives(129 and 131) by the Eglinton's oxidative coupling of pentenynals(41a and 41b) in the presence of methanol can be regarded as a result of secondary reaction of initially formed dialdehydes(122 and 123) respectively, i.e., addition of methanol to carbonyl carbon of dialdehyde forms hemiacetal(138), and nucleophilic attack of oxygen atom of hemiacetal(138) to acetylenic carbon atom gives



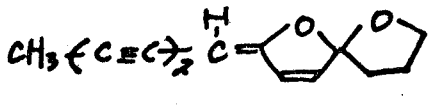
rise to dihydrofuranylidene compound(139). Because the cyclization reaction did not proceed without pyridine, it is evident that pyridine has a role of proton acceptor.

In the case of dialdehyde(121), no cyclization took place by pyridine-methanol. However, treatment of (121) in ether with sodium methoxide-methanol at 0°C afforded dihydrofuranylidene derivatives(140 and 141). The dihydrofuranylidene compounds could be separated into cis-isomer(140) and trans-isomer(141) on chromatography on silica gel.

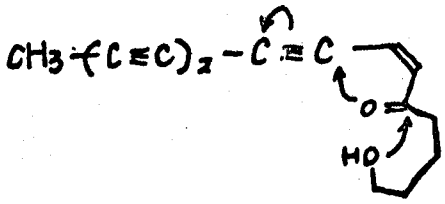
It is noted that acetylenic compounds with analogous dihydrofuranylidene system(142, 143 and 145) have been found in naturally occurring poly-ynes[86]. An intramolecular cyclization of keto-alcohol(144) in biogenetic path way to form (145) has been postulated by Bohlmann and Florenz[87].



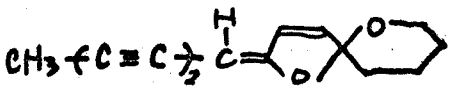
(142)



(143)

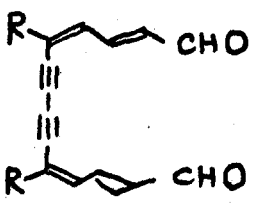


(144)



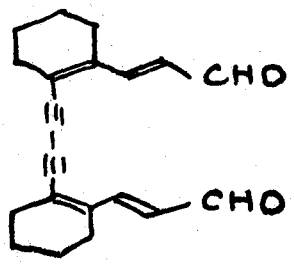
(145)

Facile intramolecular cyclization observed in decadiendiyndials (121, 122 and 123) can be attributed to the proximate position of oxygen atom of formyl group to acetylenic carbon atom favorable for the formation of stable five-membered ring which is caused by the cis-configuration of ethylenic linkage with respect to acetylene and formyl functions. We have mentioned to prepare diphenyl-(51) and di-t-butyltetradecatetraendiyndials(56) in previous chapter (p. 22). Expectedly, intramolecular cyclization could not have been observed in such a case. Quite recently the preparation of 4,5 10,11-bis(tetramethylene)-2,4,10,12-tetradecatetraen-6,8-diyndial(146), a vinylog of (121), was reported by Sondheimer and Yamamoto[88].



(51) R=Ph

(56) R=$B\overset{t}{u}$

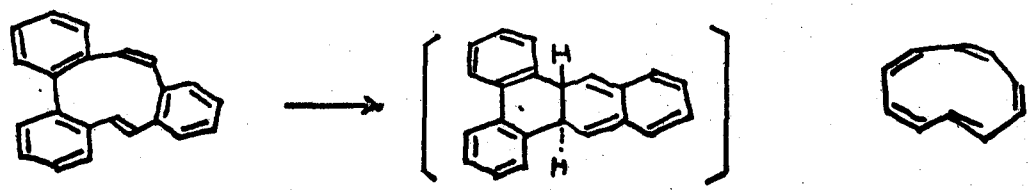


(146)

IX. SYNTHESIS OF DINAPHTHO-DI-t-BUTYL-DIDEHYDRO[14]ANNULENE AN AROMATIC ANNELATED ANNULENE* [89]

The properties of [4n + 2]annulenes annelated with benzenoid nuclei are of considerable interest with regard to the participation of benzenoid π-electrons to the macrocyclic systems. Some planar and non-planar annelated annulenes have been recently synthesized[90),91),92),93] with a view to examine the peripheral conjugation of aromatic character on the central ring systems containing [4n + 2]π-electrons.

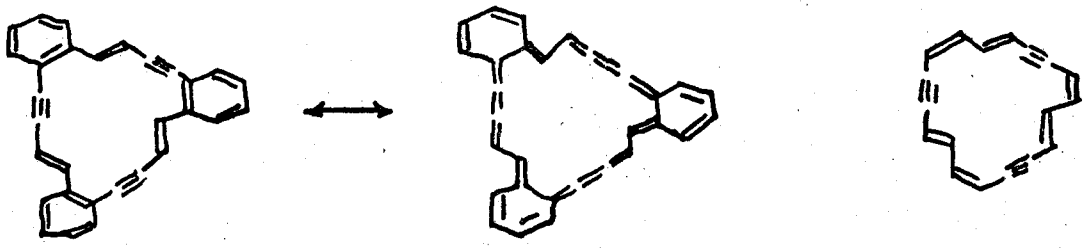
Mono-trans-1,2:3,4:7,8-tribenzo[10]annulene(146) was synthesized by Grohmann and Sondheimer[91]. The benzo[10]annulene can be written for a Kekulé structure incorporatiog the cyclodecapentaene system. However, it appears that the ten-membered ring in (146)is non-planar and does not represent a delocalized ten π-electron system. A reason for the greatly increased stability of (146), as compared with [10]annulene(7) itself, is presumably that the isomerization to the 9,10-didehydronaphthalene derivative(147) in this case involves disruption of cyclic delocalization of a benzene ring.



(146) (147) (7)

* These experiments were carried out in colaboration with Masakazu Morigaki.

A planar annelated derivative of aromatic 1,7,13-tridehydro-[18]annulene(18) was synthesized by Endo, Sakata and Misumi, i.e., tribenzotridehydro[18]annulene(148)[92]. The shift of the inner protons toward higher field due to induced diamagnetic ring current cannot be observed on the spectrum of (148) in contrast with that of tridehydro[18]annulene(18). These inner protons are found to resonate at rather low field owing to shielding effect of other unsaturated bonds and aromatic nuclei. The olefinic nature of 18-membered ring in (148) is due to the strong perturbation of the three benzene nuclei, which causes the completely nondelocalized alternate bond structure to be energetically prefered to the delocalized system*. Delocalization in aromatic system is dependent on the extent of contribution of another resonance hybrid in this molecule. Taking into consideration that resonance energy of benzene is 36 kcal/mol, it is actually impossible to assume the contribution of the structure(149) in tribenzotridehydro[18]-annulene(148).

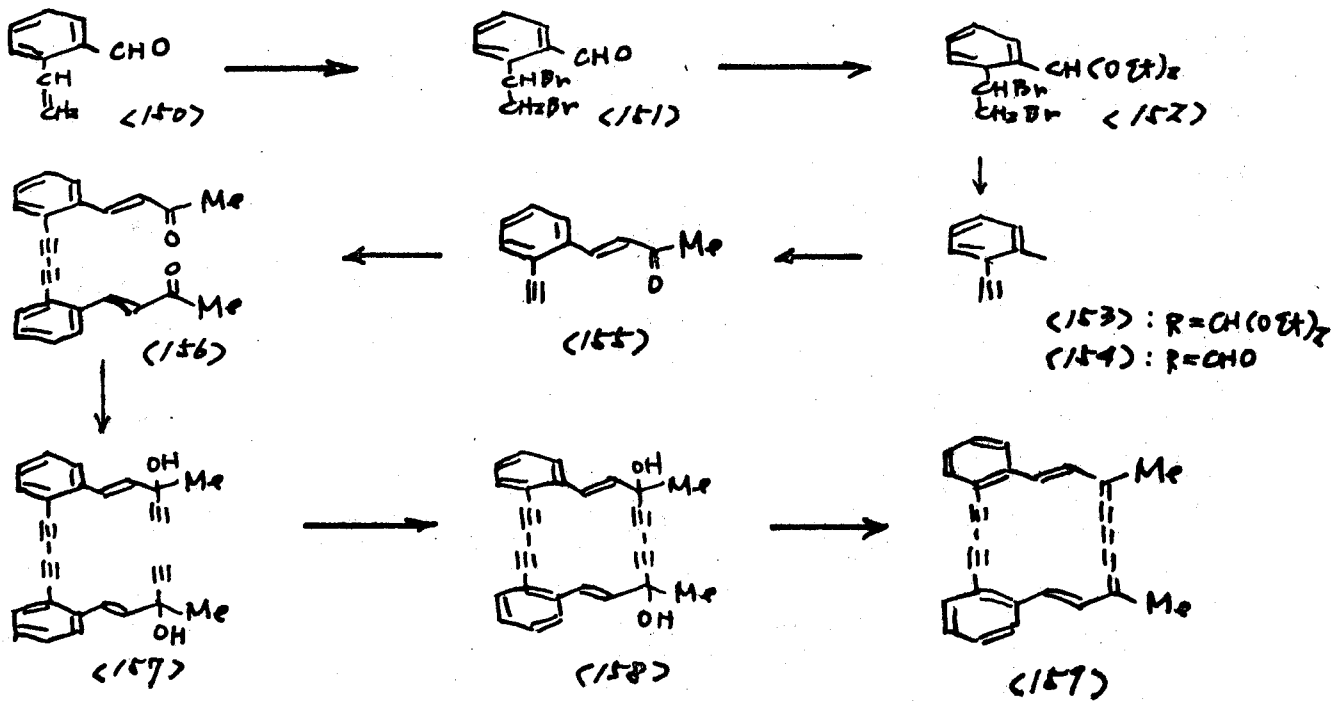


(148) (149) (18)

*The empirical resonance energy of [18]annulene(16) was determined from the heat of combustion, and found to be 100 ± 6 kcal/mol. Recently the other detailed study was reported[93], and showed that the resonance energy in this aromatic molecule cannot be greater than 19 kcal/mol.

1,8-Didehydro[14]annulenes seem to be an appropriate system for the examination of the effect of fused benzenoid nuclei, because the didehydroannulenes have been found to be highly stable, entirely planar and strongly aromatic.

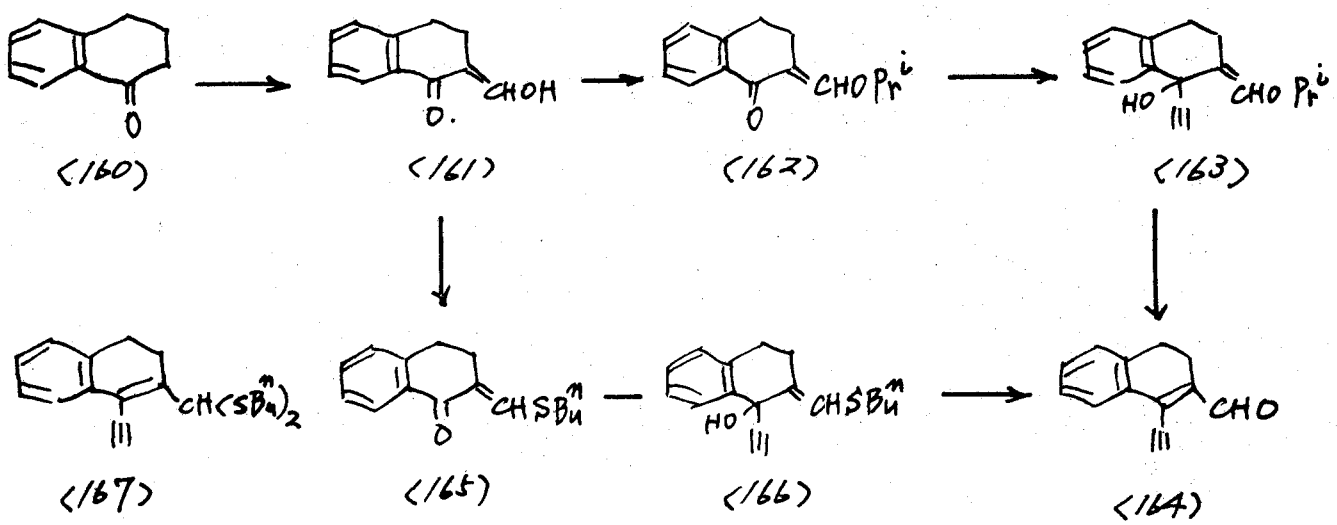
1,3,10,12-Tetradehydro[18]annulenes as described previously are analogue of the didehydro[14]annulenes, and an approach to dibenzotetradehydro[18]annulene was done by Ojima, Yokomachi and Yokoyama (shown in Scheme XXI)[94]. The reductive dehydroxylation of cyclic glycol(158) thus prepared was effected by use of stannous chloride in concentrated hydrochloric acid to give a very unstable compound. The substance could be kept at room temperature only in relatively diluted solution for less than half an hour. Unfortunately, because of its extreme instabilility, the n.m.r. spectrum of the product could not be measured.



Scheme XXI

The resonance energies of naphthalene and 1,2-dihydronaphthalene have been estimated to be 61 kcal/mol and 40 kcal/mol, respectively[95]. Therefore, destruction of one benzene system in naphthalene nucleus to form 1,2-naphthoquinone type structure may require about 21 kcal/mol(61-40 = 21 kcal/mol). This energy should be much less as compared with the energy of transformation of benzene into o-quinoid structure(ca. 36 kcal/mol). Taking this into consideration, we have carried out the synthesis of didehydro[14]annulene annelated with two naphthalene nuclei.

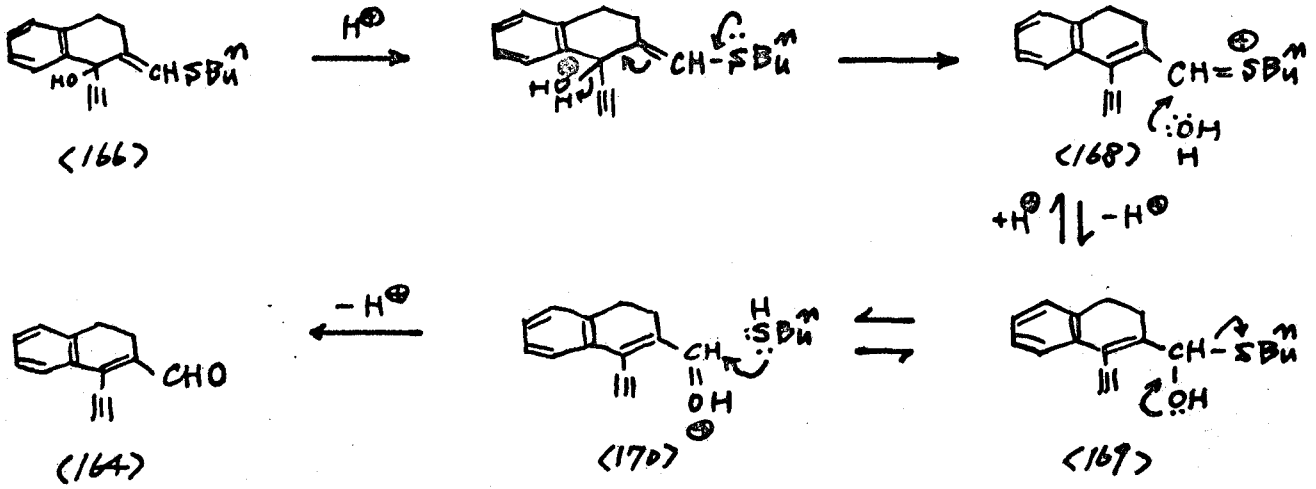
1-Ethynyl-2-naphthaldehyde(173), a key intermediate in this synthesis, was unknown and difficult to derive from other naphthalene derivatives by conversion of subsituent or by introduction of groups into naphthalene nucleus. Therefore, we attempted to synthesize dihydronaphthalene-aldehyde(164), which might be converted into naphthalene-aldehyde(173). Additionally, bis(dihydronaphtho)-didehydro[14]annulene(180) could be easily obtained by transformation of the aldehyde(164) in the usual way.



(160) (161) (162) (163)

(167) (165) (166) (164)

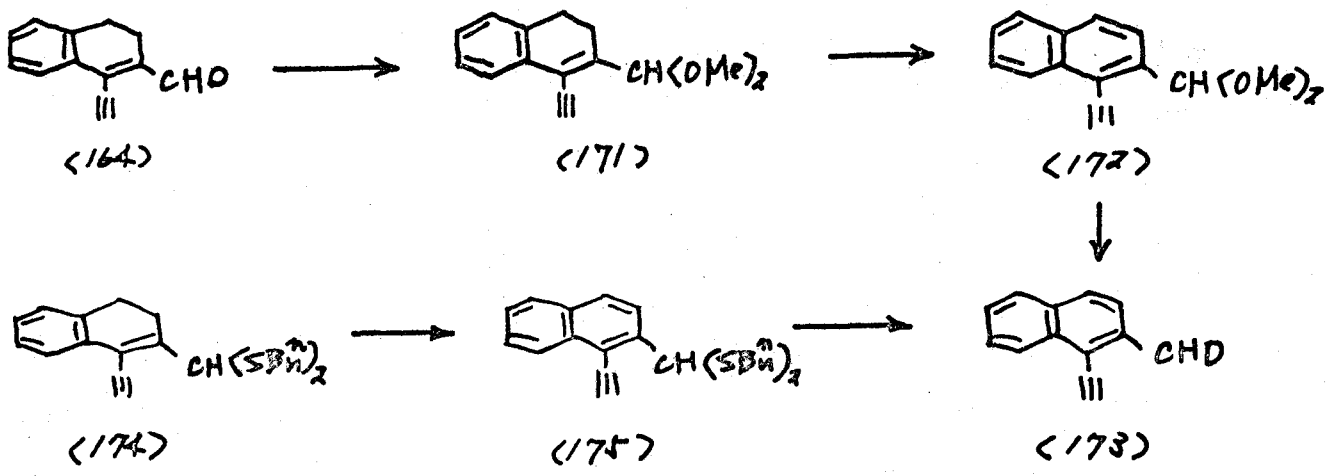
Scheme XXII



Scheme XXIII

Condensation of tetralone(160) with ethyl formate gave 2-hydroxymethylenetetralone(161) in a 88.6 % yield. 2-Isopropoxymethylenetetralone(162) was prepared by the reaction of isopropyl iodide with (161), and ethynylated with lithium acetylide-ethylenediamine complex to give ethynyl alcohol(163). (163) was treated without purification with dilute sulfuric acid to give brown oily products. Isolation of (163) was carried out by column chromatography on silica gel to give (164) in a poor yield. An alternative synthesis of (164) was therefore investigated. This proceeded from enolthioether(165), which was prepared from 2-hydroxymethylenetetralone(161) by the reaction of n-butylmercaptan[96]. Sulfur atom stabilizes a cationic center more than oxygen atom does, and would be expected to facilitate the hydrolysis of ethynyl alcohol. Enolthioether(165) was ethynylated with lithium acetylide-ethylenediamine complex to give ethynyl alcohol(166). As we would expect, (166) was hydrolyzed with ease. Treatment of (165) with lithium acetylide-ethylenediamine and subsequent hydrolysis with dilute sulfuric acid aldehyde(164) in a 32.5 % yield and thioacetal(167)

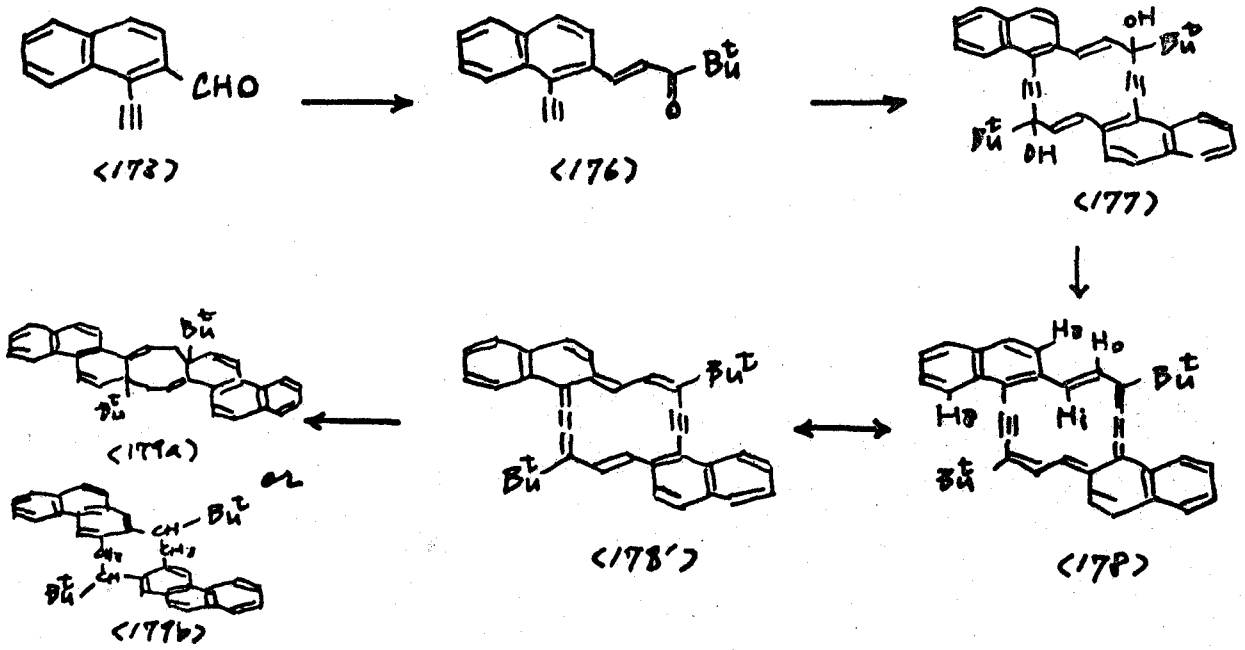
in a yield of 40.8 %. A possible mechanism was illustrated in Scheme XXIII. In this case, cation(168) is much more stable than cation (170), and thioacetal(167) was produced stoichometrically. Ethynylation of (165) followed by treatment with n-butylmercaptan in the presence of p-toluenesulfonic acid to afford ethynylthioacetal (167)(indistillable yellow liquid, 97 % based on (166)).



Scheme XXIV

1-Ethynyl-2-naphthaldehyde(173), the key intermediate of the synthesis of dinaphthodidehydro[14]annulene, was obtained shown in Scheme XXIV. First dehydrogenation of aldehyde(164) with DDQ (dichlorodicyanoquinone) was attempted to transform into (173) because of its simplicity. But the reaction was slow and needed higher temperature to result in the decomposition of (164). Next dimethyl acetal derived from (164) was dehydrogenated with DDQ. It proceeded at room temperature and gave the desired naphthalene-acetal(171) as crystals only in a low yield. Finally, dehydrogenation of thioacetal(174) with DDQ was successful to obtain naphthalene derivative (175). Since naphthalenethioacetal(175) contained ethynyl group, in order to hydrolyze (175) usual heavy metal salts, i.e., cupric

chloride, mercuric chloride and mercuric oxide could not be used. Quite recently, convenient method was reported to hydrolyze thioacetal[97] with methyl iodide-aqueous acetonitrile. By use of this method, (175) was hydrolyzed to give the desired aldehyde(173, yellow plates) in a 37 % yield based on (174). 1-Ethynyl-2-naphthaldhyde(173) was converted into t-butylketone(176), pale yellow leaflets, in a yield of 39.2 %, by the condensation with pinacolone. A solution of (176) in tetrahydrofuran was added to a stirred suspension of potassium hydroxide in liquid ammonia. The reaction mixture was worked up by usual way to give cyclic glycols(177), colorless crystals, m.p. 279.0-279.5°C(dec.), Mass(m/e) 524 M^+, Calcd. for $C_{38}H_{36}O_2$, in a yield of 90 %.



Scheme XXV

Development of deep blue violet color was observed on addition of finely powdered stannous chloride dihydrate to a solution of (177) in ether or tetrahydrofuran saturated with hydrogen chloride. It was found that the deep blue violet solution was fairly unstable, and rapid fading of the color was observed at room temperature. The solution was also sensitive to oxygen even at -78°C. However, in the absence of oxygen, the solution could be kept without appreciable color change at -78°C for a day. Although all attempts to isolate the reaction product were unsuccessful, the formation of dinaphtho-di-t-butyl-didehydro[14]annulene(178) could be confirmed on the basis of electronic and n.m.r. spectroscopy. The reactions and spectroscopic measurements were performed under argon atmosphere using degassed solvent. Accurately weighed (177) dissolved in tetrahydrofuran was mixed at -20°C with stannous chloride dihydrate and the same solvent saturated with hydrogen chloride. The resulting solution was directly subjected to the measurement of electronic spectrum at -78°C. The electronic spectrum was found to be closely related with that of bis(dihydronaphtho)-di-t-butyl-didehydro[14]-annulene(180)*, indicating the formation of (178)(Fig. 14). The ε-value of (178) were calculated assuming quantitative conversion of (177) into (178).

Deuteriotetrahydrofuran and (177) placed in a n.m.r. tube were mixed at -78°C with a solution of stannous chloride dihydrate in the same solvent saturated with deuterium chloride. The mixture was shaken at -30°C for 5 minutes and used for the measurement of 100 MHz n.m.r. spectra at -54°C(Fig. 15)(see Experimental). The

*The synthesis and properties of (180) will be reported elsewhere[98].

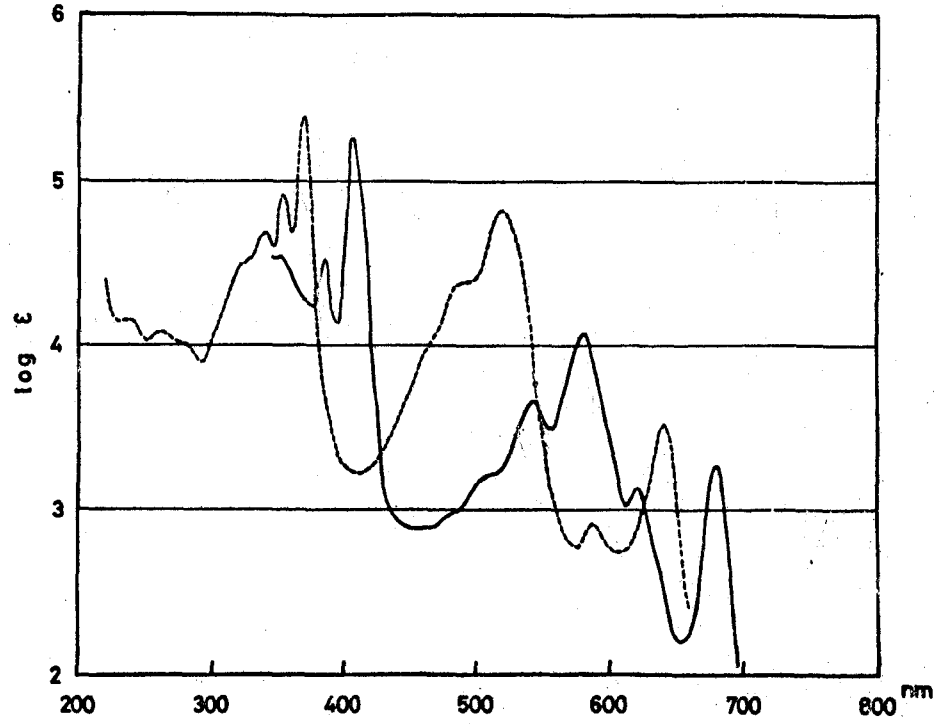


Fig. 14. Electronic spectra of (178) and (180)

—— (178), ---- (180)

doublets at τ -0.22(J=15 Hz, 2H) and τ 13.45(J=15 Hz, 2H) could be assigned to outer protons(H^o) and inner protons(H^i), respectively. The assignment could be further confirmed by a double resonance technique, i.e., the doublet at τ -0.22 changed to a sharp singlet on irradiation at τ 13.45. The doublets at τ 0.46(J=10 Hz, 2H) and τ 0.29(J=8Hz, 2H) were assigned to H^{3*},H^{8*} and the sharp singlet at τ 7.89(18H) to t-butyl protons, respectively. The n.m.r. spectrum clearly indicates the induction of a diamagnetic ring current

$^*H^3$ and H^8 were confirmed by a double resonance technique(see Experimental).

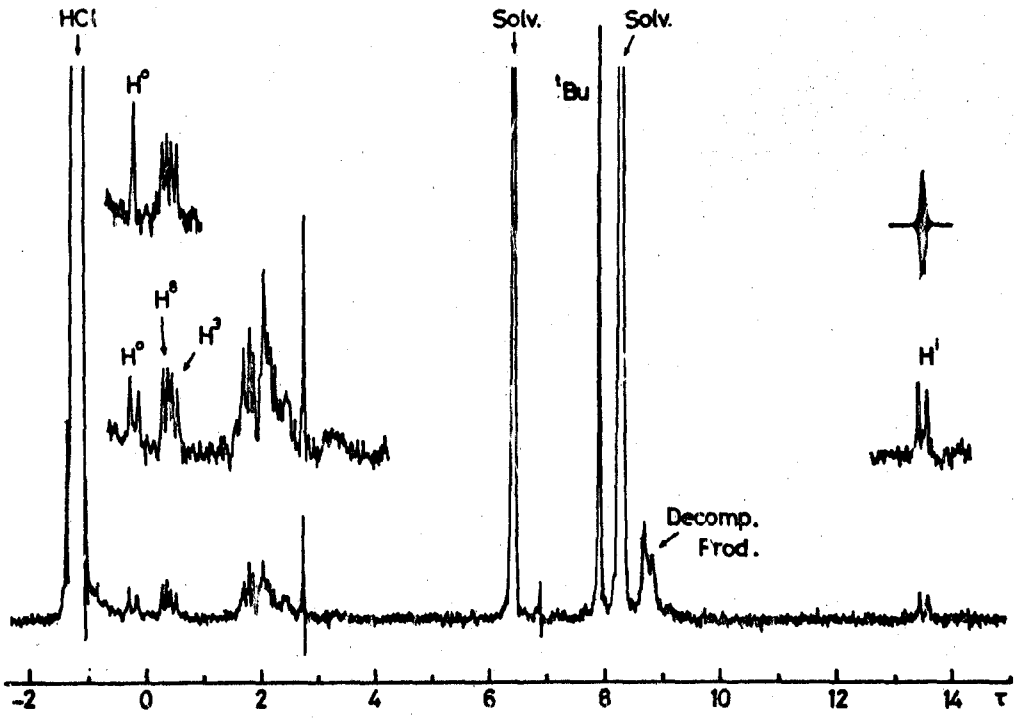


Fig. 15. The n.m.r. spectra of (178) prepared 2.0mg of (177) and deuteriotetrahydrofuran containing DCl (-54°C, 100MHz)

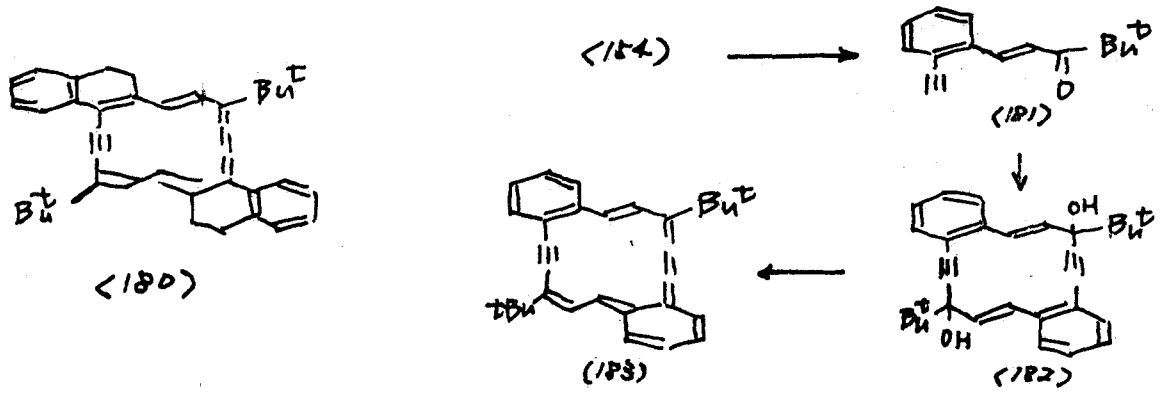
in the annelated dehydroannulene ring (178) ⟷ (178').

The dinaphthodidehydro[14]annulene(178) can be written in the two Kekulé-type structures(178 ⟷ 178'). Though the structure(178) contains an o-naphthoquinone-skeleton which causes the loss in energy(ca. 21 kcal/mol), the annulene gains the resonance energy of didehydro[14]annulene-form estimated about 20 kcal/mol. Cosidering this equality of energy, dinaphthodidehydro[14]annulene(178) is an appropriate annelated system. Because the difference in energy between two forms(178 ⟷ 178') is nothing, it is contemplated that the annelated annulene(178) should show definite induction of

diamagnetic ring current in n.m.r. spectrum. To our knowledge, this is the first example of diatropic non-bridged neutral annulated annulene*.

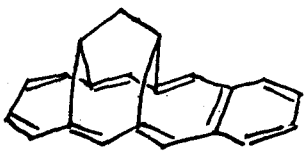
Reduction of (178) gave the unsaturated hydrocarbon, which has proved to be the structure (179). Further characterization of this compound is currently under way.

Attempted synthesis of dibenzo-didehydro[14]annulene (183) was carried out by the sequence shown in Scheme XXVI by Yasuhara and Nakagawa[99]. The annulene was found to be the most unstable compound of our synthesized annulenes. The solution of (183) is dark blue. Since it showed no signals in e.s.r. spectrum, (183) does not adopt a radical structure. The investigation to measure the u.v. and n.m.r. spectra is in progress.



Scheme XXVI

*The 14 π-electron system in 3,4-benzo-1,6:8,18-propanediylidene[14]annulene (184) has been reported to be diatropic[100].



(184)

X. RESULT AND DISCUSSION.

X-1. DEFINITION OF AROMATIC CHARACTER.

The original definition equating aromaticity with odour is only of historical interest. The 'clasical' definition, considered acceptable until fairly recently, equated aromaticity with benzene-like stability and chemical behavior. A definition of aromatic character based on criteria of chemical reactivity is inherently unsound, based as it is on the difference in free energy between the initial molecule and that of the transition state of the reaction which ensues.

As mentioned previously, some theoretical justification of benzene-like stability was gained in the principle of the aromatic sextet[4] and subsequently the Hückel's rule[5]. Structural factors became the primary consideration for the basis of classification and associated physical properties used as a measure of gradations in aromatic character. It has been considered increasingly desirable to attach a quantitative criterion to aromatic character in oredr to avoid the exceptions which inevidently arise from the use of empirical considerations such as symmetry properties.

As many authors have been described, the definition of aromatic character is bound up with attempts to classify cyclic, conjugated systems. The past decade has been marked by great progerss in the synthesis of non-benzenoid aromatic systems, which has robbed the special position of classical aromatic substance, benzene, and has necessiated a wider and deeper definition of the aromatic concepts. It is unfortunately true that whichever of the classifications we chose, some anomalies can be

pointed out, and thus generation of a definition of aromatic character, which will embrance all of the requirements set out, is difficult, if not impossible, to achieve.

The molecular orbital definition of aromatic character has been considered the most favourable and as a consequence the attempts to attach quantitative signification to the aromaticity phenomenon have been based on the maasurment of physical properties which can be accounted for in terms of the π-electron delocalization. Thus those properties depend upon of delocalization of a cyclic conjugated system and permit statements concerning the ground state.

Spectroscopically, aromatic compounds are not only characterized by the shift of their absorption to longer wavelengths compared with olefinic compounds (a property of the excited state) but also by the anisotropy of their diamagnetic susceptibility, by changes in bond lengths and charge distribution related to the delocalization of the π-eleotrons, and by their resonance energy.

The proposals for establishing n.m.r. ring current as a criterion of aromaticity has emerged subsequently[101),102),103)]. The ring current model and its bearing on diamagnetic anisotropy and chemical shifts in aromatic systems provides no exception to this general trend. Perhaps the primary feature revealed in some reservations is the recognition that while the ring current model provides a reasonable amount for the quantitative trends in the chemical shifts of a variety of molecules, it does not permit assertions concerning the degree of aromatic character in these systems.

Ultimately, it is apparent that the physical properties used must be chosen to fit the compound in question and that the appropriate model compounds must be available for theoretical and experimental comparison.

X-2, THE THERMODYNAMIC CRITERION.

THE RESONANCE ENERGY OF THE ANNULENES.

Both by Pople's self-consistent field (SCF) molecular orbital (MO) theory[104] and by Hückel theory [5], provided the variation of the core resonance integrals β^{0}_{ij} or the exchange integrals βij with bond length are taken into account by an interactive procedure[104)105], the classical linear even polyenes might be represented in terms of localized 'single' and 'double' bonds. In other words, if we assume that σ-bond energy is an additive property of the number of formal C_{sp_2}-C_{sp_2} single and double bonds and C_{sp_2}-H bonds, this means that the total π-energy E_π of these molecules can be written:

$$E_\pi = n \cdot E^s_\pi + n' \cdot E^d_\pi \qquad (1)$$

where n and n' are the number of CC 'single' and 'double' bonds respectively, E^s_π and E^d_π being their π-energies.

The improved Pople method[106] were applied to the calculation of the resonance energy in the different members of the annulene series up to $C_{30}H_{30}$[107]. In this series, we have the same number (n) of formal 'single' and 'double' bonds; accordingly, the π-energy of the 'localized' structure may be written:

$$E_\pi(\text{loc}) = n \cdot (E^s_\pi + E^d_\pi) \qquad (2)$$

Thus, the π-contribution to the resonance energy $E_R(\pi)$ of the

[2n]annulene is:

$$E_R(\pi) = E_\pi - E_\pi(loc) \qquad (3)$$

where E_π is the total molecular π-energy calculated by the improved Hückel theory for this annulene. Table 8 lists resonance energies calculated in this way for the series of compounds investigated by the improved Hückel method. Fig. 16 shows the plot obtained for $E_R(\pi)$ as a function of the dimension of the ring[N].

Obviously, the thermodynamic criterion devides the annulenes into two well separated series: the $(4n + 2)$ π-electron ring systems with stabilizing resonance energy (positive values of $E_R(\pi)$ expressed in $|\beta|$-units) and the $(4n)$ π-electron ring systems showing decreased stabilization as compared with the 'localized' model compounds.

Table 8, π-Electron Contribution to the Resonance Energy of Annulenes according to Breslow's and Dewar's definition.

[N]annulene	$E_R(\pi)$	[N]annulene	$E_R(\pi)$
4	-0.8588	18	0.1752
6	0.3992	20	-0.1160
8	-0.4148	22	0.1616
10	0.2628	24	-0.0760
12	-0.2550	26	0.1556
14	0.2024	28	-0.0452
16	-0.1704	30	0.1538

X-3, MAGNETIC BEHAVIOUR AS A CRITERION OF AROMATICITY. MAGNETIC ANISOTROPY AND N.M.R. CHEMICAL SHIFTS.

The theoretical investigation of the magnetic properties of annulenes (and benzo-annulenes) other than benzene and benzenoid hydrocarbons has received attention only in very recent years. First it was pointed out by Longuet-Higgins[108] and Nakajima and Kohda[109] that, when a cyclic conjugated molecule is placed in an external magnetic field, the π-electronic ring current is the difference between a diamagnetic part depending only on the electonic structure in the ground-state of the molecule, and a paramagnetic part which is a sum of contributions implying excited states. The paramagnetic part will be particularly large if the molecule possesses suitable very low-lying excited states. This is exactly the situation obtained by introducing the Jahn-Teller effect in the series of [4n]annulenes. As a result, paramagnetic ring currents should occur in these molecules, which should give rise to a positive susceptibility exaltation or anisotropy.

Under these circumstances, the usual diamagnetic n.m.r. rules have to be reversed: protons outside the ring will show an increased shielding relative to the 'olefinic' reference compound, and those inside the ring should be deshielded. Similar conclusions were obtained by Pople and Untch[110] and by Baer, Kuhn and Regel[111].

The influence of bond alternation on the magnetic properties of the annulenes was investigated by several authors. For all sizes of rings, the theory predicts that the magnitude of the calculated ring current should be partially quenched if bond alternation occurs. In the [4n + 2]as well as in the [4n]annulene

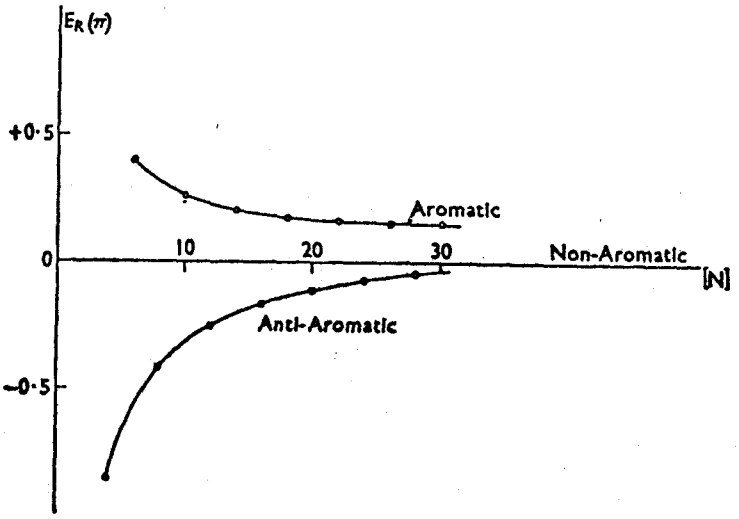


Fig. 16. π-Electron contribution to the resonance energy in the annulene series. Reprinted from "Topics in Carbocyclic Chemistry", Vol. 1, Logos Press Limited, London, p.275 (1969).

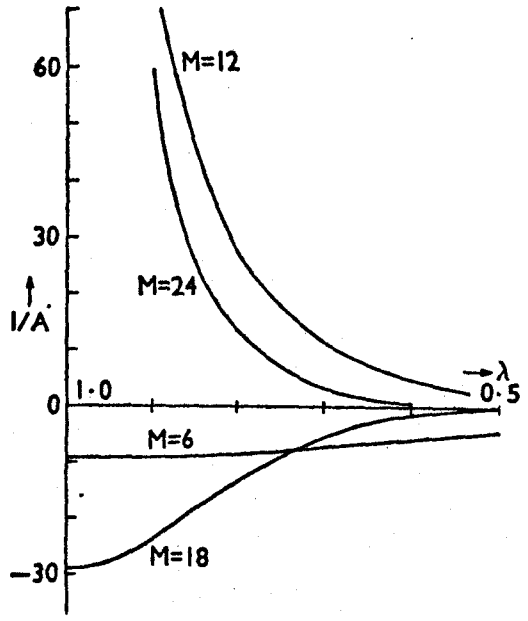


Fig. 17. Dependence of ring-current on alternation parameter for some annulenes, $J_\mu = A \cdot f(N,\lambda)$. Reprinted from the J. Amer. Chem. Soc., 88, 4811 (1966).

series, it appears that the larger the ring, the more effective is the quenching due to a given amount of alternation. This is very clearly shown in Fig. 17, where the variable part of the ring current J_μ is plotted for certain annulenes as a function of the bond alternation parameter $\beta_1/\beta_2 = \lambda$, β_1 and β_2 being the exchnge integrals of the 'long' and 'short' bonds respectively. As a result, the calculated contribution χ_π of the π-electrons to the diamagnetic susceptibility of the annulenes becomes negligible if bond alternation is significant, and the chemical shifts for the inner and outer protons tend rapidly to the 'olefinic' frequency[61] (Table 9).

Table 9. Calculated Proton Chemical Shifts in $C_{18}H_{18}$ and $C_{30}H_{30}$ as a function of bond alternation *

	$C_{18}H_{18}$			$C_{30}H_{30}$			
λ	inner H	outer H	Δ**	inner H	outer H (corner)	outer H (edge)	Δ**
1.0000	-7.44	10.42	17.86	-12.42	13.26	13.26	26.41
0.9657	-7.21	10.27	17.48	-11.43	12.88	12.88	25.00
0.8107	-0.85	8.28	9.13	2.45	7.58	7.58	5.25
0.6500	4.60	6.59	1.99	5.90	6.21	6.21	0.31
0.4903	5.98	6.21	0.23	6.13	6.13	6.13	0.00

* The chmical shift is expressed in ppm relative to TMS; the 'olefinic' resonance frequency is evaluated at 6.129 ppm and the ring current effect for the benzene protons is assumed to be 1.15 ppm.

** $\Delta = \tau(\text{inner H}) - \tau(\text{outer H})$.

The table shows that the magnetic properties of the annulenes are exceedingly sensitive to the ammount of distortion from the symmetrical structure. Neverthless, several authors have used proton n.m.r. spectroscopic arguments in order to decide whether or not an uncharged cyclic conjugated molecule is aromatic. The presence of an induced diamagneic ring current (as in benzene), detected by n.m.r. spectroscopy and susceptibility measurments, should be used as a criterion of aromatic character. Thus [4n + 2]annulenes should be aromatic and will show benzene-like magnetic properties. Fig. 18 shows the evolution of the ring-currents per unit benzene area as a function of ring size; qualitatively, the conclusions concerning the aromaticity of these compounds are in excellent agreement with those obtained from the thermodynamic criterion (see Fig. 16).

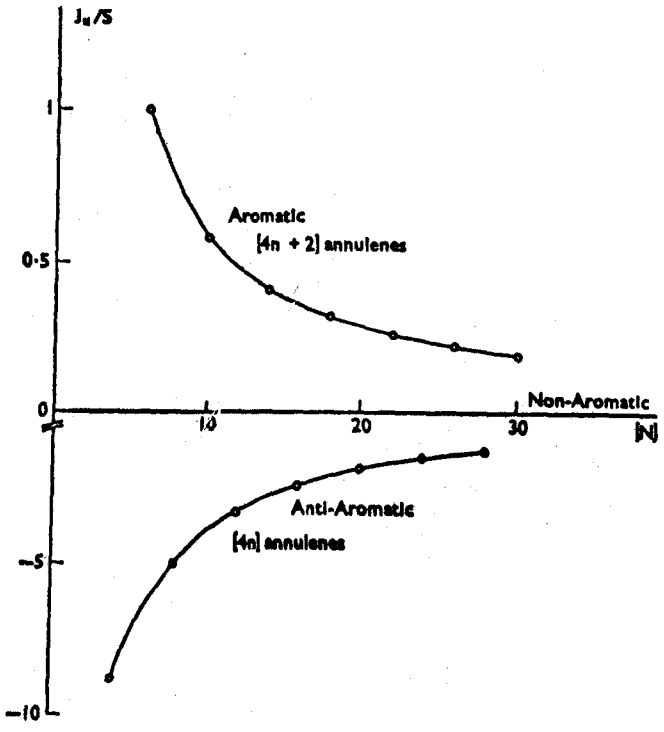
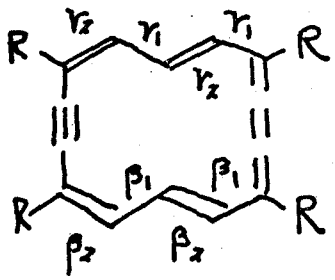


Fig. 18. Ring current intensity per unit benzene area ($J\mu/S$) in the annulenes as a function of ring size. Printed from "Topics in Carbocyclic Chemistry", Vol. 1, Logos Press Limited, London, p.289 (1969).

X-4, AROMATICITY IN THE DEHYDROANNULENES.

We have mentioned the synthesis of tetradehydro[4n + 2]- and didehydro[4n + 2]annulenes containing acetylenic and cumulenic linkages in the cyclic system. These annulenes possess the essentially same molecular geometry and the same degree of planarity and , consequently, the approximately same circumstances in the magnetic field of n.m.r. spectroscopy. Therefore, we have assumed the difference of chmical shifts between inner and outer protons is an index of the magnitude of the ring current (p.51, Table 5).

We consider that the single and double bonds are alternately of length r_1 and r_2 ($r_1 \geq r_2$) with resonance integrals β_1 and β_2, respectively ($\beta_1 \leq \beta_2 < 0$) shown bellow:



$$\beta_1 \cdot \beta_2 = \beta^2$$

$$\frac{\beta_2}{\beta_1} = \lambda$$

If all the bonds were equal in length, we should have $r_1 = r_2$, but we are allowing for the possibility of a twofold alternation. (Higher-oder periodicities could conceivably occur, but seen unimportant).

1,8-Didehydro[14]annulene (26) has been proved to be a highly planar and delocalized molecule on the basis of X-ray crystal structure analysis (p.11, Fig. 2); r_1 and r_2 is equal. A quite recent work on bond alternation of annulenes showed that λ value of (26) is 0.892[113]. In this caluculation the Biot-Savart low was used to caluculate the ring current of proton

chemical shifts. We will estimate the resonance energy of tetra-t-butyldidehydro[4n + 2]annulenes.

We will assume that a λ value is proportional to the ring current, since the curve of λ vs. J_μ gives an approximately linear relationship between λ = 0.65 and 0.95 (fig. 17). The λ value of nonaromatic annulene is estimated by extrapolation to be 0.60 (estimated on the basis of the curve, M = 18, in Fig. 17). We chose the glycol (64) as nonaromatic model compound*. Although the glycol is not annulene and perhaps not completely planar molecule, this compound is equipped with roughly same molecular circumstances in the magnetic field of n.m.r. spectroscopy.

Table 10 shows the bond alternation factor (λ) in tetra-t-butyldidehydro[4n + 2]annulenes. We calculated the λ value based on the relationship written as follows.

$$\lambda = k\Delta' \qquad (4)$$

Similarly the λ value in tetra-t-butyltetradehydro[4n + 2]annulenes is shown in Table 11. λ vs. Δ' plot displays downward curvature and eventually approaches 0.6 (Fig. 18).

* By Haddon's definition[113], a non-aromatic annulene in the absence of steric inhibition of resonance is assumed to have the same degree of bond alternation (and bond lengths) as a classical polyene (neglecting end effects). A similar approach is adopted by Binsch, Heilbronner and Murrell[114]. A classical polyene is considered to be a molecule for which only one unexcited resonance structure can be written.

Table 10. The Bond Alternation Factor (λ) vs. in Tetra-t-butyl-didehydro[4n + 2]annulenes.

	[4n + 2]	Δ	Δ'	λ
(64)	glycol	-1.33	0.00	0.600
(67)	14	13.76	15.09	0.892
(71)	18	12.80	14.13	0.873
(83)	22	9.58	10.91	0.811
(84)	26	6.13	7.46	0.744
(91)	30	4.00	5.33	0.703

* N.m.r. spectra were measured in $CDCl_3$ at room temperature except for (91), which was measured at -60 °C.

** $\Delta = \tau$(inner H) -τ(outer h). $\Delta' = \Delta + 1.33$.

Table 11. The Bond Alternation Factor (λ) vs. in Tetra-t-butyl-tetradehydro[4n +2]annulenes.

	[4n + 2]	Δ	Δ'	λ
(36)	18	14.93	16.26	0.914
(50)	22	13.11	14.44	0.879

* N.m.r. spectra were measured in $CDCl_3$ at room temperature.

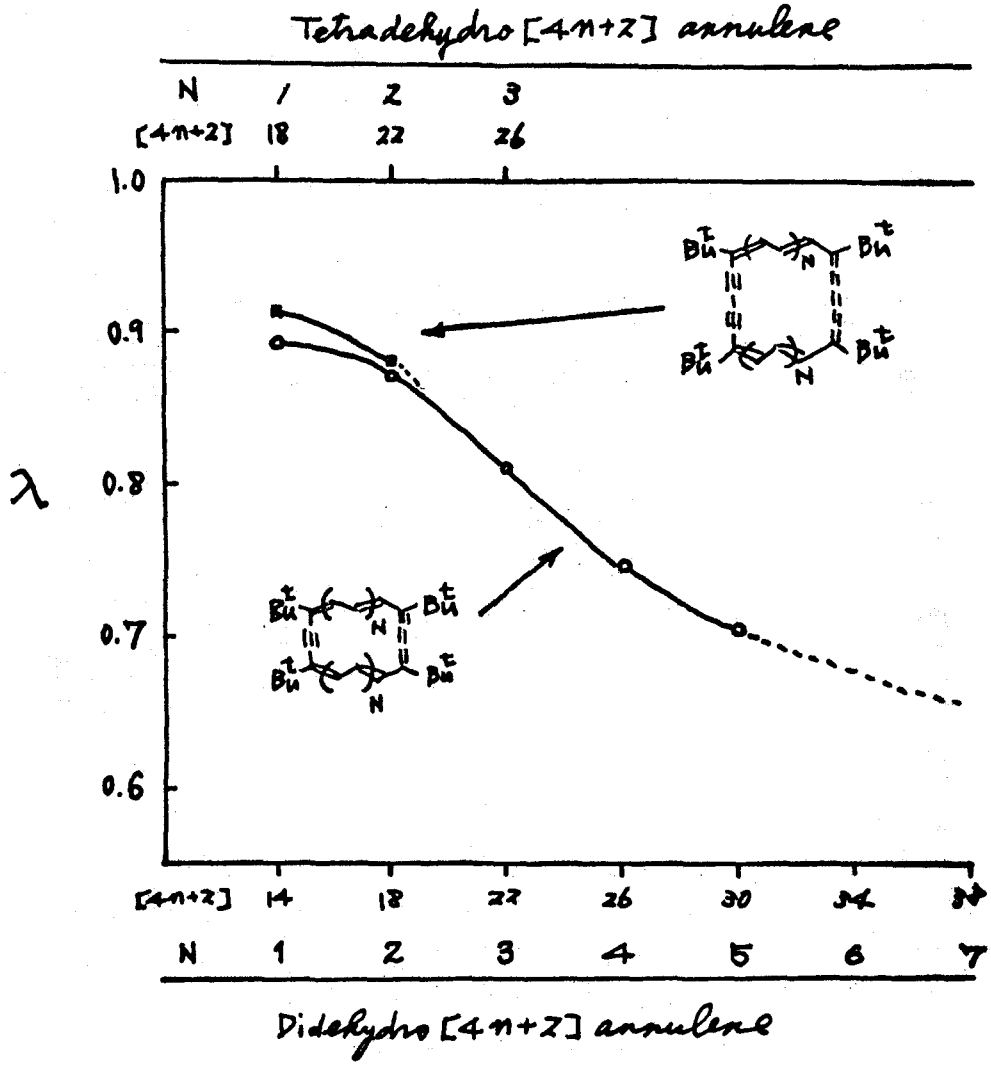
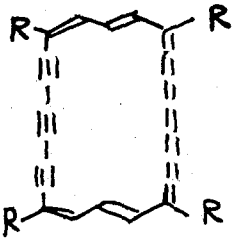
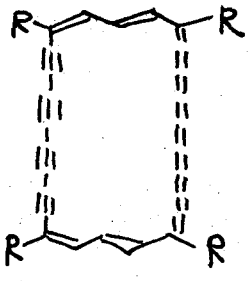


Fig. 19. Relation between bond-alternation parameter (λ) vs. ring size and N.



Hexadehydro-[22]annulene

(185)



Octadehydro-[26]annulene

(186)

As the original suggestion by Dewar and Gleicher[60] that [26]annulene should be the first non-aromatic [4n + 2]annulene (on the basis of a negative resonance energy), it is by no means clear how one could test such a statement. Haddon has indicated the possibility of presence of "non-aromatic ring currents" (although very low temperature may be needed for observation[113]), and stressed that the magnetic criterion does not constitute a direct experimental test for the presence or absence of resonance energy; as pointed ont by Pople and Untch[110], ring currents (if present) will always parallel the Hückel's rule.

Fig. 19 may suggest that the extent of bond alternation in the [4n + 2]annulenes is due to the number of the double bonds (N) which quench the resonance between two Kekulé structures. It is contemplated that if it is possible to synthesize hexadehydro-[22]annulene or octadehydro[26]annulene, these annulenes show larger ring current, and there is no limit applying Huckel's rule*. However, these compounds can be very unstable and there is a practical limit to examine the Hückel's rule.

* For slight bond alternation the magnitude of the ring current increases with ring size. However, for the bond alternation expected at the non-aromatic limit, the ring current will die away quite rapidly with increasing ring size.

Experimental Section

General Procedures

All the melting points were determined on a Mettler EP2 apparatus and uncorrected. Infrared spectra were measured on a Hitachi EPI-2 or EPI-G3 spectrophothometer(s=strong, m=medium, w=weak); only significant maxima are reported. Electronic spectra were measured on a Hitachi ESP-3T spectrophotometer; shoulder was indicated by an asterisk. N.m.r. spectra were measured on a Varian A-60(60MHz) or XL-100(100MHz) spectrometer using tetramethylsilane as an internal standard and recorded in τ-unit. Mass spectra were measured on a Hitachi RM-50 spectrometer operating at 70 eV. T.l.c. was performed on Kieselgel GF_{254} (Merk) plates. Silica gel(Merk, Kiesel gel 60) or alumina(Merk act. II-III) were used for column chromatography, unless stated otherwise.

I. Synthesis of 5,11,16,22-tetra-t-butyl-1,3,12,14-tetradehydro[22]annulene(50).

5-Phenyl-2,4-heptadien-6-ynal(43a). a) By the Modified Wittig Reaction: Sodium hydride dispersion in mineral oil (50%, 1.84g, 0.383mol) was washed under nitrogen atmosphere with petroleum ether(3 ml×4). The sodium hydride, after being dried in vacuo, was mixed with tetrahydrofuran(10 ml) and a solution of diethyl 2-(cyclohexylimino)ethylphosphonate[46](10.0g, 0.0383 mol) in the same solvent(30 ml) was added under ice-cooling and the mixture was stirred for 15 min. A solution of (41a)(2.00g, 0.0128 mol) in the same solvent(15 ml) was then added at -15°C.

The mixture was stirred at -10--15°C for 15hr, then poured onto ice-water, and extracted with ether(30 ml × 3). After being washed and dried, the extract was evaporated under reduced pressure to yield a crude mixture containing (42a), dark brown oil, 8.07g. The material was dissolved in benzene(60 ml) and mixed with 1% aqueous solution of oxalic acid(180 ml). After being stirred for 15 hr at 20-25°C, the organic layer was separated and the aqueous layer was extracted with dichloromethane(20 ml × 2). The combined organic layer was washed and dried. The residue obtained by evaporating the solvent was chromatographed on silica gel. Elution with carbon tetrachloride and dichloromethane afforded (43a), yellow crystals(from carbon tetrachloride-methanol), mp 69.5-70.3°C, 1.18g(51%), infrared spectrum($CHCl_3$): 3300m(≡CH), 2085w, 2710w (CHO), 1686vs(C=O) cm^{-1}, n.m.r. spectrum(CCl_4): τ 0.33(d, J=7.5 Hz, 1H, CHO), 2.06-2.95(m, 8H, phenyl and olefinic), 3.75(dd, J=7.5 and 15 Hz, α-position of CHO), 6.32(s, 1H, ≡CH).

Found: C, 85.73; H, 5.48%. Calcd for $C_{13}H_{10}O$: C,85.69; H, 5.53%.

b) By the Isler's Method: 3-Phenyl-2-penten-4-ynal Diethyl Acetal(44a). A solution of p-toluenesulfonic acid monohydrate (0.385g, 2.02 mmol) in ethanol(2 ml) was added to a mixture of (41a)(3.852g, 24.7 mmol) and ethyl orthoformate(13.25g, 89.4 m mol). After being stirred for 24 hr at room temperature, the reaction mixture was chilled in an ice-bath and then poured onto ice-water containing sodium hydrogen carbonate, and extracted with ether. The extract, after being washed and dried(potassium carbonate), was concentrated under reduced pressure. The residue was distilled in vacuo to yield (44a), 4.948g(87%), bp 93-96°C

/0.005 mmHg, Mass(m/e): 230(M^+), infrared spectrum(CCl_4): 3321s (≡CH), 2090vw(-C≡C-), 1615m(C=C), 1000-1150vs(C-O-C) cm^{-1}. N.m.r. spectrum(CCl_4):τ2.31-2.82(m, 5H, phenyl), 3.62(d, J=7.5Hz, 1H, olefinic), 4.60(d, J=7.5Hz, 1H, acetal), 6.38(q, J= 7.0Hz, 2H, CH_2), 6.42(q, J=7.0Hz, 2H, CH_2), 6.70(s, 1H, C≡CH), 8.82(t, J= 7.0Hz, 6H, CH_3).

5-Phenyl-2,4-heptadien-6-ynal(43a). A solution of borontrifluoride etherate(72mg) in benzene(1 ml) was added to a solution of acetal(44a,16.98g, 0.0737 mol) in the same solvent(23 ml) at 40°C and a solution of ethyl vinyl ether(6.233g, 0.0864 mol) in the same solvent(10 ml) was slowly added at 40-45°C. The mixture was kept at the same temperature for 4 hr and then allowed to cool on standing. Finely powdered potassium carbonate was added to the mixture. The filtrate was concentrated under reduced pressure to give crude (45a), brown oil, 22.68g. A mixture of crude(45a), tetrahydrofuran(187 ml) and 3M hydrochloric acid (125 ml) was vigorously stirred at 25°C for 48 hr. The reaction mixture was extracted with ether. The extract, after being washed and dried, was concentrated under reduced pressure. Oily residue containing crystals was purified by a chromatography on silica gel to yield pure (43a), 8.168g(61% based on (44a)).

3-t-Butyl-2-penten-4-ynal Diethyl Acetal(44b). A solution of t-butyl-β-chlorovinyl-ethynylcarbinol[43] 88.00g(0.510 mol) in dioxane(180 ml) was added to 4N sulfuric acid at 50°C under nitrogen atmosphere. The mixture was vigorously stirred at 50°C for 3 hr and then at 35°C for 26 hr. The mixture was allowed to cool on standing and the organic layer was separated. The aqueous layer

was extracted with ether(150 ml×3). The combined organic layer was washed successively with water, saturated sodium hydrogen carbonate solution and saturated sodium chloride solution, and dried over anhydrous magnesium sulfate. The residue obtained by evaporating the solvent in vacuo was distilled to yield crude (41b), 63.70g, bp 47-50°C/3 mmHg. To a solution of crude aldehyde (41b) in orthoethylformate(160 ml, 0.968 mol) was added a solution of p-toluenesulfonic acid monohydrate(6.00g, 0.0315 mol) in ethanol (2 ml). The solution was stirred at 30°C for 24 hr under nitrogen atmosphere and then chilled in an ice-bath. The reaction mixture was poured onto ice-water containing sodium hydrogen carbonate. The organic layer was separated and the aqueous layer was extracted with ether(100 ml×2). The combined organic layer was washed successively with saturated sodium hydrogen carbonate and sodium chloride solution, and dried over anhydrous potassium carbonate. The residue obtained by evaporating the solvent in vacuo was distilled to yield (44b), 84.11g(78.5% based on the carbinol), bp 78-79°C/3 mmHg, mass spectrum(m/e), 210(M^+), infrared spectrum (CCl_4), 3320m(≡CH), 2085vw(-C≡C-), 1628w(C=C), 1200-1000vs(C-O-C) cm^{-1}. N.m.r. spectrum(CCl_4), τ 4.24(d, J=7.5Hz, 1H, olefinic), 4.78(d, J=7.5Hz, 1H, acetal), 6.48(m, 4H, $-CH_2-$), 6.89(s, 1H, C≡CH), 8.83(t, J=7.0Hz, CH_3), 8.83(s, 9H, t-Bu).

Elemental analysis gave unsatisfactory result owing to extremely unstable nature of (44b) to hydrolysis.

5-t-Butyl-3-ethoxy-4-hepten-6-ynal Diethyl Acetal(45b).

A mixture of borontrifluoride etherate(20mg) in dry benzene(1 ml) was added to a solution of acetal(44b)(7.40g, 0.0352 mol) in dry

benzene(20 ml) at 40 °C. A solution of ethyl vinyl ether(2.79g, 0.0387 mol) in the same solvent(5 ml) was slowly added at 40 °C. The mixture was kept at the same temperature for 2 hr and then allowed to cool on standing. Finely powdered potassium carbonate was added to the mixture to afford a light yellow solution. The potassium carbonate was filtered off and washed with ether. The filtrate and washings were concentrated under reduced pressure. The residue was distilled in vacuo to yield (45b), 8.98g(90.4%), bp 110-111 °C/3 mmHg. Mass spectrum(m/e), 282(M^+), infrared spectrum(CCl_4), 3320m(≡CH), 2070w(-C≡C-), 1620w(C=C), 1150-1050 vs(C-O-C), n.m.r. spectrum(CCl_4), τ 4.36(d, J=9.0Hz, 1H, H^4= olefinic H), 5.42(m, 1H, H^1=acetal H), 5.64(m, 1H, H^3), 6.56 (m, 6H, O-CH_2-), 6.83(s, 1H, C≡CH), 8.30(m, 2H, H^2=-CH_2-), 8.85 (t, J=7.0Hz, 9H, CH_3), 8.85(s, 9H, t-Bu).

Found: C,71.89; H,10.61%. Calcd for $C_{17}H_{30}O_3$: C,72.30; H,10.71%.

5-t-Butyl-2,4-heptadien-6-ynal(43b). A mixture of t-butyl-ethoxyacetal(45b)(10.00g, 0.0354 mol), dioxane(60 ml) and 3N hydrochloric acid(50 ml) was vigorously stirred under nitrogen atmosphere at 50 °C for 3 hr and then 40 °C for 18 hr. The reaction mixture was chilled and the organic layer was separated and the aqueous layer was extracted with ether. The combined organic layer was washed successively with saturated sodium hydrogen carbonate and sodium chloride solutions, dried(Na_2SO_4) and evaporated under reduced pressure. Rapid distillation under nitrogen atmosphere through a short-path apparatus gave a yellow liquid (43b), 4.06g(70.7%), bp 60-70 °C/1.5 mmHg. Infrared spectrum(CCl_4),

3300m(≡CH), 2810w, 2730w(CHO), 1687vs(C=O), 1616s(C=C), 977s (trans-CH=CH-) cm^{-1}. N.m.r. spectrum(CCl_4), τ 0.46(d, J=7.5Hz, 1H, CHO), 2.47(dd, J=11 and 15Hz, 1H, β-position of CHO), 3.46 (d, J=11Hz, 1H, γ-position of CHO), 6.45(s, 1H, C≡CH), 8.81(s, 9H, t-Bu). Elemental analysis gave unsatisfactory result owing to unstable nature of (43b) to oxygen at room temperature. The yellow sample became a red viscous oil within a hour at room temperature, but could be kept for several days at -20 °C under nitrogen, and was best stored in ether solution at 0 °C.

2,4-Dinitrophenylhydrazone of the dienyne-aldehyde(43b). A solution of 2,4-dinitrophenylhydrazine(100mg, 0.50 mmol) in phosphoric acid(0.6 ml)-ethanol(0.4ml) was added to a solution of (43b)(88mg, 0.54 mmol) in ethanol(7 ml) and the mixture was allowed to stand overnight at room temperature. Red crystals deposited were filtered off and chromatographed on silica gel. Elution with petroleum ether-benzene afforded pure 2,4-dinitrophenylhydrazone of (43b), 160mg, yield 93%. The sample for analysis was recrystallized from petroleum ether-benzene to afford red crystals, mp 194.0-194.9 °C.

Found: C,59.39; H, 5.35; N, 16.59%. Calcd for $C_{17}H_{18}O_4N_4$: C, 59.64; H,5.30; N, 16.37%.

Since the dienyne-aldehyde(43b) was very unstable and partly decomposed during distillation, the aldehyde was isolated by short column chromatography on alumina and without further purification the dienyne-aldehyde was used for next aldol condensation reaction.

1,7-Di-t-butyl-1-oxo-2,4,6-nonatrien-8-yne(46) from the Ethoxyacetal(45b). A mixture of t-butyl-ethoxyacetal(45b)(12.2g, 0.0433 mol), dioxane(80 ml) and 3N hydrochloric acid(60 ml) was vigorously stirred under nitrogen atmosphere at 50 °C for 2 hr and then 40 °C for 20 hr. The reaction mixture was chilled and the organic layer was separated. The aqueous layer was extracted with benzene(20 ml×3) and the combined organic layer was worked up by the usual way. Crude oily residue thus obtained was purified by short column chromatography on alumina. Elution with carbon tetrachloride afforded (43b) as brown oil, 4.91g.

A solution of sodium hydroxide(2.00g, 50.0 mmol) in ethanol (5 ml) and water(5 ml) was added to a solution of the aldehyde (43b)(4.91g) and pinacolone(5.00g, 50.0 mmol) in ethanol(60ml) at 0 °C under nitrogen atmosphere. The mixture was kept at 22 °C for 36 hr and then poured onto ice-cooled 3N hydrochloric acid(50 ml). The reaction mixture was extracted with ether(20 ml×3) and the organic layer was washed successively with water and saturated sodium chloride solution and dried. The extract was concentrated under reduced pressure. The residue was chromatographed on alumina and crystallized from methanol to give trienyne-ketone(46) as pale yellow crystals, 3.20g. The mother liquor was chromatographed on silica gel to afford a further amount of the ketone, 2.08g. The total yield of the ketone was 5.28g(50.0%). The analytical sample of (46) was recrystallized from pentane to afford pale yellow crystals, mp 92.5-93.5 °C, infrared spectrum(CCl_4), 3300m(≡CH), 1678s(C=O), 1591s(C=C), 999s(trans-CH=CH-). N.m.r. spectrum(CCl_4), τ 2.40-3.85(m, 5H, olefinic), 6.59(s, 1H, C≡CH), 8.83(s, 9H, t-Bu), 8.88(s, 9H,

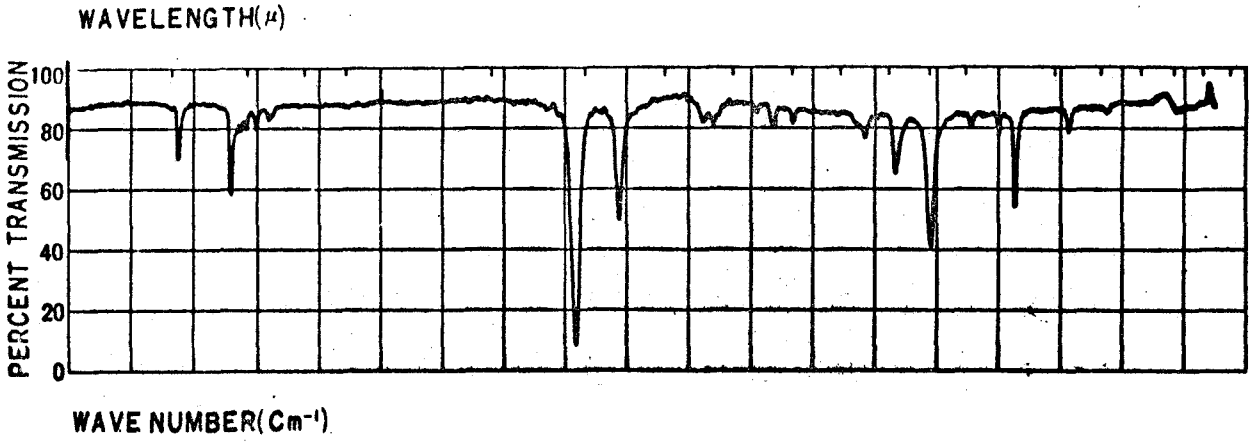
t-Bu). U.v. spectrum, $\lambda_{max}^{99\%EtOH}(\varepsilon)$, 230*(5520), 239(6670), 336 (37,900) nm.

Found: C, 83.80 ; H, 9.97 %. Calcd for $C_{17}H_{24}O$: C, 83.55 ; H, 9.90 %.

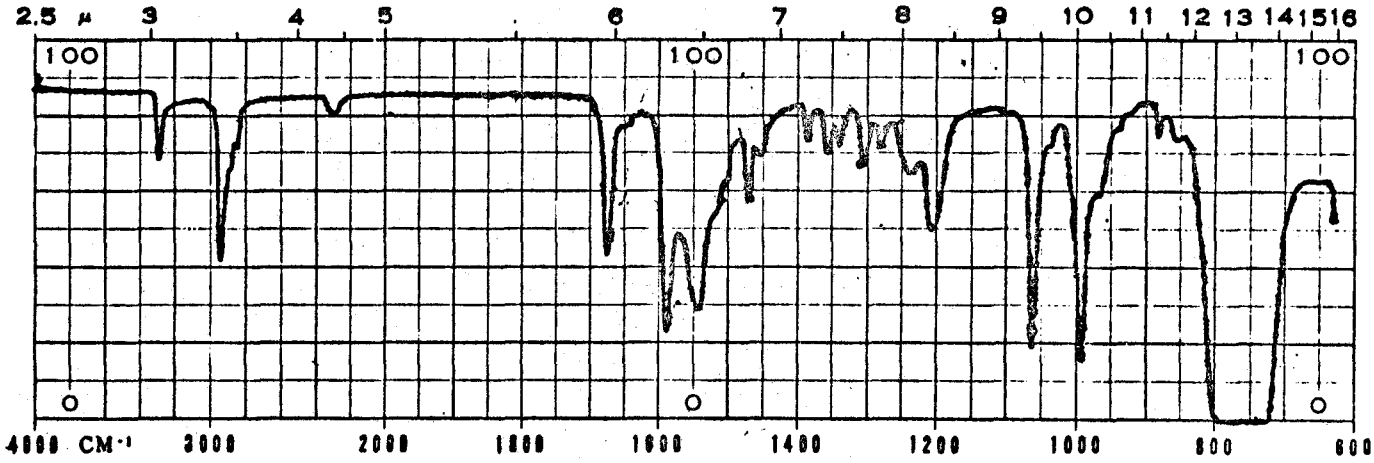
1,7,12,18-Tetra-t-butyl-1,18-dioxo-2,4,6,12,14,16-octadecahexaen-8,10-diyne(47). A solution of trienyne-ketone(46)(3.00g, 0.0123 mol) in pyridine(15 ml) and methanol(15 ml) was added to a mixture of cupric acetate monohydrate(15.00, 0.0752 mol), pyridine(50 ml) and methanol(50 ml) at 30°C. The mixture was stirred at 30-35°C for 15 hr and poured onto ice-cooled 2N hydrochloric acid. The reaction mixture was extracted with ether(100 ml×4) and the organic layer was washed with dilute hydrochloric acid, saturated sodium hydrogen carbonate solution and saturated sodium chloride solution and dried over anhydrous magnesium sulfate. Removal of the solvent in vacuo afforded a crystalline residue. Column chromatography on alumina and elution with benzene gave orange yellow crystals, which was washed with methanol to give pure hexaendiyne-ketone(47), as yellow crystals, 2.49g (83.3%). The analytical sample of (47) was recrystallized from methanol to give yellow crystals, mp 171.5-172.5°C, mass spectrum(m/e), 486(M^+), 429(M-57), infrared spectrum(CCl_4), 1678m(C=O), 1591s (C=C), 999s(trans-CH=CH-). N.m.r. spectrum($CDCl_3$) 2.40-3.81 (m, 10H, olefinic), 8.78(s, 18H, t-Bu), 8.84(s, 18H, t-Bu), u.v. spectrum, $\lambda_{max}^{99\%EtOH}(\varepsilon)$, 246.5(23,100), 288*(22,300), 325* (39,800), 343(46,200), 385(41,200), 425*(24,300) nm.

Found: C, 83.73 ; H, 9.41 %. Calcd for $C_{34}H_{46}O_2$: C, 83.90 ; H, 9.53 %.

Infrared spectrum of (43b),(CCl_4).



Infrared spectrum of (46),(CCl_4).



Infrared spectrum of (47),(CCl_4).

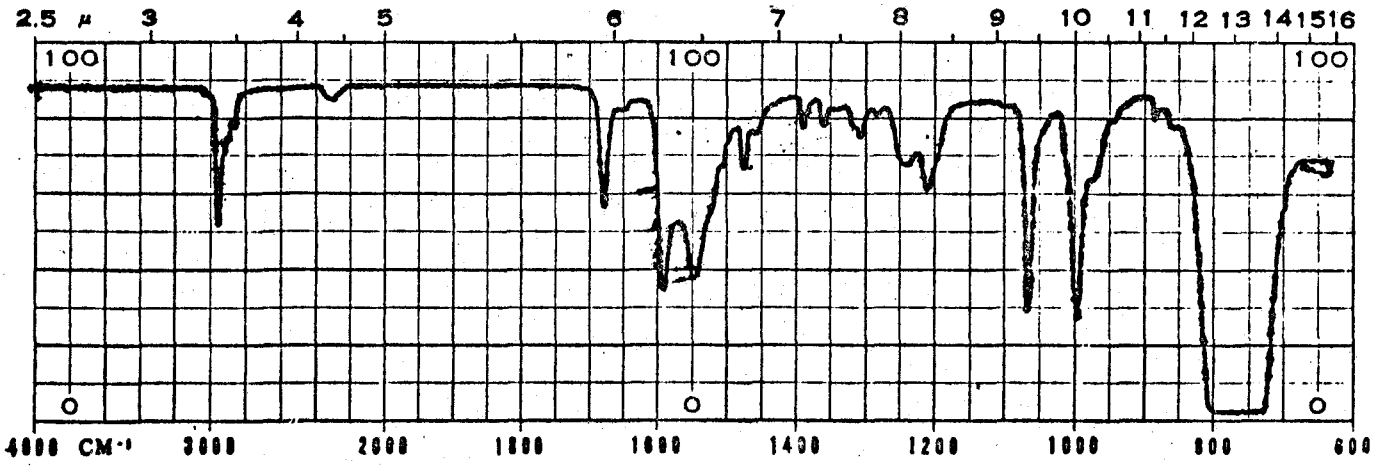


Fig. 20.

3,9,14,20-Tetra-t-butyl-4,6,8,14,16,18-docosahexaen-1,10-12,21-tetrayn-3,20-diol(48). Absolute tetrahydrofuran(60 ml) was saturated with acetylene. Lithium acetylide-ethylenediamine (3.00g, 0.0326 mol) was added and then a solution of the diketone (47)(1.60g, 0.00329 mol) in absolute tetrahydrofuran(15 ml) was added with stirring at 30°C. The mixture was stirred at 30°C for 2 hr in an atmosphere of acetylene and was chilled in an ice-salt bath. Saturated ammonium chloride solution was added dropwise, an internal temperature of -5-0°C being maintained by ice-salt cooling. Water was added and the organic layer was separated. The aqueous layer was extracted with ether(30 ml×3) and the combined organic layer was washed successively with dilute hydrochloric acid and saturated sodium chloride solution, dried($MgSO_4$) and evaporated under reduced pressure. Chromatograpy on alumina and elution with benzene gave the diethynyl-glycol(48), 1.71g(96.6%) as a amorphous solid. The sample for analysis was washed thoroughly with pentane to afford a pale yellow powder, mp 148-150°C. Mass spectrum(m/e) 538(M^+), 481(M-57), 436(M-57-18), infrared spectrum($CHCl_3$), 3590m(-OH), 3317m(≡CH), 2193w(-C≡C-), 2106w(-C≡C-), 1600w(C=C), 995s(trans-CH=CH-) cm^{-1}. N.m.r.spectrum ($CDCl_3$), τ, 2.80-4.26(m, 10H, olefinic), 7.40(s, 2H, C≡CH), 7.87 (br s, 2H, -OH), 8.83(s, 18H, t-Bu), 8.98(s, 18H, t-Bu), u.v. spectrum, $\lambda_{max}^{99\%EtOH}$ (ε), 223.5(29,500), 262.5(27,500), 280*(31,900), 293(43,300), 305(49,100), 327(39,300), 347(38,300), 369(31,500), 397.5(22,600) nm.

Found: C, 84.38 ; H, 9.34 %. Calcd for $C_{38}H_{50}O_2$: C, 84.71 ; H, 9.35 %.

1,6,12,17-Tetra-t-butyl-7,9,11,17,19,21-cyclodocosahexaen-2,4,13,15-tetrayn-1,6-diol (49). A solution of the diethynyl glycol(48) in ether(90 ml)-pyridine(90 ml)-methanol(60 ml) was added during 12 hr to a refluxing solution(the internal temperature, 50°C) of cupric acetate monohydrate(18.0g, 0.0902 mol) in ether (180 ml)-pyridine(180 ml)-methanol(40 ml), in a high-dilution apparatus[115]. After a further 2-hr reflux the resultant mixture was evapolated under reduced pressure to 200 ml. The mixture was poured onto ice-cooled 2N hydrochloric acid(600 ml) and extracted with ether(100 ml×4). The organic layer was washed with 2N hydrochloric acid, saturated sodium bicarbonate solution and saturated sodium chloride solution, and dried($MgSO_4$). Removal of the solvent in vacuo afforded a crystalline residue. Column chromatography on alumina and elution with benzene gave cyclic glycol(49), 1.32g(yield, 77.5%). The analytical sample was recrystallized from methylenechloride-n-pentane to afford yellow crystals, which turned dark brown at ca. 240°C but not melted until 280°C. Mass spectrum(m/e), 536(M^+), 479(M-57), infrared spectrum(KBr), 3340m br(OH), 988vs(trans-CH=CH-) cm^{-1}, n.m.r. spectrum($CDCl_3$), τ 2.64-4.28(m, 10 H, olefinic), 7.91(br s, 2H, OH) dissappeared on shaking with D_2O, 8.81(s, 18H, t-Bu), 8.89 (s, 18H, t-Bu), u.v. spectrum, $\lambda_{max}^{99\%EtOH}$(ε), 279*(45,400), 292 (83,400), 303(102,000), 323.5*(12,700), 360*(12,500), 385(17,200), 409(16,200).

Found: C, 84.92 ; H, 9.03 %. Calcd for $C_{38}H_{48}O_2$: C, 85.02 ; H, 9.01 %.

5,11,16,22-Tetra-t-butyl-1,3,12,14-tetradehydro[22]annulene (50). To cyclic glycol(49)(150 mg, 0.279 mmol) was added ether (10 ml) saturated hydrogen chloride at -60 °C under nitrogen atmosphere. Finely powdered stannous chloride dihydrate(450 mg, 1.99 mmol) was added with stirring at -60 °C. Immediately there appears a dark blue violet color. The mixture was stirred for half an hour at the same temperature and ether(30 ml) was then added. The organic layer was washed with cold water and cold saturated sodium bicarbonate solution. The extract was dried, evaporated under reduced pressure on a rotary evaporator(internal temperature < 0 °C), and the dark violet residue was immediately chromatographed on alumina at -20 °C. Elution with methylenechloride -n-pentane(3:7) gave the tetradehydro[22]annulene(50), 119 mg(85 %), as dark violet crystals, which became colorless at ~100 °C on melting point determination. Infrared spectrum(nujol, low temperature), 988(trans-CH=CH-) cm^{-1}(see Fig. 2); u.v. spectrum, λ_{max}^{THF} (ε), 222(37,000), 231(37,000), 263.5(16,000), 299(13,000), 311 (11,000), 369*(41,000), 382(47,000), 414(350,000), 552*(14,000), 596(46,000), 732(130), 768(130), 858(490) nm(see Fig. 4 and Fig. 8); n.m.r. spectrum see Table 1 and Figure 3.

Found: C, 89.92 ; H, 9.32 %. Calcd for $C_{38}H_{46}$: C, 90.78 ; H, 9.22 %. Analysis performed as rapidly as possible after being washed with cold methylenechloride.

Substance(50) was soluble in ether, benzene, chloroform and dichloromethane and considerably soluble in tetrahydrofuran. (50) was moderately soluble in carbon tetrachloride, slightly soluble in n-pentane and insolble in methanol. The crystals rapidly decomposed on standing in light and air at room temperature.

After standing for 24 hr, analysis of a sample had gave a very different result. (Found: C, 74.09 ; H, 7.70 %.)

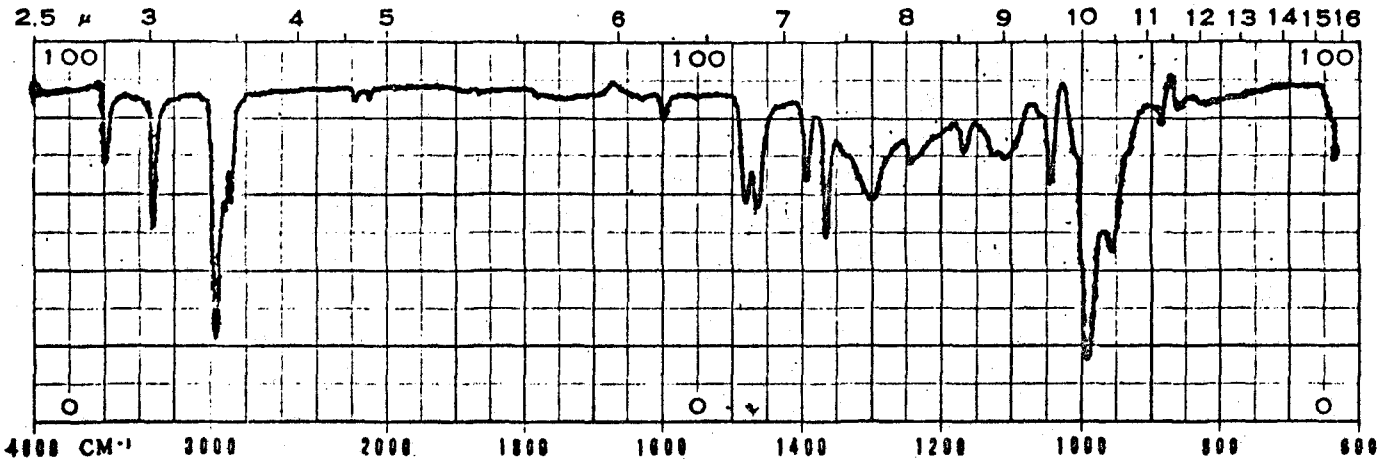
n-Pentane, ether and dichloromethane solutions of (50) on standing at 0 °C gradually turned yellow. T.l.c. examination showed the presence of much material at the solution. The compound was usually stored in dilute dichloromethane solution or in crystalline state at -78 °C under nitrogen.

Catalytic hydrogenation of the tetradehydro[22]annulene(50). A cold solution of (50)(46 mg) in ethyl acetate(10 ml) was added to platinum(from 200 mg of platinum oxide) in glacial acetic acid (20 ml) and ethyl acetate(10 ml) at -20 °C. The mixture was stirred under hydrogen at -15~-20 °C for 3hr, and overnight at room temperature. The catalyst was removed by filtlation, and the filtrate was diluted with ether. The solution was washed successively with water, saturated sodium bicarbonate solution and saturated sodium chloride solution, and was then dried($MgSO_4$) and evaporated under reduced pressure. The resulting pale yellow oil, which crystallized on standing. Chromatography on alumina(Woelm act.I) and elution with n-pentane gave 1,6,12,17-tetra-t-butylcyclodocosane, 42 mg(86 %), which was recrystallized from ethyl acetate-methanol to afford colorless crystals, mp 97-101 °C. Mass spectrum(m/e), 532(M^+), 477(M-57), 57(base peak); infrared spectrum(CCl_4), 2940 vs, 2860s, 1476m, 1393w, 1365m cm^{-1}; n.m.r. spectrum(CCl_4), τ 8.32 (m, $-CH_2-$, -CH=), 9.15(s, CH_3)(the ratio of 10 : 9).

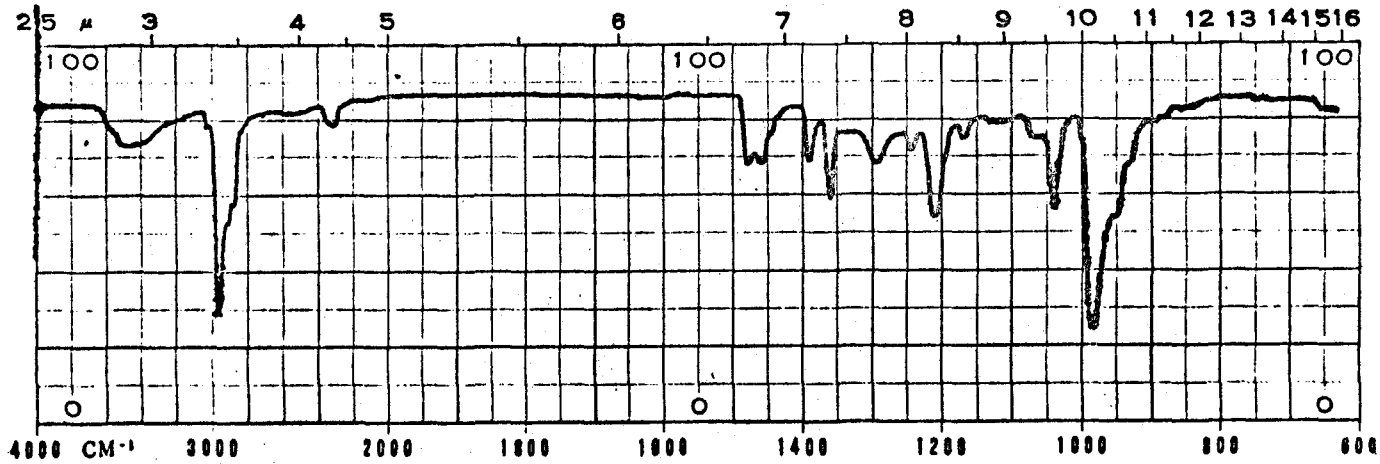
Found: C, 85.81 ; H, 14.36 %. Calcd for $C_{38}H_{76}$: C, 85.63 ; H, 14.37 %.

Fig. 21.

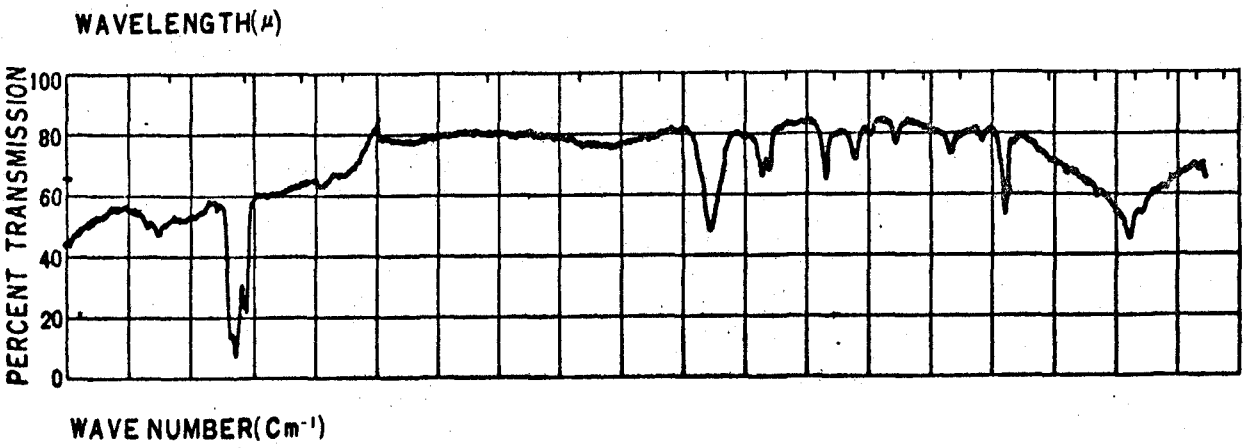
Infrared spectrum of (48),($CHCl_3$).



Infrared spectrum of (49),(KBr).



Infrared spectrum of (50),(nujol, low temp.).



II. SYNTHETIC STUDIES OF DISUBSTITUTED TETRADEHYDRO[18]-ANNULENES.

5,10-Diphenyl-2,4,10,12-tetradecatetraen-6,8-diyndial(51).

To a mixture of (43a)(740 mg, 4.07 mmol), methanol(5 ml) and pyridine(5 ml) was added a solution of cupric acetate monohydrate (3.50 g) in methanol(25 ml) and pyridine(25 ml). After being stirred for 3 hr at 25°C, the mixture was chilled on an ice-bath, mixed 3M hydrochloric acid, and extracted with chloroform(30 ml×3). The extract was washed, dried and concentrated under reduced pressure. The residue was chromatographed on silica gel(30 g) and eluted with carbon tetrachloride-dichloromethane to yield (51), yellow crystals, 691 mg(Y: 94 %). The crystals dissolved in benzene were passed through a short column of alumina. Concentration of the filtrate afforded pure (51), orange yellow crystals, mp ca. 155°C(dec.)(from benzene-cyclohexane); infrared spectrum($CHCl_3$), 1677(C=O), 1603 (C=C)ν cm^{-1}; n.m.r. spectrum($CDCl_3$),τ 0.31(d, J= 8.0 Hz, 2H, CHO), 1.93-2.78(m, 16H, phenyl and olefinic), 3.58(dd, J= 8.0 Hz, and 15Hz, 2H, olefinic H_2).

Found: C, 85.56 ; H, 4.98 %. Calcd for $C_{36}H_{18}O_2$: C, 86.16 ; H, 5.01 %.

7,12-Diphenyl-4,6,12,14-cyclooctadecatetraen-8,10-diyn-3,16-diol(53). A solution of lithium acetylide in liquid ammonia (30 ml) was prepared in a Dewar vessel by passing a steady stream of acetylene into a stirred solution of lithium(50 mg, 7.2 mmol). A solution of the dialdehyde(51)(100 mg, 0.276 mmol) in absolute tetrahydrofuran(15 ml) was added at -60°C. The mixture was stirred at -50°C for 4 hr and -34 °C for 6 hr. The ammonia was allowed

to evaporate off and the residue was mixed with a saturated solution of ammonium chloride at -40°C. Ether was added and the organic layer was separated, washed successively with water and saturated sodium chloride solution, dried($MgSO_4$) and evaporated. The dark brown residue(105 mg) was chromatographed on silica gel to give (53), as a yellow oil, 25 mg(Y: 22 %); infrared spectrum (film) 3500~3000br(-OH), 3250(≡CH), 2180,2100(-C≡C-), 968(trans-CH=CH-), 755(phenyl) cm^{-1}; n.m.r. spectrum($CDCl_3$) τ 2.27~3.05(m, 16H, olefinic and phenyl), 3.85(d, J= 14.5 Hz, 2H, allylic), 7.00 (br s, 2H, -OH) disappeared on shaking with D_2O, 7.20(s, 2H, C≡CH).

An attempt to synthesize 5,18-diphenyl-1,3,10,12-tetradehydro-[18]annulene(55) from the ethynyl glycol(53). A solution of (53) (36 mg) in pyridine(40ml) was added to a mixture of cupric acetate monohydrate(3.00 g, 15.0 mmol) in pyridine(24 ml)-methanol(24 ml) over a period of 2 hr and the mixture was stirred for a further 16 hr at room temperature. The mixture was acidified with 3N hydrochloric acid and extracted with ether. The extracts were washed with water and saturated sodium chloride solution and dried ($MgSO_4$). Removal of the solvent in vacuo gave a residue, which was dissolved in benzene(5 ml). A solution of stannous chloride dihydrate(50 mg, 0.222 mmol) in conc. hydrochloric acid(5 ml) was added and the resulting green solution was vigorously stirred for 30 min at room temperature. The organic layer was separated, washed with water, saturated sodium bicarbonate and sodium chloride solutions and dried($MgSO_4$). U.v. spectrum of the benzene solution, $\lambda_{max}^{benzene}$, 344, 416*, 622, 778 nm.

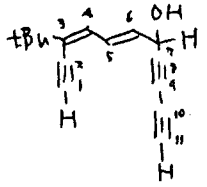
5,10-Di-t-butyl-2,4,10,12-tetradecatetraen-6,8-diyndial(56).

A solution of the dienyne-aldehyde(43b)(1.20 g, 7.4 mmol) in pyridine(10 ml) and methanol(10 ml) was added to a mixture of cupric acetate monohydrate(5.00 g), pyridine(40 ml) and methanol(40 ml). After being kept at 25°C for 21 hr, the reaction mixture was worked up by the way used for (51). Crude yellow crystals thus obtained were chromatographed on alumina to yield pure (56), 1.01 g(Y: 85%), as yellow crystals, mp 154.4~155.7°C(from benzene-n-hexane); infrared spectrum(KBr),2745(CHO), 2230(-C≡C-), 1677(C=O), 1604 (C=C) cm^{-1}; n.m.r. spectrum($CDCl_3$) τ 0.29(d, J= 8.0 Hz, 2H, CHO), 2.39(dd, J= 11 and 15 Hz, 2H, H_3 and H_{12}), 3.30(d, J= 11 Hz, 2H, H_4 and H_{11}), 3.67(dd, J= 8.0 Hz and 15 Hz , 2H, H_2 and H_{13}), 8.73 (s, 18H, t-Bu).

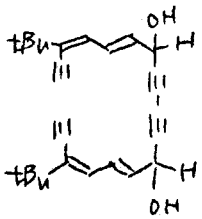
Found: C, 81.91 ; H, 8.17 %. Calcd for $C_{22}H_{26}O_2$: C, 81.95 ; H, 8.13 %.

Reaction of the dienyne-aldehyde(43b) with diacetylene bis-Grignard reagent. Diacetylene(250 mg, 5.00 mmol) in tetrahydrofuran(5.1 ml) was added to a solution of ethynyl magnesium bromide (from magnesium, 240 mg, 9.87 mmol) in tetrahydrofuran(20 ml). The solution was stirred for a further 1.5 hr and then the flask was cooled to -10°C in an ice-salt bath. A solution of t-butyl-dienyne-aldehyde(43b)(1.62 g, 9.99 mmol) in tetrahydrofuran(5 ml) was added at -10°C and the mixture was stirred at the same temperature for 1 hr and then at room temperature for 1.5 hr. The reaction mixture was worked up by the usual way. The oily residue obtained by evaporating the solvent in vacuo was chromatographed

on silica gel (n-hexane~benzene) to give recovered (43b), 360 mg; mono-adduct(57), 180 mg as a yellow oil, n.m.r. spectrum(CCl_4) τ 3.14(dd, J= 15 and 10.5 Hz, 1H, H_5), 4.53(d, J= 10.5 Hz, 1H, H_4), 4.23(dd, J= 15 and 6.5 Hz, 1H, H_6), 5.06(d, J= 6.5 Hz, 1H, H_7), 6.47(s, 1H, -OH), 6.67(s, 1H, H_1), 7.80(s, 1H, H_{11}), 8.84(s, 9H, t-Bu); di-adduct(58), as a yellow oil, n.m.r. spectrum(CCl_4) τ 3.0 5.0(m, 6H, olefinic), 5.9(d, 2H, allylic), 6.68(s, 2H, -OH), 6.72(s, 2H, C-CH), 8.85(s, 18H, t-Bu).



(57)



(58)

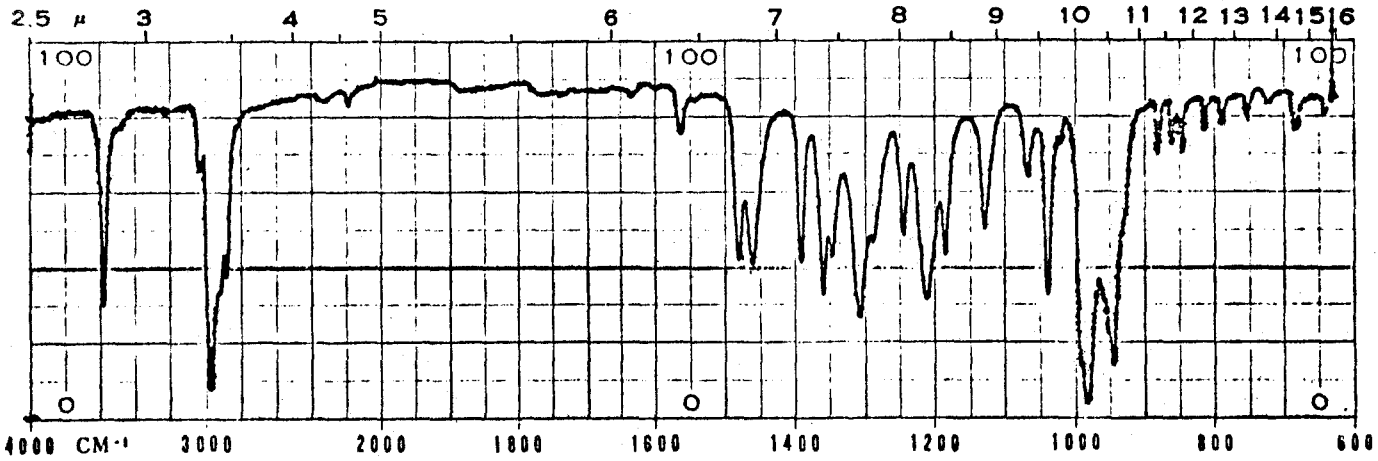
An attempt to synthesize 5,18-di-t-butyl-1,3,10,12-tetradehydro[18]annulene(60). Oxidative coupling reaction of (58) by the same way used for (53)(Eglinton's method) and dehydroxylative aromatization reaction (stannous chloride dihydrate-conc. hydrochloric acid) gave a red solution, u.v. spectrum, $\lambda_{max}^{benzene}$, 372, 400*, 505,520,713.

III. SYNTHESIS OF TETRA-t-BUTYL- AND DI-t-BUTYLDI-PHENYL-DIDEHYDRO[18]ANNULENES (71 AND 74).

1,4,10,13-Tetra-t-butyl-4,6,8,13,15,17-cyclooctahexaen-2,11-diyn-1,10-diol (70). To a suspension of finely powdered potassium hydroxide(900 mg, 1.60 mmol) in liquid ammonia(180ml) was added very slowly a solution of the trienyne-ketone(46) (320 mg, 1.13 mmol) in absolute tetradydrofuran(30 ml) at -34°C for 5 hr. After being stirred for 3 hr at -34 °C, ammonium chloride(1.80 g, 33.6 mmol) was added and the ammonia was allowed to evaporate off and the residue treated with water and ether(20 ml). The aqueous layer was then further extracted with ether(15 ml × 2). The combined organic layer was washed successively with water and saturated sodium chloride solution. Drying($MgSO_4$), evaporation under reduced pressure yielded pale yellow crystals, which were washed with n-hexane to give a mixture of diastereomers(70a and 70b), colorless crystals, 212 mg(Y: 66.3%). The diastereomers were chromatographed on silica gel. Elution with benzene gave (70a), colorless crystals, mp 230.5~231.5°C; mass spectrum(m/e), 488(M^+), 470(M-18), 431 (M-57), 57(t-Bu, base peak); infrared spectrum(KBr), 3560m (-OH), 2180vw(-C≡C-), 1563w(C=C), 985vs(trans-CH=CH-) cm^{-1}; n.m.r. spectrum($CDCl_3$) τ 2.75 4.20(m, 10H, olefinic), 8.2(br s, 2H, -OH), 8.80(s, 18H, t-Bu), 8.92(s, 18H, t-Bu); u.v. spectrum, $\lambda_{max}^{99\%EtOH}$(ε), 230(21,100), 280.5(86,900), 291(113,000), 327.5 (13,800).

Found: C,83.53; H, 9.93 %. Calcd for $C_{34}H_{48}O_2$: C, 83.55 ; H, 9.90 %.

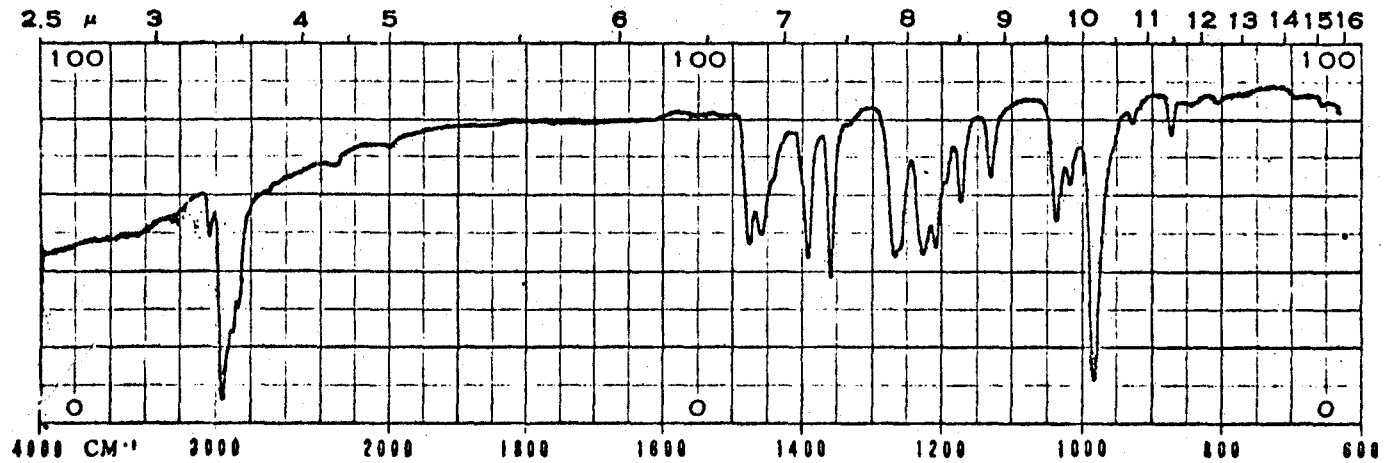
Infrared spectrum of (70a),(KBr).



Elution with benzene~benzene-ether(19:1) gave (70b), mp 170.0 ~171.0°C; mass spectrum(m/e), 488(M^+), 470(M-18), 431(M-57), 57(t-Bu, base peak); infrared spectrum(KBr), 3480m, 3340m(-OH), 2180vw(-C≡C-), 1563w(C=C), 985vs(trans-CH=CH-) cm^{-1}; n.m.r. spectrum($CDCl_3$), τ 2,75~4.20(m, 10H, olefinic), 8.01(s, 2H, -OH), 8.80(s, 18H, t-Bu), 8.92(s, 18H, t-Bu); u.v. spectrum, $\lambda_{max}^{99\%EtOH}$(ε) 230(18,200), 280.5(76,300), 291(98,400), 327.5 (12,300) nm.

Found: C,83.72 ; H, 10.76 %. Calcd for $C_{34}H_{48}O_8$: C,83.55 ; H, 9.90 %.

Infrared spectrum of (70b),(KBr).



3,9,12,18-Tetra-t-butyl-1,10-didehydro[18]annulene (71).

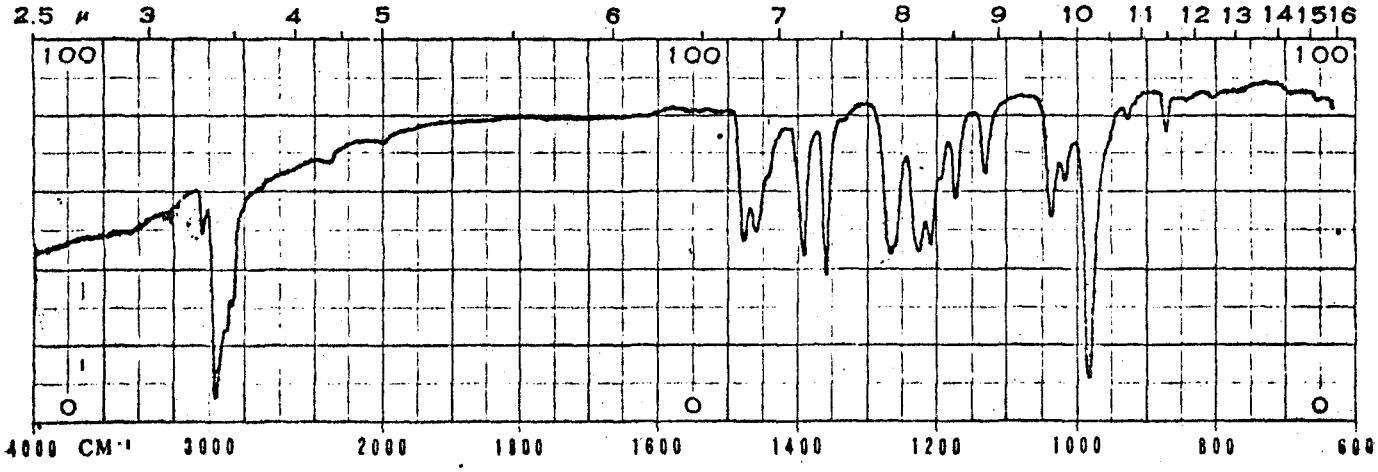
The cyclic glycol(70)(105 mg, 0.215 mmol) was mixed with ether (10 ml) saturated with hydrogen chloride at - 60°C under nitrogen atmosphere. Finely powdered stannous chloride dihydrate (400 mg, 1.77 mmol) was added to the mixture at -60°C. The mixture was vigorously stirred at the same temperature for 10 min and then poured onto ice-cooled sodium bicarbonate solution and ether was added. Separation, drying(K_2CO_3) and evaporation of the ether layer furnished the dark red crystals, which were chromatographed on alumina(Woelm act. I) and eluted with n-hexane-dicloromethane(19:1) to afford pure annulene (71), 91 mg(Y: 93 %), as dark reddish violet crystals. The sample for analysis was rechromatographed on alumina and washed successively with ether and then n-hexane, mp 260°C (dec.); mass spectrum(m/e), 454(M^+), 397(M-57), 57(t-Bu, base peak); infrared spectrum(KBr), 3030w, 2950s, 2000vw (-C≡C- or C=C=C), 1041m, 987vs, 878w cm^{-1}; u.v. spectrum, $\lambda_{max}^{THF}(\varepsilon)$, 217(11,300), 255*(5,810), 267.5(8,360), 342*(44,400), 356(94,400), 372(447,000), 464*(4,790), 499(10,600), 530 (19,100), 607(100), 647*(89), 669(116), 681(116), 720*(138), 751(316) nm, see Fig. 7; n.m.r. spectrum, see Table 2, Table 3 and Fig. 5.

Found: C, 89.72 ; H, 10.18 %. Calcd for $C_{34}H_{46}$: C,89.80 ; H, 10.20 %.

Tetra-t-butyldidehydro[18]annulene(83) is much more stable than tetra-t-butyltetradehydro[18]annulene(36). (83) shows

pink in a dilute solution and reddish brown in a concentrated solution. The compound is soluble in ether, benzene, chloroform and dichloromethane and resonably soluble in tetrahydrofuran. (83) is moderately soluble in carbon tetrachloride, slightly soluble in pentane and insoluble in methanol. The crystals hardly decompose in light and air and can be stored in a sample tube at room temperature more than a month.

The annulene is thermally stable but in the presence of Lewis acid(for example, $AlCl_3$, $SnCl_4$, BF_3 etc.) rapidly decomposes to give a polymeric material. Therefore, substitution reaction like benzene cannot have been successful so far.



Formation of C-T complex between the annulene(71) and 2,4,7-trinitrofluorenone. A solution of (71)(31.5 mg, 0.0694 mmol) in benzene(20 ml)-methanol(20 ml) was warmed at 40～50°C and a solution of 2,4,7-trinitrofluorenone(43.5 mg, 0.138 mmol) in benzene(6 ml)-methanol(3 ml) was added. The solution was kept at 0°C to deposite the deep violet needles, 41 mg(Y: 77

%), mp ~260 °C.

Found: C, 73.37 ; H, 6.63 ; N, 5.43 %. Calcd for $C_{47}H_{51}N_3O_7$: C, 73.32 ; H, 6.68 ; N, 5.46 %.

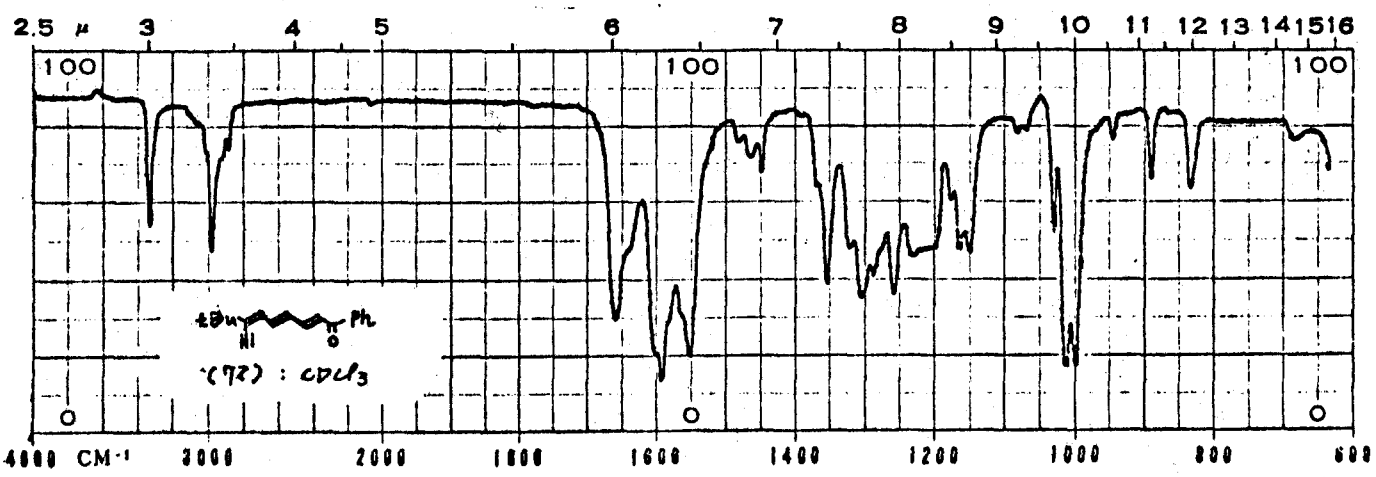
C-T complex of (71) was found to be more dark bluish compound and less soluble in organic solvents than parent annulene and the stability of C-T complex was change better. U.v. spectrum of the C-T complex showed a superposed one of (71) and 2,4,7-trinitrofluorenone, and could not detect the charge-transfer band.

Catalytic hydrogenation of the didehydro[18]annulene(71). A solution of (71)(42 mg, 0.0924 mmol) in ethyl acetate(25 ml) was added to platinum(from 150 mg of platinic oxide) in glacial acetic acid(25 ml) at room temperature. The mixture was vigorously stirred under hydrogen for 2.5 hr and the catalyst was removed by filtration and platinum was washed with ether(50 ml). The organic layer was washed successively with water, saturated sodium bicarbonate solution and saturated sodium chloride solution and dried($MgSO_4$). Evapolation of the solvent *in vacuo* gave a crystalline residue, which was chromatographed on alumina(Woelm act. I) and eluted with n-hexane to afforded 1,4,10,13-tetra-t-butylcyclooctadecane, 40 mg(Y: 91 %). The sample for analysis was recrystallized from ethyl acetate-methanol to give colorless crystals, mp 151~154$_0$C; mass spectrum(m/e), 476(M^+), 419(M - 57), 57(t-Bu, base peak) ; infrared spectrum(CCl_4), 2940s, 2860m, 1475m, 1393m, 1365m cm^{-1}; n.m.r. spectrum(CCl_4) τ 8.63(br s, $-CH_2-$, -CH=), 9.11(s, t-Bu)(the ratio of 8 : 9).

Found: C, 85.62 ; H, 14.13 %. Calcd for $C_{34}H_{68}$: C, 85.63 ; H, 14.37 %.

7-t-Butyl-1-oxo-1-phenyl-2,4,6-nonatrien-8-yne(72) from the t-Butyldienyne-aldehyde(43b). A solution of sodium hydroxide(0.88 g, 0.022 mol) in ethanol(3 ml)-water(3 ml) was added a solution of the aldehyde(43b)(3.56 g, 0.0219 mol) and acetophenone(2.64 g, 0.0220 mol) in ethanol(30 ml) at 0°C under nitrogen atmosphere. The mixture was kept at 0 °C for 3 hr and then acidified with 2N sulfuric acid(20 ml). The mixture was extracted with ether(50 ml×3). The extracts were washed successively with water, saturated sodium bicarbonate solution and saturated sodium chloride solution and dried($MgSO_4$). The organic solvent was evaporated under reduced pressure and the residue was chromatographed on silica gel (eluent: n-hexane→benzene→ether-benzene) to give pure the ketone(72), 4.41 g(Y: 76.0%). The sample for analysis was recrystallized from petroleum ether(bp 40~60°C) to afford yellow crystals, mp 59.5~60.0°C; mass spectrum(m/e), 264(M^+); infrared spectrum($CHCl_3$), 3320m(≡CH), 2060vw(-C≡C-), 1658s(C=O), 1590s, 1550s(C=C), 1016s, 1002s(trans-CH=CH-) cm^{-1}; n.m.r. spectrum($CDCl_3$) τ 1.98~3.72(m, 10H, olefinic and phenyl), 6.50 (s, 1H, C≡CH), 8.81(s,9H, t-Bu); u.v. spectrum, $\lambda_{max}^{99\%EtOH}(\varepsilon)$, 225*(8,710), 267.5(10,300), 359(39,100).

Found: C, 86.27 ; H, 7.56 %. Calcd for $C_{38}H_{38}$: C, 86.32 ; H, 7.63 %.



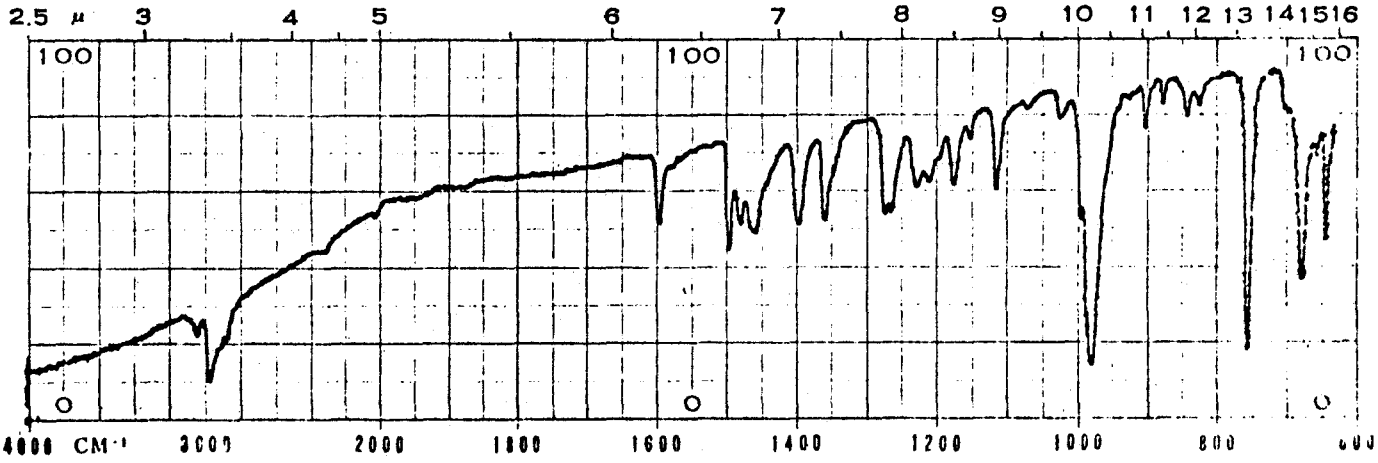
3,12-Di-t-butyl-9,18-diphenyl-1,10-didehydro[18]annulene (74) from the trienyne-ketone(72). A solution of the trienyne-ketone(72)(350 mg, 1.32 mmol) in absolute tetrahydrofuran (50 ml) was added very slowly to a suspension of finely powdered potassium hydroxide(1.00 g, 17.8 mmol) in liquid ammonia (200 ml) at -34°C for 8 hr. After being stirred for 2 hr at -34 °C, ammonium chloride(2.00 g, 37.4 mmol) was added and the ammonia was allowed to evaporate off and the residue was treated with water and ether(20 ml). The aqueous layer was then further extracted with ether(15 ml×2). The combined organic layer was washed successively with water and saturated sodium chloride solution. Drying($MgSO_4$), evaporation under reduced pressure yielded a light brown solid(ca. 350 mg), which was found to contain the cyclic glycol(73) on the basis of spectroscopy and t.l.c. analysis.

To a solution of crude cyclic glycol(ca. 350 mg) in ether (10 ml) was added ether(10 ml) saturated with hydrogen chloride at -60°C under nitrogen atmosphere. Finely powdered stannous chloride dihydrate(1,00 g, 4.43 mmol) was added to the solution at -60°C. The reaction mixture was vigorously stirred at the same temperature for 10 min and then poured onto ice-cold sodium bicarbonate solution. Ether was added and the organic layer was separated. Drying(K_2CO_3) and evaporation in vacuo furnished the violet crystals, which were chromatographed on alumina(Woelm act. I) and eluted with n-hexane-benzene(4:1～1:1) to afford pure annulene(74), 108 mg(Y: 33.0 % based on the ketone(72)), as deep violet crystals. The sample for analysis was recrystallized from benzene-methanol, mp 235°C

(dec.); mass spectrum(m/e), 494(M^+), 57(t-Bu, base peak); in infrared spectrum(KBr), 3025w, 2950m, 2010vw(-C≡C- or C=C=C), 1595m(C=C), 983s(trans-CH=CH-), 766s(phenyl); u.v. spectrum $\lambda_{max}^{THF}(\varepsilon)$, 240*(12,900), 249.5(14,000), 267*(12,000), 281.5 (16,200), 367*(51,800), 389*(171,000), 401(330,000), 534* (17,900), 575(48,000), 673*(150), 701(231), 785(980) nm; n.m.r. spectrum($CDCl_3$) τ -0.21~0.62(m, 6H, outer protons), 1.33(m, 4H, phenyl o-protons), 2.33(m, 6H, phenyl m,p-protons), 7,98(s, 18H, tBu), 13.28(m, 4H, inner protons) see Fig. 6.

Found: C, 92.16 ; H, 7.67 %. Calcd for $C_{38}H_{38}$: C, 92.26 ; H, 7.74 %.

Infrared spectrum of (74)(KBr).



Formation of the C-T complex between the annulene(7) and 2,4,7-trinitrofluorenone. A solution of (74)(45,3 mg, 0.0916 mmol) in benzene(20 ml)-methanol(20 ml) was warmed at 40°C and a solution of 2,4,7-trinitrofluorenone(57.7 mg, 0.183 mmol) in benzene(10 ml)-methanol(10 ml) was added. The solution was allowed to stand at 0°C to deposite the deep violet needles, 46.6 mg(Y: 62.8%), mp ~ 250°C(dec.).

Found: C,75.06 ; H, 5.23 ; N, 5.49 %. Calcd for $C_{51}H_{43}N_3O_7$: C,75.63 ; H, 5.35 ; N, 5.19 %.

IV. SYNTHESIS OF TETRA-t-BUTYL-DIDEHYDRO[22]ANNULENE(83).

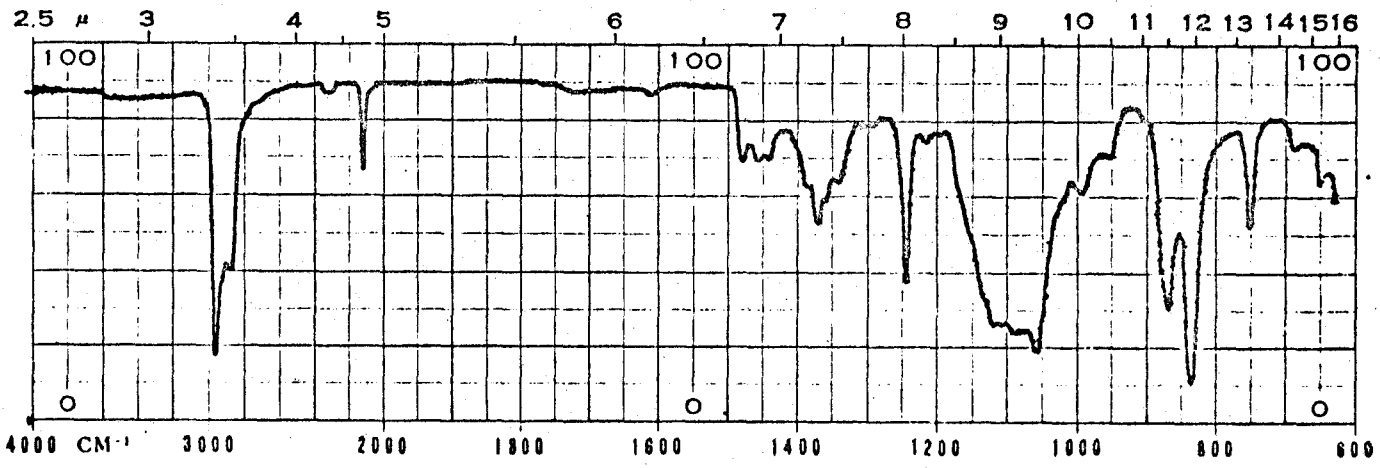
5-t-Butyl-2,4-heptadien-6-ynal Diethyl Acetal(75). A solution of p-toluenesulfonic acid monohydrate(300 mg, 1.58 mmol) in etanol (1 ml) was added to a solution of the dienyne-aldehyde(43b)(2.88 g, 0.178 mol) in ethyl orthoformate (7.70 g, 0.0520 mol). After being stirred overnight, the reaction mixture was worked up by the usual way. Evaporation of the solvent and distillation through a short column furnished (75), 2.60 g (62%), as a yellow liquid, bp 105°C /2mmHg; n.m.r. spectrum (CCl_4)τ 3.27 (dd, J=10.0 and 15.5 Hz, 1H, H_3= β-position of acetal), 3.79 (d, J=10H_z, 1H, H_4= γ-position of acetal), 4.47 (dd, J=5.0 and 15.5 Hz, 1H, H_2= α-position of acetal), 5.09 (d, J=5.0^{H_a}, 1H, acetal), 6.46 (q, J=7.0Hz, 4 H, $-CH_2-$), 6.52 (q, J=7.0Hz, 6H), 8.85 (S, 9H, tBu).

5-t-Butyl-3-ethoxy-7-trimethylsilyl-4-hepten-6-ynal Diethyl Acetal (76). To a solution of ethylmagnesium bromide under nitrogen [from magnesium (1.91 g, 0.0786 mol), ethyl bromide (10.30 g, 0.0945 mol), and absolute tetrahydrofuran (30 ml)] was added dropwise a solution of (45b) (14.80 g, 0.0524 mol) in tetrahydrofuran (20 ml) at 10~20°C with stirring and ice-cooling. The mixture was stirred at 20°C for a further 30 min and then chilled in an ice-bath. Trimethylchlorosilane (10.26 g, 0.945 mol) was added to the mixture at 0°C and the reaction mixture was stirred for 1 hr at the same temperature. (A crystalline precipitate of magnesium chloride waa deposited.) Ammonium chloride solution was added dropwise and the organic layer was separated. Aqueous layer was extracted with ether (50 ml x 3) and the combined organic layer was washed with water and saturated sodium chloride solution and dried ($MgSO_4$). Removal of the solvent in vacuo and distillation gave (76), 17.02 g (Y:91.6 %), as a pale yellow liquid, bp 122~130°C/2.5mmHg; mass spectrum (m/e), 354(M^+);

infrared spectrum (film), 2125 m (-C≡C-), 1616 vw (C=C), 1250 S ($Si-CH_3$), 875 s, 842 vs, 758 m (Si-C); n.m.r. spectrum (CCl_4) τ 4.45 (d, J=8.5Hz, 1H, H_4), 5.43 (t, J=6Hz, 1H, H_1=acetal), 5.67 (m, 1H, H_3), 6.56 (m, 6H, $O-CH_2-$), 8.32 (t, J=6Hz, 2H, H_2), 8.84 (t, J=7Hz, 9H, $-CH_3$), 8.88 (s, 9H, t-Bu), 9.80 (s, 9H, $-SiMe_3$).

Found: C, 67,48; H, 10.58 %. Calcd for: $C_{20}H_{38}O_3Si$: C, 67.75 ; H, 10.80 %.

Infrared spectrum of (76),(film).

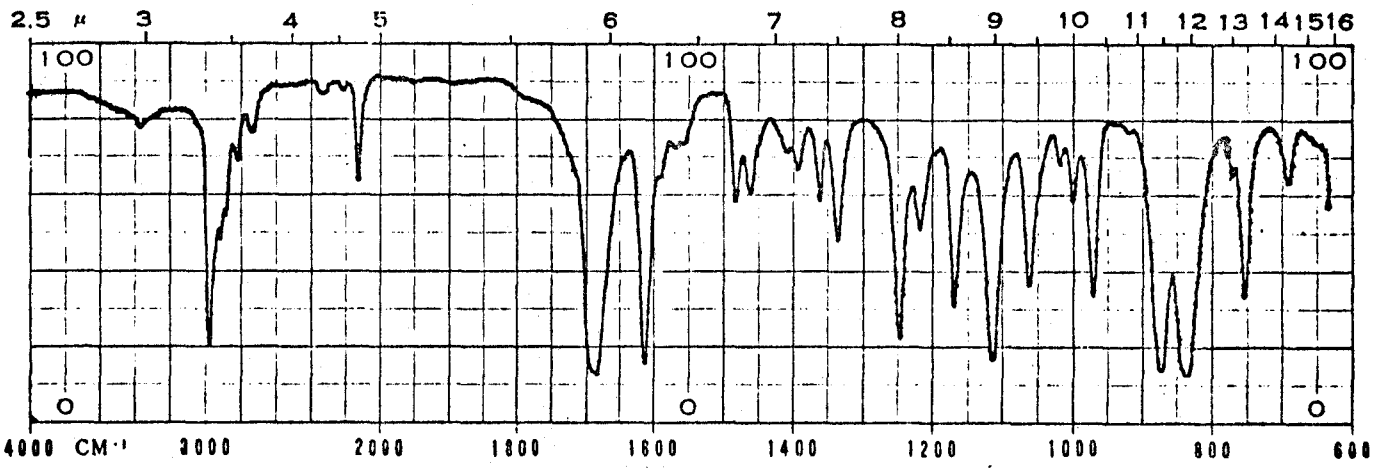


5-t-Butyl-7-trimethylsilyl-2,4-heptadien-6-ynal (77). A mixture of (76) (6.74 g, 0.0190 mol), sodium acetate (6.50 g, 0.0792 mol), acetic acid (56 ml) and water (4 ml) was stirred at 80°C for 6 hr under mitrogen and allowed to stand at room temperature overnight. The reaction mixture was poured onto saturated sodium carbonate solution and extracted with ether (50 ml×3). The extracts were washed successively with saturated sodium carbonate and sodium chloride solutions and dried ($MgSO_4$). Evaporation of the solvent in vacuo and distillation through a short-path apparatus afforded (77), 3.98g (Y ≒ 89.3 %), as a yellow liquid, bp 105~108°C/2.5 mmHg; mass spectrum (m/e), 234 (M^+); infrared spectrum (film), 2810w, 2725w (CHO), 2120 m (-C≡C-), 1687 vs (CHO), 1613 vs (C=C), 1244 s, 1221 m

($Si-CH_3$), 878 vs, 843 vs, 759 s (Si-C); n.m.r. spectrum (CCl_4) τ 0.42 (d, J=8Hz, 1H, H_1=aldehyde), 2,49 (dd, J=11.5 and 15.5 Hz, 1H, H_3), 3.50 (d, J=11.5 Hz, 1H, H_4), 3.88 (dd, J=8.0 and 15.5 Hz, 1H, H_2), 8.78 (s, 9H, t-Bu), 9.70 (s, 9H, $Si-CH_3$).

The aldehyde (76) was more stable than (436) but gradually decompose on standing in air and light at room temperature. Elemental analysis gave unsatisfactory result owing to the unstable nature.

Infrared spectrum of (77),(film).



2,4-Dinitrophenylhydrazone of the dienyne-aldehyde(77).

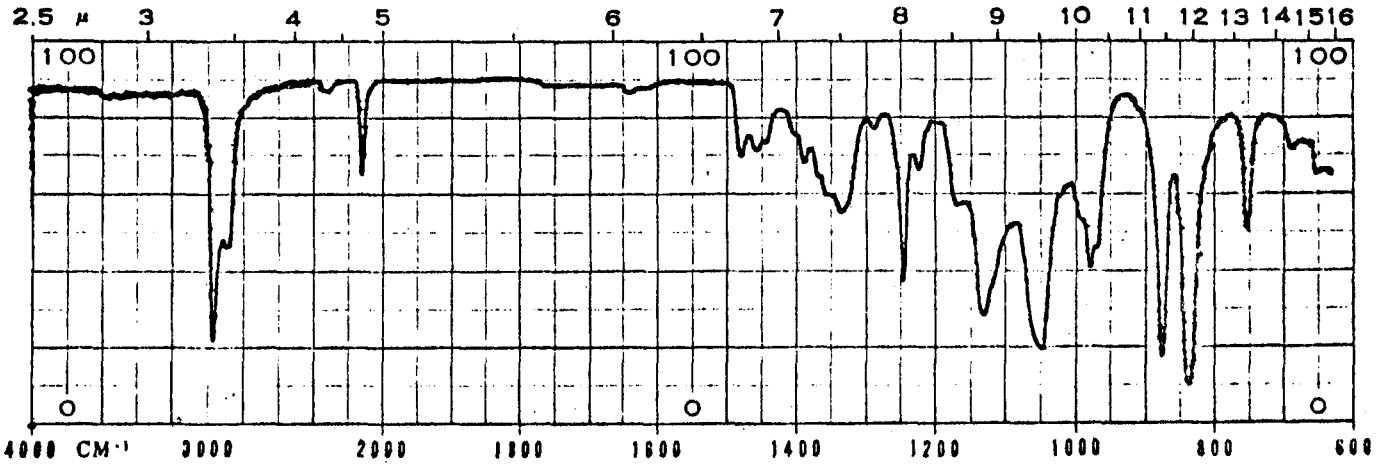
A solution of 2,4-dinitrophenylhydrazine(95 mg, 0.48 mmol) in phosphoric acid(1 ml)-ethanol(1 ml) was added to a solution of (77) (56 mg, 0.24 mmol) in ethanol(15 ml) and the mixture was allowed to stand at room temperature for 30 min. Red precipitate deposited was filtered off and washed with ethanol to give the hydrazone, 62 mg(Y: 63 %), which was recrystallized from ethyl acetate to give red crystals, mp 201~202°C(dec.).

Found: C, 57.81 ; H, 6.39 ; N, 13.27 %. Calcd for $C_{30}H_{36}N_4O_4Si$: C, 57.95 ; H, 6.32 ; N, 13.52 %.

5-t-Butyl-7-trimethylsilyl-2,4-heptadien-6-ynal Diethyl Acetal (78). A solution of p-toluenesulfonic acid monohydrate(400 mg, 2.10 mmol) in ethanol(4 ml) was added to a solution of the trimethylsilyldienyne-aldehyde(77)(3.98 g, 0.017 mol) in ethyl orthoformate(30 ml). After being stirred for 20 hr at room temperature, the reaction mixture was chilled an ice bath and poured onto ice-cold sodium carbonate solution. The mixture was extracted with ether(30 ml × 3). The extracts were washed with saturated sodium carbonate, and sodium chloride solutions and dried(K_2CO_3). Evaporation of the solvent in vacuo and distillation yielded (78), 4.92g (Y: 94 %) as a pale yellow liquid, bp 118 ~120°C / 2.5 mmHg; mass specturm(m/e), 308(M^+), 263(M - 45); infrared spectrum(film), 2125m (-C≡C-), 1644vw(C=C), 1248s, 1227w(Si-CH_3), 881vs, 842vs, 760m (Si-C) cm^{-1}; n.m.r. spectrum(CCl_4) τ 3.20(dd, J= 11.0 and 15.5 Hz, 1H, H_3=β-position of acetal), 3.77(d, J= 11.0 Hz, 1H, H_4=γ-position of acetal), 4.37(dd, J= 5.0 and 15.5 Hz, 1H, H_2=α-position of acetal), 5.07(d, J= 5.0 Hz, 1H, acetal), 6.49(m, 4H, -CH_2-). 8.83 (t, J= 7.0 Hz, 6H, -CH_3), 8.85(s, 9H, t-Bu), 9.76(s, 9H, Si-Me_3).

Found: C, 70.50 ; H, 10.30 %. Calcd for $C_{18}H_{32}O_2Si$: C, 70.08 ; H, 10.46 %.

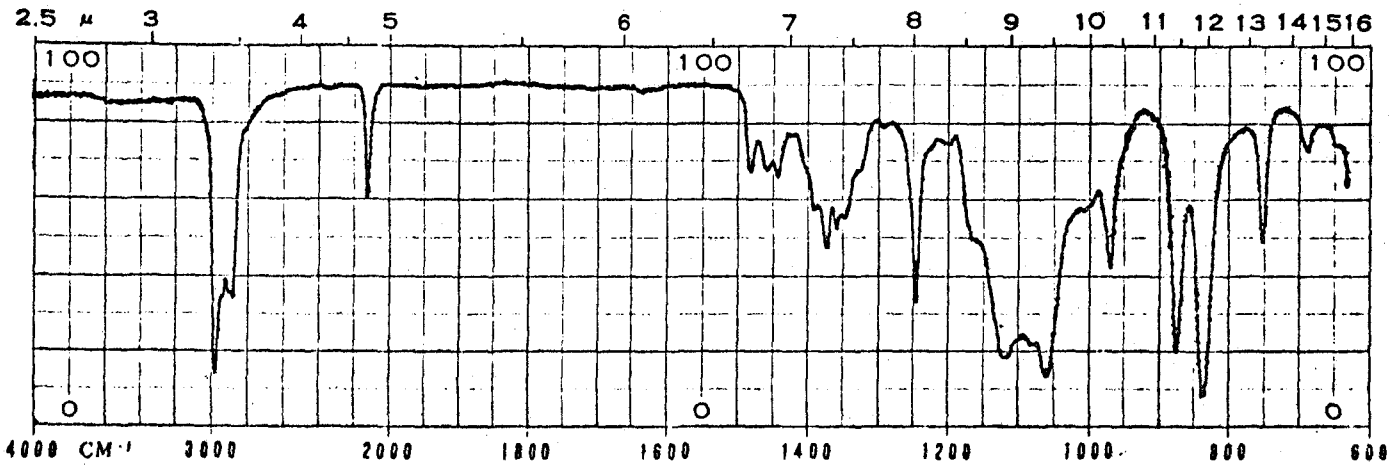
Infrared spectrum of (78),(CCl_4).



7-t-Butyl-3-ethoxy-9-trimethylsilyl-4,6-nonadien-8-ynal Diehyl Acetal(79). A mixture of boron trifluoride etherate(20 mg) in dry benzene(1 ml) was added to a solution of the acetal(78)(4.92 g, 0.0159 mol) in dry benzene(20 ml) at 35 °C. Subsequently, a solution of ethyl vinyl ether(1.40 g, 0.0194 mol) in the same solvent (5 ml) was slowly added at 35 °C. The mixture was kept at the same temperature for 20 min and then finely powdered potassium carbonate (1.0 g) was added to the mixture. The color of the solution changed to light yellow. The potassium carbonate was filtered off and washed with ether. The filtrate and washings were concentrated under reduced pressure. The residue was distilled in vacuo to yield (79), 5.20 g(86 %), as a pale yellow liquid, bp 120~124 °C / 0.009 mmHg; mass spectrum(m/e), 380(M^+), 334(M -46); infrared spectrum(film), 2120m(-C≡C-), 1640vw(C=C), 1248s(Si-CH_3), 880vs, 842vs, 758m(Si-C) cm^{-1}; n.m.r. spectrum(CCl_4) 3.39(dd, J= 10.5 and 14.5 Hz, 1H, H_5), 3.81(d, J= 10.5 Hz, 1H, H_6), 4.42(dd, J=7 and 14.5 Hz, 1H, H_4), 5.44(t, J= 5.5 Hz, 1H, H_1= acetal), 6.04~6.88(m, 7H, O-CH_2- and O-CH-), 8.29(m, 2H, H_2= -CH_2-), 8.85(t, J= 7 Hz, 18H, -CH_3), 8.86(s, 9H, t-Bu), 9.78(s, 9H, Si-Me_3).

Found: C, 69.14 ; H, 10.38 %. Calcd for $C_{22}H_{40}O_3Si$: C, 69:42 ; H, 10.59 %.

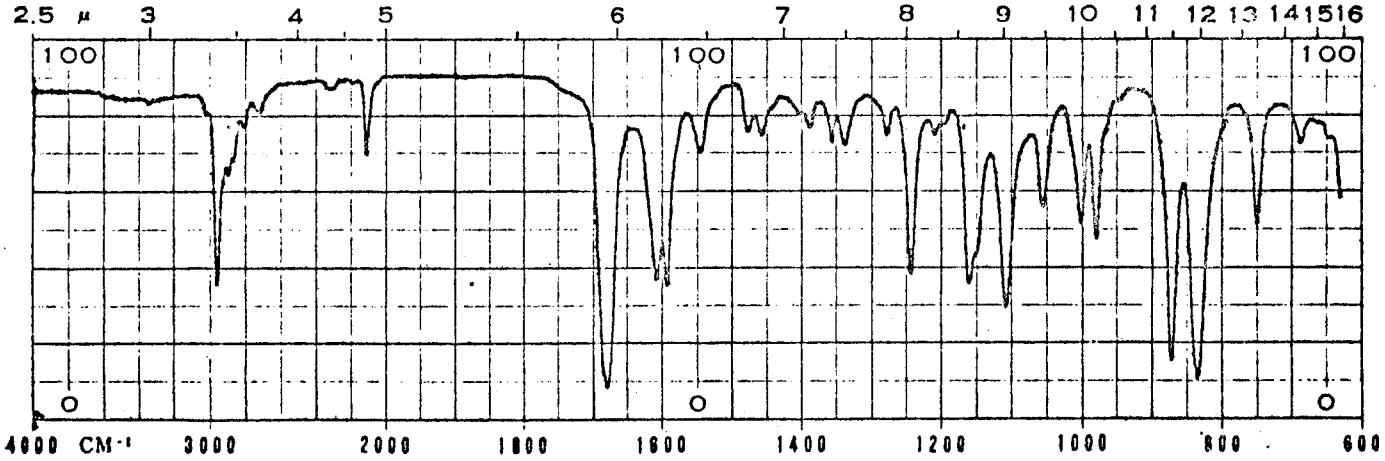
Infrared spectrum of (79),(CCl_4).



7-t-Butyl-9-trimethylsilyl-2,4,6-nonatrien-8-ynal(80).

A mixture of (79)(2,00 g, 5.26 mmol), sodium acetate(2.00 g, 24.4 mmol), acetic acid(18 ml) and water(2 ml) was stirred at 60°C for 6 hr under nitrogen and cooled to room temperature. The mixture was poured onto saturated sodium carbonate solution and extracted with ether(20 ml×3). The extracts were washed successively with saturated sodium carbonate solution and sodium chloride solution and dried($MgSO_4$). Removal of the solvent under reduced pressure and distillation through a short-path apparatus gave (80), 1.19 g (Y: 86.9%), as a viscous yellow liquid, bp 111～114 °C / 0.02mmHg; mass spectrum(m/e), 260(M^+); infrared spectrum(film) 2810w, 2725w (CHO), 2120m(-C≡C-), 1683vs(C=O), 1612s, 1597s(C=C), 1247s(Si-CH_3), 1007m, 987m(trans-CH=CH-), 880vs, 843vs, 759m(Si-C) cm^{-1}; n.m.r. spectrum(CCl_4) 0.43(d, J= 4 Hz, 1H, CHO), 2.65～4.13(m, 5H, olefinic), 8.81(s, 9H, t-Bu), 9.72(s, 9H, Si-Me_3).

Infrared spectrum of (80),(film).



2,4-Dinitrophenylhydrazone of the trienyne-aldehyde(80).

A solution of 2,4-dinitriphenylhydrazone(119 mg, 0.601 mmol) in phosphoric acid(1 ml)-ethanol(1 ml) was added to a solution of (80)(134 mg, 0.515 mmol) in ethanol(8 ml) and the mixture was

allowed to stand at room temperature for 30 min. Reddish brown precipitate deposited was filtered off and washed with ethanol to give the hydrazone, 164 mg(Y: 72.3 %), which was short column-chromatographed on silicagel(benzene) and recrystallized from *n*-hexane-benzene(3 : 1) gave reddish brown crystals, mp 208~211 °C.

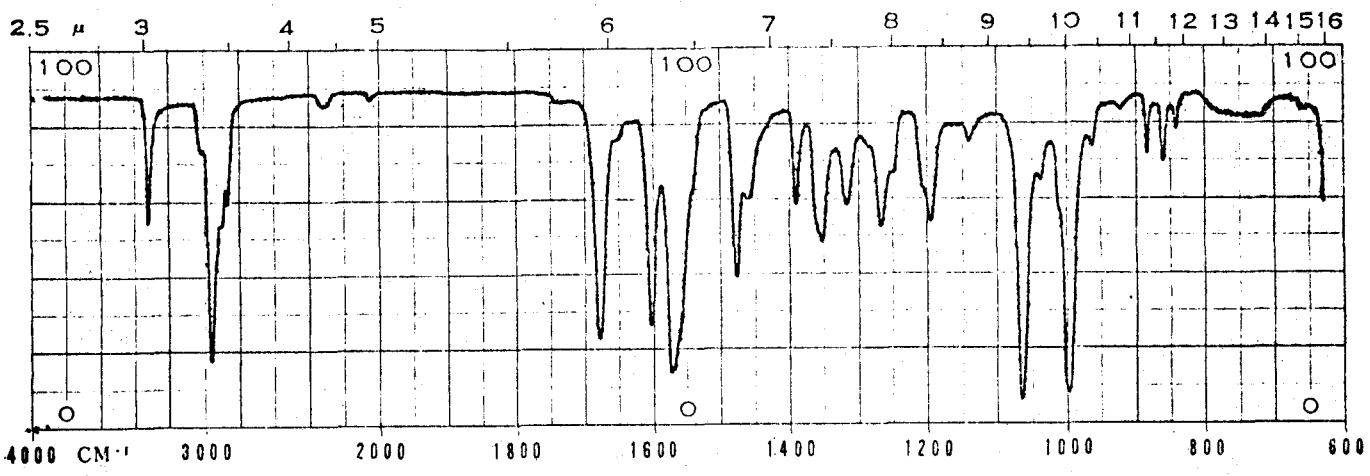
Found: C, 60.09 ; H, 6.38 ; N, 12.69 %. Calcd for $C_{22}H_{28}N_4O_4Si$: C, 59.98 ; H, 6.41 ; N, 12.72 %.

1,9-Di-t-butyl-1-oxo-2,4,6,8-undecatetraen-10-yne(81).

A solution of sodium hydroxide(209 mg, 5.22 mmol) in ethanol(1 ml) -water(1 ml) was added to a solution of the aldehyde(80)(100 g, 3.84 mmol) and pinacolone(522 mg, 5.21 mmol) in ethanol(10 ml) at 0 °C under nitrogen atmosphere. The mixture was kept at room temperature for 24 hr and then acidified with 3N hydrochloric acid (10 ml). The mixture was extracted with ether(20 ml × 3). The extracts were washed successively with sodium bicarbonate and saturated sodium chloride solutions and dried($MgSO_4$). The solvent was evaporated under reduced pressure and the residue was chromatographed on alumina. Elution with n-hexane-benzene(9 : 1) gave crystals, which was washed with methanol to afford pure (80), 618 mg(Y: 59.5 %). The analytical sample was recrystallized from methanol to give yellow crystals, mp 133.5~134.0 °C; mass spectrum (m/e), 270(M^+); infrared spectrum(CCl_4), 3325m(≡CH), 2060vw(-C≡C-), 1684s(C=O), 1607s(C=C), 1574vs(C=C), 1070vs, 1003vs(trans-CH=CH-) cm^{-1}; n.m.r. spectrum(CCl_4)τ 2.52~3.92(m, 7H, olefinic), 6.63 (s, 1H, -C≡CH), 8.82(s, 9H, t-Bu), 8.86(s, 9H, t-Bu); u.v. spectrum $\lambda_{max}^{99\%EtOH}$(ε), 261(5,870), 359*(52,000), 369(53,000).

Found: C, 84.74 ; H, 9.75 %. Calcd for $C_{19}H_{26}O$: C, 84.39 ; H, 9.69 %.

Infrared spectrum of (81),(CCl_4).

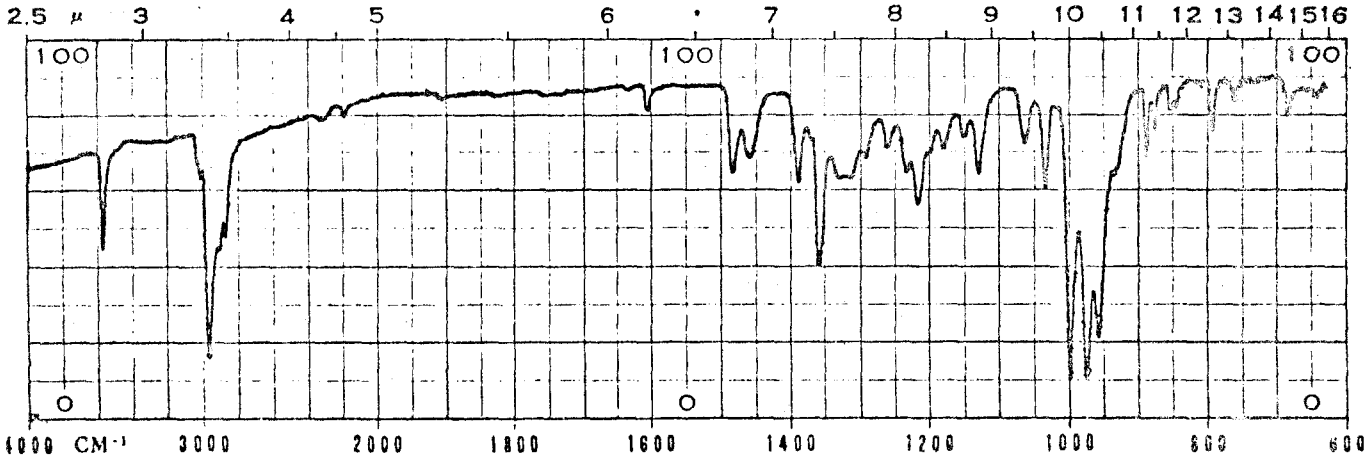


1,4,12,15-Tetra-t-butyl-4,6,8,10,15,17,19,21-cyclodocosaocta-en-2,13-diyn-1,12-diol(82). A solution of the tetraenyne-ketone (81)(160 mg, 0.592 mmol) in absolute tetrahydrofuran(60 ml) was added very slowly to a suspension of finely powdered potassium hydroxide(2.00 g, 35.7 mmol) in liquid ammonia(150 ml) at -34°C for 8 hr(the apparatus Fig. 22). After being stirred for 6 hr at -34°C, ammonium chloride(4.00 g, 0.0748 mmol) was added and the ammonia was allowed to evaporate off and the residue was treated with water and ether(20 ml). The aqueous layer was then further extracted with ether(15 ml×2). The combined organic layer was washed successively with water and saturated sodium chloride solution. Drying($MgSO_4$), evaporation under reduced pressure yielded yellow crystals. Chromatography on alumina(40 g) and elution with ether-benzene(1:49～1:19) gave a diastereomer(82a), 56 mg(Y: 31 %), as colorless crystals. The analytical sample was washed thoroughly with ethyl acetate, mp 252°C(dec.); mass spectrum(m/e), 540(M^+), 483(M -57), 57(base peak); infrared spectrum(KBr), 3570m(-OH), 2190vw(-C≡C-), 1638vw, 1607w(C=C), 1001vs, 977vs,960s(trans-CH=CH-) cm^{-1}; n.m.r. spectrum($CDCl_3$), τ 2.8～4.2(m, 14H, olefinic), 8,35

(s, 2H, -OH)disappeared on shaking with D_2O, 8.79(s, 18H, t-Bu), 8.90(s, 18H, t-Bu); u.v. spectrum, $\lambda_{max}^{99\%EtOH}(\varepsilon)$, 248.5(22,600),292* (50,600), 307(120,000),320(173,000), 341*(34,800), 359(27,800) nm.

Found: C, 84.15 ; H, 9.61 %. Calcd for $C_{38}H_{52}O_2$: C, 84.39 ; H, 9.69 %.

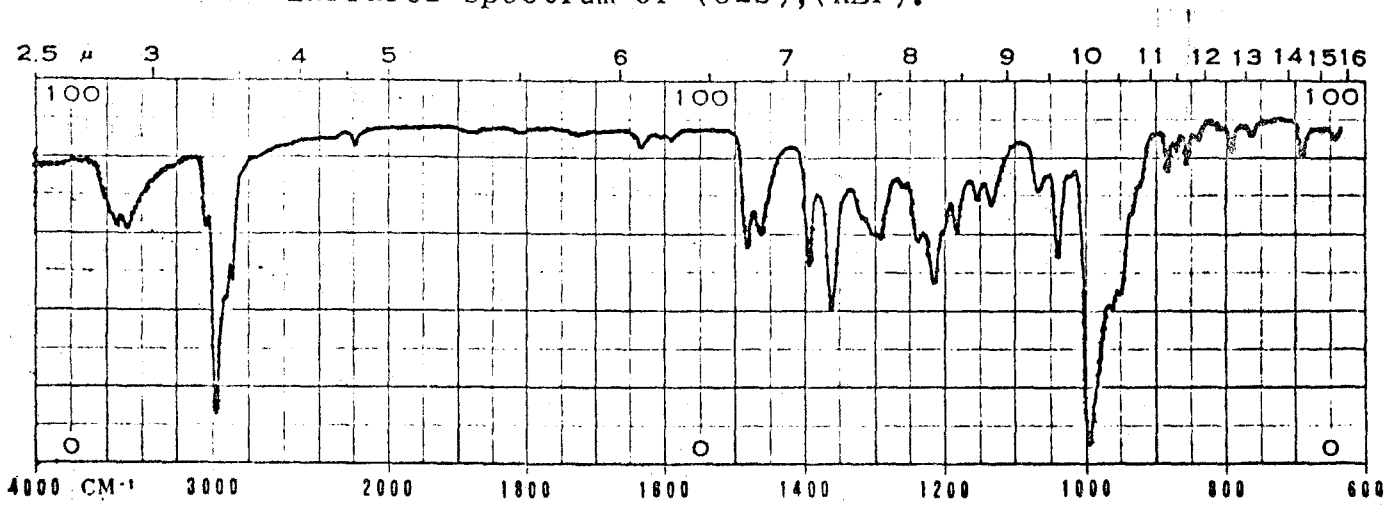
Infrared spectrum of (82a),(KBr).



Elution with ether-benzene(1:3) gave another diastereomer(82b), 105 mg(Y: 58%), as colorless crystals. The sample for analysis was washed with ethyl acetate, mp 220～221°C; mass spectrum(m/e), 540(M^+), 483(M - 57, base peak), 57(t-Bu); infrared spectrum(KBr), 3530m, 3465m(-OH), 2180vw(-C≡C-), 1634w,1590vw(C=C), 993vs(trans-CH=CH-) cm^{-1}; n.m.r. spectrum($CDCl_3$) τ 2.8～4.2(m, 14H, olefinic), 8.31(s, 2H,-OH) disappeared on shaking with D_2O, 8.80(s, 18H, t-Bu); u.v. spectrum $\lambda_{max}^{99\%EtOH}(\varepsilon)$, 248.5(22,200), 292*(45,400), 307 (109,000), 320(160,000), 341*(34,200), 359(26,100) nm.

Found: C, 84.56 ;; H, 9.84 %. Calcd for $C_{38}H_{52}O_2$: C, 84.39 ; H, 9.69 %.

Infrared spectrum of (82b),(KBr).



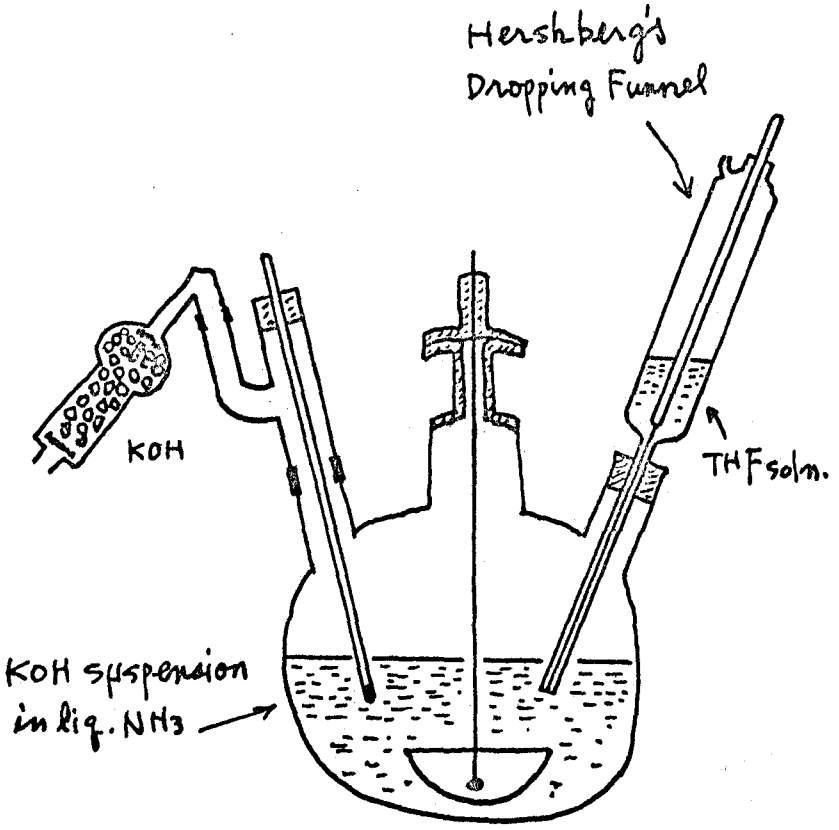


Fig. 22. The apparatus of cyclic dimerization.

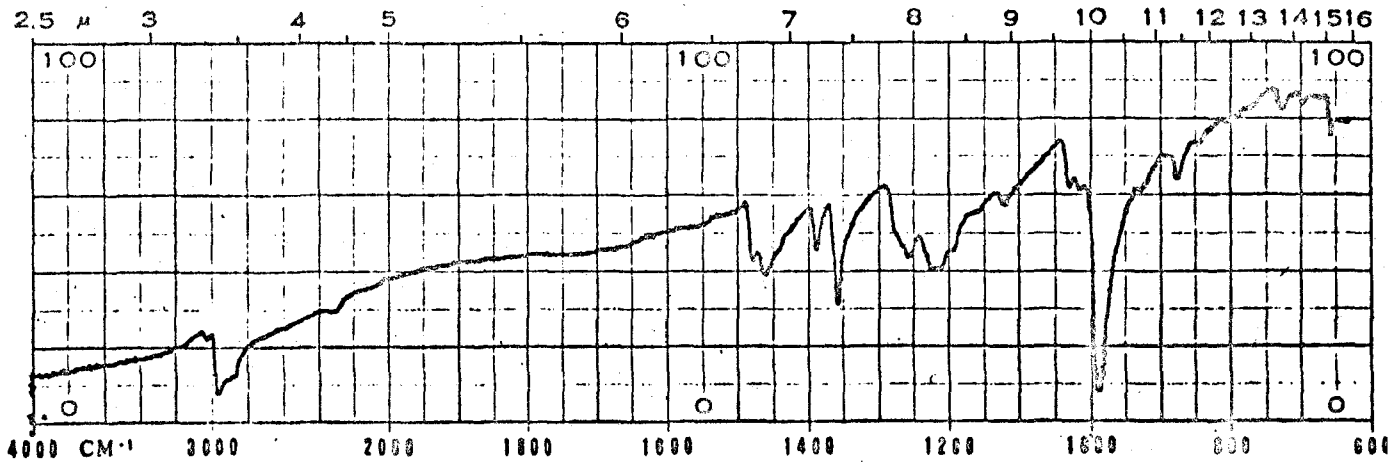
3,11,14,22-Tetra-t-butyl-1,12-didehydro[22]annulene(83).

To a suspension of (82, a mixture of diastereomers)(136 mg, 0.251 mmol) in ether(10 ml) was added ether(10 ml) saturated with hydrogen chloride at -60 °C under nitrogen atmosphere. Finely powdered stannous chloride dihydrate(600 mg, 2.66 mmol) was added to the mixture at -60 °C. The reaction mixture was vigorously stirred at the same temperature for 15 min and then poured onto ice-cold sodium carbonate solution. Dichloromethane was added and the organic layer was separated, washed with saturated sodium chloride solution and dried(K_2CO_3). Evaporation of the solvent in vacuo gave a dark violet residue, which was chromatographed on alumina(Woelm act. I) and eluted with carbon tetrachloride-dichloromethane(19:1) to afford pure annulene(83), 120 mg(Y: 94.2%). The sample for analysis was recrystallized from benzene-methanol to give dark violet crystals, mp ~230 °C(dec.); mass spectrum(m/e), 506(M^+), 449(M - 57), 57(t-Bu, base peak); infrared spectrum(KBr), 3020w, 2950s, 992vs, 881w; u.v. spectrum $\lambda_{max}^{THF}(\varepsilon)$, 221.5(10,400), 248(11,900), 261*(8,810), 277*(9,200), 290(12,100), 302.5(17,100), 316.5*(9,610), 377*(7,720), 395(147,000), 412.5(300,000), 512*(6,640), 556(10,400), 591(11,300), 712*(83), 757*(72), 782(77), 853*(66), 895(106) see Fig. 8(p. 34); n.m.r. spectrum, see Fig. 9(p. 35) and Table 4(p. 34).

Formation of C-T complex between the annulene(83) and 2,4,7-trinitrofluorenone. To a solution of (83)(25 mg, 0.049 mmol) in benzene(20 ml)-methanol(20 ml) was added a solution of 2,4,7-trinitrofluorenone(31 mg, 0.098 mmol) in benzene(5 ml)-methanol(5 ml) at room temperature and the mixture was allowed to stand at room temperature(18 °C) to deposite the black violet crystals, 32 mg(Y: 79%), mp ~260 °C(dec.).

Found: C, 74.39 ; H, 6.67 %. Calcd for $C_{51}H_{55}N_3O_7$: C, 74.52 ; H, 6.74 ; N, 5.11 %.

Infrared spectrum of (83),(KBr).



Catalytic hydrogenation of the didehydro[22]annulene(83).

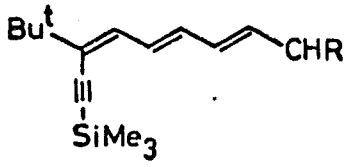
A mixture of (83)(32 mg, 0.063 mmol), platinic oxide(100 mg) in acetic acid(20 ml)-ethyl acetate(20 ml) was vigorously stirred under hydrogen at -15～-20°C overnight. The catalyst was removed by filtration and platinum was washed with ether(30 ml). The organic layer was washed successively with water, saturated sodium carbonate and sodium chloride solutions, and dried($MgSO_4$). Evaporation of the solvent in vacuo gave a crystalline residue, which was chromatographed on alumina(Woelm act. I) and eluted with n-hexane to afford 1,4,12,15-tetra-t-butyl-cyclodocosane, 31 mg(Y: 92%). The analytical sample was recrystallized from ethyl acetate-methanol to give colorless crystals, 15 mg, mp 104～112°C; mass spectrum (m/e), 532(M^+), 475(M -57), 57(base peak); infrared spectrum(KBr), 2930vs, 2860s, 1475m, 1393m, 1365m cm^{-1}; n.m.r. spectrum(CCl_4), τ 8.72(br s, $-CH_2-$,-CH-), 9.05(s, t-Bu), the ratio of 10:9.

Found: C, 85.35 ; H, 14.19 %. Calcd for $C_{36}H_{76}$: C, 85.63 ; H, 14.37 %.

The filtrate was evaporated and recrystallized from ethyl acetate-methanol to afford colorless crystals, 8 mg, mp 91～95°C (Found: C, 86.11 ; H, 14.21 %.)

V. SYNTHESIS OF TETRA-t-BUTYL-DIDEHYDRO[26]ANNULENE(84).

7-t-Butyl-9-trimethylsilyl-2,4,6-nonatrien-8-ynal Diethyl Acetal(85). To a solution of (80)(2.62 g, 10.1 mmol) in ethyl orthoformate(25 ml) was added a solution of p-toluenesulfonic acid (300 mg, 1.58 mmol) in ethanol(3 ml) at 20°C under nitrogen. The mixture was stirred at room temperature for 18 hr and then cooled in an ice bath. The reaction mixture was poured onto ice-cold sodium carbonate solution and extracted with ether(25 ml×3). The combined organic layer was washed successively with saturated sodium carbonate and sodium chloride solutions and dried(K_2CO_3). Removal of the solvent in vacuo and distillation yielded (85), 3.07 g(Y: 91.2 %) as a yellow viscous liquid, bp 126~128°C / 0.013 mmHg; mass spectrum(m/e), 334(M^+), 288(M - 46); infrared spectrum(film), 2130m(-C≡C-), 1685vw, 1645vw(C=C), 1248s(Si-CH_3), 878vs, 840vs, 757m(Si-C) cm^{-1}; n.m.r. spectrum(CCl_4), τ 3.01~4.01(m, 4H, olefinic), 4.41(dd, J= 5.0 and 14.5 Hz, 1H, α-position of acetal), 5.07(d, J= 5Hz, 1H, acetal), 6.50(m, 4H, O-CH_2-), 8.83(t, J= 7.5 Hz, 6H, -CH_3), 8.85(s, 9H, t-Bu), 9.76(s, 9H, -$SiMe_3$).



(80) R=O
(85) R=(OEt)$_2$

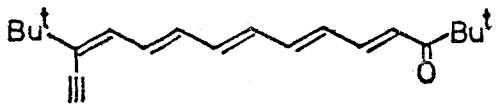
1,11-Di-t-butyl-1-oxo-2,4,6,8,10-tridecapentaen-12-yne(88) from the trienyne-acetal(85). To a solution of the acetal(85) (2.04 g, 6.10 mmol) in dry benzene(15 ml) was added a drop of boron trifluoride etherate at 35°C and immediately a solution of ethyl vinyl ether (475 mg, 6.59 mmol) in dry benzene(5 ml) was slowly

added at 35°C. After being stirred for 30 min at the same temperature, potassium carbonate was added to result in a light yellow solution. The potassum carbonate was filtered off and washed with ether. The filtrate and washings were concentrated under reduced pressure to give crude (86), 2.50 g(homogeneous on t.l.c.).

A mixture of (86, 2.50 g), sodium acetate(2.50 g, 30.5 mmol), acetic acid(28 ml) and water(2 ml) was stirred at 60°C for 12 hr under nitrogen. The reaction mixture was poured onto saturated sodium carbonate solution and extracted with ether. The extracts were washed with saturated sodium carbonate solution and saturated sodium chloride solution and dried($MgSO_4$). Removal of the solvent and column chromatography on alumina(50 g-eluent:benzene) gave (87), 1.45 g, as a reddish brown oil.

To a solution of crude (87, 1.45 g) and pinacolone(556 mg, 5.55 mmol) in ethanol(20 ml) was added a solution of sodium hydroxide(320 mg, 8.00 mmol) in ethanol(2 ml)-water(2 ml) at 0°C under nitrogen. The mixture was stirred at 30°C for 20 hr and then poured onto ice-cold 3N hydrochloric acid(10 ml). The mixture was extracted with ether and the extracts were washed with saturated sodium bicarbonate and sodium chloride solutions and dried($MgSO_4$). Evaporation of the solvent under reduced pressure gave a oily residue, which was chromatographed on silica gel(30 g) and eluted with n-hexane-benzene(1:1)~benzene to afford (88), 741 mg(Y: 41.0 % based on the acetal(85). The analytical sample was recrystallized from ether at -75°C to give yellow crystals, mp 92~94°C; mass spectrum(m/e), 296(M^+), 239(M - 57), 57(t-Bu, base peak); infrared spectrum(KBr), 3290m(≡CH), 2080vw(-C≡C-), 1678(C=O) cm^{-1}. n.m.r. spectrum(CCl_4) τ 2.48~3.90(m, 9H, olefinic), 6.62(s, 1H, C≡CH), 8.82(s, 9H,t-Bu), 8,85(s, 9H, t-Bu).

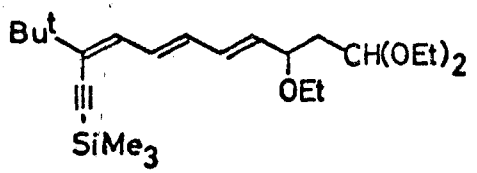
Found: C, 84.82 ; H, 9.52 %. Calcd for $C_{21}H_{28}O$: C, 85.08 ; H, 9.52 %.



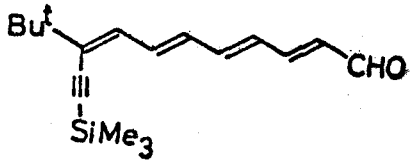
(88)

The ketone was fairly unstable and rapidly decomposed on exposure to air and light at room temperature, becoming a brown solid. Samples stored under nitrogen at -20°C suffered only slight decomposition after several days, and ether solutions of (88) at 0°C were also relatively stable.

The spectral data of the intermediates(86) and (87) were as follows. The ethoxyacetal(86), as a pale yellow liquid; mass spectrum(m/e), 334(M^+); infrared spectrum(film), 2130m(-C≡C-), 1685w(C=C), 1250s(Si-CH_3), 880vs, 840vs, 757m(Si-C) cm^{-1}; n.m.r. spectrum(CCl_4) τ 5.46(m, 1H, acetal), 8.25(m, 2H, H_2= -CH_2-), 9.76(s, 9H, -$SiMe_3$). The tetraenyne-aldehyde(87) as a yellowish brown liquid; mass spectrum(m/e), 406(M^+); infrared spectrum(film), 2805w, 2720w(CHO), 2135m(-C≡C-), 1679vs(C=O), 1617m, 1576vs(C=C), 1250s(Si-CH_3), 1009s, 992s(trans-CH=CH-), 879vs, 843vs, 760m(Si-C) cm^{-1}; n.m.r. spectrum(CCl_4) τ 0.46(d, J= 7.0 Hz, 1H, CHO), 2.49~4.12(m, 7H, olefinic), 8.83(s, 9H, t-Bu), 9.74(s, 9H,-$SiMe_3$).



(86)



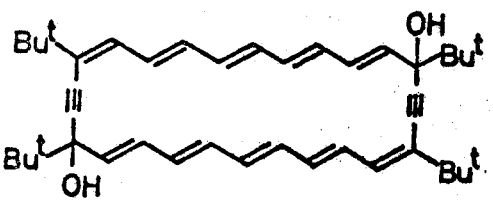
(87)

1,4,14,17-Tetra-t-butyl-4,6,8,10,12,17,19,21,23,25-cyclohexacosadecaen-2,15-diyn-1,14-diol(90). To a stirred suspension of finely powdered potassium hydroxide(5.00 g) in liquid ammonia (250 ml) was added very slowly a solution of the ketone(88)(160 mg, 0.540 mmol) in absolute tetrahydrofuran(40 ml) at -34°C for 12 hr. The mixture was stirred for a further 2 hr, and ammonium chloride (10 g) was added. The ammonia was allowed to evaporate off and the residue was treated with ether. The organic layer was separated and the aqueous layer was extracted with ether. The combined organic layer was washed successively with water and saturated sodium chloride solution and dried($MgSO_4$) and evaporated under reduced pressure. The crystalline residue thus obtained was chromatographed on alumina and eluted with THF-benzene(3:17~1:4) to give firstly (90a), a diastereomer of (90) as pale yellow crystals, 53 mg(Y: 33 %), mp 277°C(dec.); mass spectrum(m/e), 592 (M^+), 535(M -57), 57(base peak); infrared spectrum(KBr), 3565m (-OH), 2205vw(-C≡C-) cm^{-1}.

Found: C, 84.86 ; H, 9.44 %. Calcd for $C_{42}H_{56}O_2$: C, 85.08 ; H, 9.52 %.

Further elution of the column with THF-benzene(1:4~1:1) gave (90b), another diastereomer of (90) as lemon yellow crystals, 96 mg(Y: 60 %), mass spectrum(m/e), 592(M^+), 535(M - 57), 57(base peak); infrared spectrum(KBr), 3540m, 3455m(-OH), 2190vw(-C≡C-) cm^{-1}.

Found: C, 84.79 ; H, 9.91 %. Calcd for $C_{42}H_{56}O_2$: C, 85.08 ; H, 9.52 %.



(90)

3,13,16,26-Tetra-t-butyl-1,14-didehydro[26]annulene(84).

From (90a). To a suspension of the cyclic glycol(90a)(27.5 mg, 0.0464 mmol) in ether(10 ml) was added ether(4 ml) saturated with hydrogen chloride at -75°C under nitrogen. Finely powdered stannous chloride dihydrate(200 mg, 0.886 mmol) was added and the resulting greenish mixture was stirred ar the same temperature for 10 min and then poured onto ice-cold sodium carbonate solution. The organic layer was separated and aqueous layer was extracted with dichloromethane. The combined organic layer was washed with saturated sodium carbonate solution and dried. The solvent was evaporated under reduced pressure on a rotary evaporator(the internal temperature of the flask $<0°C$) and immediately chromatographed on alumina at -15°C. Elution with n-pentane-dichloromethane(9:1$\sim$4:1) gave (84), 23 mg(Y: 89 %).

From (90b). To a solution of (90b)(26 mg, 0.044 mmol) in ether (5 ml) was added ether(2 ml) saturated with hydrogen chloride at -75°C under nitrogen. Finely powdered stannous chloride dihydrate (200 mg, 0.886 mmol) was added and the resulting greenish mixture was stirred at the same temperature for 10 min and worked up by the same way as above mentioned procedure. Evaporation and chromatographic purification at low temperature gave (84), 21 mg(Y: 86 %).

The annulene was recrystallized from dichloromethane-ether at -78°C to afford black violet crystals, which decomposed on attempted melting point determination; mass spectrum(m/e), 558 (M^+), 501(M - 57), 57(base peak); u.v. spectrum $\lambda_{max}^{THF}(\varepsilon)$, 223.5 (15,000),268*(14,000), 280(15,000),285.5(15,000), 316(24,000), 330 (25,000), 427(170,000), 442*(150,000), 584(9,600), 840*(64), 930

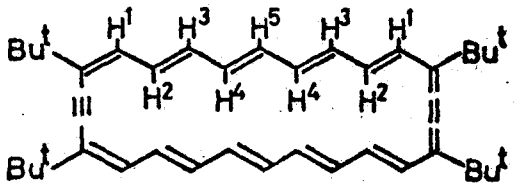
(41), 975(43)(the spectrum was measured at 25°C and showed no differences of the shape from the spectrum measured after 1 hr); n.m.r. spectrum ($CDCl_3$), τ 1.73(m, H_3 and H_5), 2.05(d, J= 13 Hz, H_1), 8.0~8.2(m, H_2 and H_4), 8.39(s, t-Bu) see Fig. 11 and Fig. 12.

The annulene was less stable and soluble than tetra-t-butyldidehydro[22]annulene(83). A saturated solution of (84) in $CDCl_3$ was decomposed gradually at room temperature (half-life $t_{1/2}$ = ca. 1 hr at 36°C) but a very dilute solution could be stored without decomposition for 1 hr at room temperature.

Catalytic hydrogenation of didehydro[26]annulene(84).

A mixture of (84)(23 mg, 0.041 mmol) and platinic oxide(100 mg) in ethyl acetate(20 ml)-acetic acid(20 ml) was added at -15 °C under hydrogen for 4 hr and at room temperature for 2 hr. The catalyst was removed by filtration, and washed with benzene(30 ml) Filtrate and washings were washed with water and saturated sodium carbonate solution and dried($MgSO_4$). Removal of the solvent in vacuo gave a crystalline residue. Chromatography on alumina(Woelm act. I) and elution with n-hexane afforded 1,4,14,17-cyclohexacosane, 22 mg(Y: 91 %). The sample for analysis was recrystallized with ethyl acetate-methanol to give colorless crystals, mp 111~113°C; mass spectrum(m/e), 588(M^+); n.m.r. spectrum(CCl_4) τ 8.73(m, $-CH_2-$, $-CH=$), 9.13(s, $-CH_3$), the ratio of ca. 4:3.

Found: C, 85.85 ; H, 14.06 %. Calcd for $C_{42}H_{84}$: C, 85.63 ; H, 14.37 %.



(84)

VI. SYNTHESIS OF TETRA-t-BUTYL-DIDEHYDRO[30]ANNULENE(91).

3-t-Butyl-2-penten-4-ynal(41b). A solution of t-butyl-β-chlorovinyl-ethynyl carbinol(20.00 g, 0.1158 mol) in dioxane(40 ml) was added to 4N sulfuric acid(600 ml) at 60°C under nitrogen and the mixture was stirred vigorously for 6 hr at the same temperature. The mixture was extracted with ether and the extracts were washed successively with water, saturated sodium bicarbonate and saturated sodium chloride solutions and dried($MgSO_4$). Evaporation of the solvent in vacuo and distillation gave pure (41b), 13.04 g(Y: 82.7%).

3-t-Butyl-2-penten-4-ynal Dimethyl Acetal(95). To a solution of (41b)(12.90 g, 94.72 mmol) in methyl orthoformate(40 ml) was added a solution of p-toluenesulfonic acid monohydrate(1.30 g, 6.83 mmol) in methanol(2 ml) at room temperature under nitrogen. The mixture was stirred for 15 hr at 15°C and then chilled in an ice-bath. The reaction mixture was poured onto ice-cold sodium bicarbonate solution and the organic layer was separated. The aqueous layer was extracted with ether(30 ml × 2). The combined organic layer was washed successively with saturated sodium bicarbonate solution and saturated sodium chloride solution and dried(K_2CO_3). Removal of the solvent in vacuo and distillation gave (95), 16.33g, (Y: 94.6 %), bp 74~76°C/8mmHg, as a colorless liquid; mass spectrum (m/e), 182(M^+), 167(M - 15), 151(M - 31); infrared spectrum(film), 3270m(≡CH), 2095vw(-C≡C-), 1628(C=C) cm^{-1}; n.m.r. spectrum($CDCl_3$) τ 4.22(d, J= 7.5 Hz, 1H, olefinic), 4.80(d, J= 7.5 Hz,1H, acetal), 6.33(s, 3H, -OMe), 6.76(s, 1H, C≡CH), 8.85(s, 9H, t-Bu).

Hydrolysis of the Acetal(95). A mixture of (95)(3.00 g, 16.5 mmol), acetic acid(6 ml) and water(2 ml) was stirred for 1.5 hr at 22°C. Water was added and the mixture was extracted with ether. The organic layer was washed with water, saturated sodium bicarbonate and saturated sodium chloride solutions and dried($MgSO_4$). Removal of the solvent in vacuo and distillation gave the aldehyde (41b), 1.95 g(Y: 87.0 %).

t-Butyl-pentenynal Dimethyl Acetal(95) from t-Butyl-β-chlorovinyl-ethynyl Carbinol. A solution of the ethynyl carbinol(20.00 g, 0.1158 mol) in dioxane(40 ml) was added to 4N sulfuric acid(600 ml) at 60°C under nitrogen. The mixture was stirred vigorously for 3.5 hr at 60°C and then worked up by the usual way. Removal of the solvent in vacuo gave crude aldehyde(41b) as a yellowish brown oil. The crude aldehyde was dissolved in methyl orthoformate (60 ml). To the solution was added a solution of p-toluenesulfonic acid monohydrate(2.00 g, 10.5 mmol) in methanol(2 ml) at room temperature. After being stirred at 15°C for 18 hr, powdered potassium carbonate(10.00 g) was added and then benzene(30 ml) was added. The mixture was srirred for 1 hr and the precipitated solid was filtered off and washed with ether. The filtrate and washings were vaporated under reduced pressure and the residue was distilled to yield pure (95), 18.06 g(Y: 85.6 %), bp 63~64°C / 4mmHg.

Preparation of methoxybutadiene(96).

(see APPENDIX p. 179)

Reaction of (96) and (95) catalyzed by boron trifluoride etherate. (see APPENDIX p. 179)

3-t-Butyl-5-trimethylsilyl-2-penten-4-ynal(103) from the dimethyl acetal(95). To a stirred solution of ethyl magnesium bromide under nitrogen from magnesium(1.00 g, 41.1 mmol), ethyl bromide(4.70 g) and tetrahydrofuran(20 ml) was added a solution of the acetal(95)(5.00 g, 27.4 mmol) in tetrahydrofuran(15 ml) at 10～15°C with ice-cooling. The mixture was stirred at room temperature for 1 hr and then cooled in an ice-bath. Trimethylchlorosilane(4.50 g, 41.4 mmol) was added at 10～15°C and the mixture was stirred for a further 1 hr at 0°C. Saturated ammonium chloride solution(20 ml) was added slowly and the mixture was poured onto water. The organic layer was separated and the aqueous layer was extracted with ether. The combined organic layer was washed with water and saturated sodium chloride solution and dried($MgSO_4$). Removal of the solvent in vacuo gave a brown residue.

The residue was dissolved in acetic acid(5 ml) and water(2 ml) was added. The mixture was vigorously stirred at 20°C for 1.5 hr. Water(50 ml) was added and the mixture was extracted with ether. The extracts were washed with water, saturated sodium bicarbonate and sodium chloride solutions and dried($MgSO_4$). Evaporation of the slovent in vacuo and distillation gave a pale yellow liquid (103), 5.31 g(Y: 92.9 %), bp 93～94°C / 6 mmHg; mass spectrum (m/e), 208(M^+); infrared spectrum(film), 2830m, 2735w(CHO), 2150m (-C≡C-), 1680vs(C=O), 1583s(C=C), 1251s, 1212m(Si-CH_3), 883vs, 846 vs, 762s(Si-C) cm^{-1}; n.m.r. spectrum($CDCl_3$) τ -0.05(d, J=8.0 Hz, 1H, CHO), 3.83(d, J= 8.0 Hz, 1H, olefinic), 8.80(s, 9H, t-Bu), 9.74(s, 9H, -$SiMe_3$).

Found: C, 69.22 ; H, 9.67 %. Calcd for $C_{18}H_{30}OSi$: C, 69.18 ; H, 9.68 %.

Condensation of the trimethylsilylpentaenyne-aldehyde(41b) with 1.5eq. crotonaldehyde. To a solution of the aldehyde(41b) (2.15g, 10.3 mmol), piperidine(400mg, 4.70mmol) and acetic acid (400mg, 6.66 mmol) in ethanol(120 ml) was slowly added a solution of freshly distilled crotonaldehyde(1.08g, 15.4 mmol) in ethanol (30 ml) over a period of 16 hr under an atmosphere of carbn dioxide and was stirred for a further 1 hr. The solvent was evaporated under reduced pressure to give a reddish brown oil, which was dissolved in dichloromethane(100 ml). The organic layer was washed succesively with water, saturated sodium bicarbonate and sodium chloride solutions and dried($MgSO_4$). The solvent was evaporated *in vacuo* and the residue was chromatographed on silica gel(250g) (eluent: n-hexane-benzene). Elution of n-hexane-benzene(1:1) and distillation(bp *ca.* 90°C/5mmHg) gave the recovered(41b), 283mg. Secondly, elution of n-hexane-benzene(1:1)~benzene gave mono-adduct(80), which was purified by distillation, 718 mg(Y: 31 %) bp *ca.* 120°C/0.03mmHg. The compound was identical with authentic sample prepared from (79), see p. 119.

Elution with benzene gave di-aduct(94), rechromatography on alumina afforded pure(94), 651 mg(Y: 23 %), as a viscous yellowish brown liquid; mass spectrum(m/e) 312(M^+); infrared spectrum(film) 2810w, 2725w (CHO), 2135m(-C≡C-), 1679vs(CHO), 1618s, 1568s(C=C)cm^{-1}; n.m.r. spectrum($CDCl_3$) τ 0.44(d, J 8HZ, 1H, CHO), 2.63~4.06(m, 9H, olefinic), 8.84(s, 9H, t-Bu), 9.76(s, 9H, $SiMe_3$).

Finally, elution of the column with benzene~benzene-ether (20:1) gave a crystalline solid, which consisted of tri-adduct(104), tetra-adduct, etc.

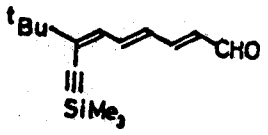
Condensation of (41b) with 2.5eq. crotonaldehyde. To a solution of the aldehyde(41b)(2.00 g, 9.60 mmol), piperidine(400 mg) and acetic acid(400 mg) in ethanol(120 ml) was slowly added a solution of freshly distilled crotonaldehyde(1.68 g, 24.0 mmol) in ethanol(40 ml) over a period of 20 hr under an atmosphere of carbon dioxide and was stirred for further 1 hr. The reaction mixture was worked up by the same way as abovementioned procedure and evaporation of the solvent in vacuo gave a residue, which was dissolved in benzene. The precipitated solid was filtered off and filtrate was evaporated under reduced pressure. Chromatographic separation on silica gel(200 g)[eluent: n-hexane-benzane] gave (80), (94) and (104).

In this reaction condition the starting aldehyde could not recovered.

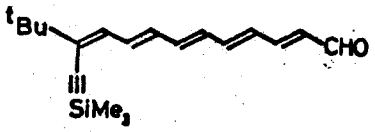
Mono-adduct(80) 280 mg(Y: 11 %).

Di-adduct(94) 755 mg(Y: 25 %).

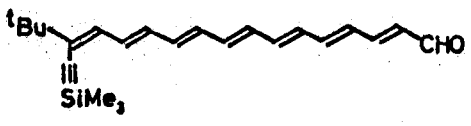
Tri-adduct(104) 120 mg(Y: 3.4%).



(80)



(94)



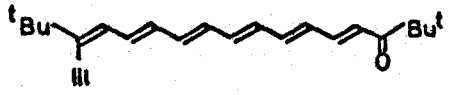
(104)

1,13-Di-t-butyl-1-oxo-2,4,6,8,10,12-pentadecahexaen-14-yne(102).

A solution of sodium hydroxide(290 mg, 7.25 mmol) in ethanol(1 ml)-water(1 ml) was added to a solution of the pentaenyne-aldehyde(94) (750 mg, 2.40 mmol) and pinacolone(290 mg, 2.90 mmol) in ethanol (15 ml) at room temperature under nitrogen. The mixture was stirred for 22 hr at 20~25°C and then poured onto ice-cold 3N hydrochloric acid(10 ml). The mixture was extracted with ether and the extracts were washed successively with water, saturated sodium bicarbonate and saturated sodium chloride solutions and dried ($MgSO_4$). Removal of the solvent in vacuo gave an oily residue, which was chromatographed on silicagel(200 g) and eluted with n-hexane-benzene(1:1) to give pure ketone(102), 295 mg(Y: 38 %), mp 49.0~49.5°C, as orange yellow crystals(from ether at -78°C); mass spectrum(m/e), 322(M^+); infrared spectrum(KBr), 3300m(≡CH), 2085w(-C≡C-), 1672s(C=O), 1588vs, 1550vs(C=C) cm^{-1}; n.m.r. spectrum ($CDCl_3$)τ 2.40~3.90(m, 11H, olefinic), 6.56(s, 1H, C≡CH), 8.83(s, 18H, t-Bu); u.v. spectrumλ_{max}^{THF}(ℓ), 235*(5,960), 243(6,330), 267 (4,310), 278(4,720), 293*(6,000), 303(7,620), 360*(31,300), 385* (61,700), 405.5(83,600), 428(73,800) nm.

Found: C, 84.90 ; H, 9.32 %. Calcd for $C_{23}H_{30}O$: C, 85.66 ; H, 9.38 %.

The ketone was unstable and the crystals turned brown on standing in air at room temperature. (102) was usually stored in an ether solution at 0°C. The elemental analysis was unsatisfactory but the ratio(H/C) was same, ie., Found: H/C= 0.1098 and Calcd: H/C= 0.1095. This result indicated that the ketone(102) was oxidized by air.



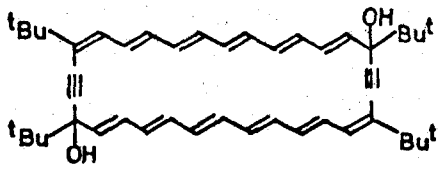
(102)

1,4,16,19-Tetra-t-butyl-4,6,8,10,12,14,19,21,23,25,27,29-cyclotriacontadodecaen-2,17-diyn-1,16-diol(105). To a solution of potassium hydroxide(5.00 g, 0.0891 mol) in liquid ammonia(400 ml) was slowly added a solution of the ketone(102)(150 mg, 0.465 mmol) in tetrahydrofuran(25 ml) at -34°C with vigorously over a period of 10 hr and the mixture was stirred for a further 6 hr. Ammonium chloride(10.00 g) was added and the ammonia was allowed to evaporate off. Water and dichloromethane was added to the residue. The organic layer was separated and washed with saturated sodium chloride solution and dried($MgSO_4$). Removal of the solvent under reduced pressure gave a crystalline residue, which was chromatographed on alumina and eluted with THF-benzene(1:9 ~ 1:4) gave (105a) a diastereomer, 52 mg(Y: 35 %) as yellow crystals, mp ca. 270°C(dec.); mass spectrum(m/e), 644(M^+); infrared spectrum(KBr), 3575s(-OH), 2200w(-C≡C-), 1635w, 1580w(C=C) cm^{-1}; u.v. spectrum, $\lambda_{max}^{THF}(\varepsilon)$, 224.5 (21,300), 268*(7,430), 280*(13,200), 292.5(23,000), 335*(65,500), 353(166,000), 370(258,000), 413.5(75,800) nm.

Found: C, 85.36 ; H, 9.41 %. Calcd for $C_{46}H_{60}O_2$: C, 85.66 ; H, 9.38 %.

Elution of the column with THF-benzene(1:1) gave (105b), another diastereomer, 84 mg(Y: 56 %) as yellow crystals, mp 260.0~260.5°C(from ethyl acetate-n-pentane); mass spectrum(m/e), 644 (M^+); infrared spectrum(KBr), 3550br m, 3450br m(-OH), 2190w(-C≡C-), 1632w(C=C) cm^{-1}; u.v. spectrum $\lambda_{max}^{THF}(\varepsilon)$, 225(19,800), 270*(7,950), 281*(13,100), 293(22,600), 335*(62,200), 354(156,000), 370.5(245,000), 414(70,600) nm.

Found: C, 85.23 ; H, 9.27 %. Calcd for $C_{46}H_{60}O_2$: C, 85.66 ; H, 9.38 %.

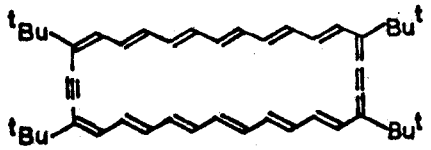


(105)

3,15,18,30-Tetra-t-butyl-didehydro[30]annulene(91). A mixture of the cyclic glycol(105a)(21 mg, 0.033 mmol), ether(10 ml) and THF(10 ml) was cooled at -78°C under nitrogen. Freshly prepared solution of stannous chloride dihydrate(200 mg, 0.886 mmol) in ether(2 ml) saturated with hydrogen chloride was added with stirring and cooling. The resuling green mixture was stirred for a further 10 min and then dichloromethane(20 ml) was added. The solution was poured onto ice-cold 1% aq. sodium carbonate solution(200 ml), and the organic layer was separated and dried($MgSO_4$). Removal of the solvent in vacuo (internal temperature of the flask <-10°C) gave black violet residue, which was immediately dissolved dichloromethane and chromatographed on alumina at -20°C. Elution with n-pentane-dichloromethane(1:1) gave the annulene(91) as black violet crystals.

The annulene was hydrogenated in order to confirm the formation of (91) in this reaction (see p. 140).

The annulene(91) was unstable and rapidly decomposed at room temperature in light and air. It was necessary to work up quickly and at low temperature in this dehydroxylative aromatization reaction. (91) decomposed on attempted melting point determination and also decomposed on measuring the n.m.r. spectrum at -20°C over a period of ca. 1 hr, but was relatively stable in a very diluted solution.



(91)

(91) was less soluble in all organic solvents, but comparatively soluble in dichloromethane, chloroform and tetrahydrofuran. A solution of (91) in chloroform or deutoriochloroform(5 ml) contained ca. 5 mg of the annulene.

The spectroscopic measurment of (91) was carried out using freshly prepared (91) by the same way mentioned above; mass spectrum (m/e), 610(M^+), 533(M - 57), 493(M - 114), 57(t-Bu, base peak); n.m.r. spectrum($CDCl_3$), see Fig. 14 (p. 50).

(see also APPENDEX p. 180)

The electronic spectrum of (91) was shown in Table 12 obtained using a solution prepared by dissolving fresh (91) derived from (105b)(1.4 mg). The ε-values were estimated assuming quantitative conversion of (105b) into (91) without decomposition or formation of by-products.

(see APPENDIX p. 180)

Table 12. Electronic Spectrum of Tetra-t-butyldidehydro-[30]annulene(91) in Tetrahydrofuran at -78°C. λ max (ε) nm

275.5(18,000), 324*(43,000), 338(56,000), 352(54,000), 401* (78,000), 451(190,000), 572(11,000), 607(11,000), 660*(8,300)

Tailing up to 1120 nm was observed.

Full hydrogenation of the didehydro[30]annulene(91).

(91)(p. 139) was suspended in ethyl acetate(20 ml) at -20°C. Platinic oxide(100 mg), ethyl acetate(10 ml) and acetic acid(10 ml) was added and the mixture was vigorously stirred under an atmosphere of hydro-

gen for 6 hr at the same temperature and then 2 hr at room temperature. Platinum was filtered off and washed with ether. Filtrate and washings were washed successively with water, saturated sodium bicarbonate and saturated sodium chloride solutions and dried($MgSO_4$). Removal of the solvent in vacuo gave a crystalline residue, which was chromatographed on alumina(Woelm act. I). Elution with n-hexane yielded 1,4,16,19-tetra-t-butylcyclotriacontane, 12 mg(57 % based on (105a)), as colorless crystals, mp 77~87°C, from ethyl acetate-methanol; mass spectrum(m/e), 644(M^+), 587(M - 57), 57(t-Bu, base peak).

Found: C, 85.63 ; H, 14.37 %. Calcd for $C_{46}H_{92}$: C, 85.77 ; H, 13.87 %.

Decomposition procucts of (91).

(see APPENDIX p. 180)

VII. ATTEMPTED SYNTHESIS OF DIDEHYDRO[14]ANNULENE-DICARBOXYLIC ACID(110a).

Condensation of the t-butylenyne-aldehyde(41b) with pyruvic acid. To a stirring mixture of the aldehyde(1.60 g,11.8 mmol), pyruvic acid(1.09 g, 12.3 mmol) and methanol(1.5 ml) was added a solution of potassium hydroxide(1.32 g, 23.5 mmol) in methanol (5 ml) at room temperature under nitrogen. The mixture was stirred for 12 hr at room temperature and then cooled on an ice-bath. 3NHydrochloric acid(10 ml) was added and the mixture was extracted with ether(20 ml×3). The organic layer was washed with water and saturated sodium chloride solution and dried($MgSO_4$). Removal of the solvent in vacuo gave an oily residue, which mainly consisted of the desired keto-carboxylic acid(108a) on the basis of n.m.r. spectrum[($CDCl_3$) τ 1.53(br s, 1H, -OH), 2.11(dd, J= 15 and 11 Hz, 1H, β-position of ketone), 3.53(d, J= 11Hz, 1H, γ-position of ketone), 5.96(d, J= 15 Hz, 1H, α-position of ketone), 6.45(s, 1H, C≡CH), 8.79(s, 1H, t-Bu)]. Attempts to purify the oily residue could not be successful.

A half volume of the oily residue was dissolved in dry ether (10 ml) and ammonia was passed into the solution to precipitate the ammonium salt. The salt was filtered off and washed with ether to give pure (108b), 0.90 g(Y: 69 % based on (41b) , as yellow crystals.

The keto-ester(108c) from (41b). Keto-carboxylic acid(108a) prepared from (41b, 1.00 g), pyruvic acid(647 mg) and potassium hydroxide(1.00 g) was dissolved in absolute ethanol(20 ml) and

ether(6 ml) saturated with hydrogen chloride was added to the solution at 0°C and the mixture was allowed to stand at room temperature overnight. The reaction mixture was worked up by the usual way to give a brown oil(1.20 g), which was short-chromatographed on alumina and eluted with benzene to afford keto-ester(108c), as a yellow oil; n.m.r. spectrum(CCl_4), τ 2.17(dd, J= 15 and 11 Hz, 1H, β-position of ketone), 3.29(d, J= 15 Hz, 1H, α-position of ketone), 3.51(d, J= 11 Hz, 1H, γ-position of ketone), 5.71(q, J= 7.0 Hz, 2H, $-CH_2-$), 6,43(s, 1H, C≡CH), 8.62(t, J= 7.0 Hz, 3H,$-CH_3$), 8.78(s, 9H, t-Bu). The keto-ester(108c) decomposed gradually on standing at room temperature or on column chromatography.

Cyclic dimerization of these keto-carboxylic acid derivatives (108a, 108b and 108c) by Favorskii reaction was unsuccessful because these compounds decomposed in the conditions of Favorskii reaction.

Condensation of the aldehyde(41b) with isonitrosoacetone.

To a mixture of the aldehyde(41b)(1.00 g, 7.34 mmol), isonitrosoacetone(0.639 g, 7.34 mmol) in ethanol(10 ml) was added a solution of sodium hydroxide(0.587 g, 14.7 mmol) in water(2 ml)-ethanol(2 ml) at -10°C under nitrogen. The mixture was stirred at -10～-15 °C for 8 hr and then acidified with 3N hydrochloric acid(10 ml) and extracted with ether. The organic layer was washed with water and saturated sodium chloride solution and dried($MgSO_4$). Removal of the solvent in vacuo yielded a crystalline residue, which was washed with n-hexane to give pure keto-oxime(108d), 1.05 g(Y: 69.7 %), as colorless crystals, mp 130.4～131.4°C(dec.); mass spectrum (m/e), 205(M^+); infrared spectrum(KBr), 3305s(≡CH), 3186s(=NOH),

2067vw(C≡C), 1658vs(C=N), 1644s(C=O), 1583vs(C=C), 987s(trans-CH=CH-), 947m(=NOH); n.m.r. spectrum($CDCl_3$) τ 2.03(dd, 1H, J= 16 and 11 Hz, 1H, β-position of ketone), 2.29(s, 1H, oxime-CH=N), 3.09 (d, J= 16 Hz, 1H, α-position of ketone), 3.47(d, J= 11 Hz, 1H, γ-position of ketone), 6.43(s, 1H, C≡CH), 8.80(s, 9H, t-Bu).

Found: C, 70.40 ; H, 7.39 ; N, 6.72 %. Calcd for $C_{12}H_{15}O_2N$: C, 70.22 ; H, 7.37 ; N, 6.82 %.

Ketalization of Acetoin(111). A mixture of acetoin(111) (17.9 g), ethylene glycol(25.0 g), p-toluenesulfonic acid monohydate (400 mg) in benzene(60 ml) was refluxed in a system equipped with a water separator. After 15 hr, the mixture was cooled and poured onto saturated sodium bicarbonate solution. The organic layer was separated and the aqueous layer was extracted with ether. The combined organic layer was washed with saturated sodium bicarbonate and sodium chloride solutions and dried(K_2CO_3). Removal of the solvent in vacuo and distillation gave the ethylene ketal(111), 6.31 g, as a colorless liquid, bp 88~89°C / 24 mmHg; n.m.r. spectrum(CCl_4) τ 6.07(s, 4H, $-CH_2-$), 6.45(q, J= 6.5 Hz, 1H, -CH-), 8.07(br s, 1H, -OH), 8.77(s, 3H, $-CH_3$), 8.91(d, J= 6.5 Hz, 3H, $-CH_3$).

Oxidation of ketal-alcohol(112). To a solution of acetoin ketal(2.40g) in acetone(30 ml) was added a solution of cromium trioxide(1.34g) in conc. sulfuric acid(1.15 ml)-water(4 ml) at 10°C on an ice-bath. The mixture was stirred at 0°C for 1 hr and then saturated sodium bicarbonate solution was added. The organic layer was separated, and the aqueous layer was diluted with water and extracted with ether. The combined organic layer was washed with saturated sodium bicarbonate and sodium chloride solutions

and dried(K_2CO_3). Removal of the solvent in vacuo and distillation gave a colorless liquid, 0.86g, bp 90~92°C/55mmHg; n.m.r. spectrum ($CDCl_3$) τ 6.00(m, 4H, $-CH_2-$), 7.80(s, 3H, $-COCH_3$), 8.53(s, 3H, $-CH_3$).

Aldol condensation of the aldehyde(41b) and biacetyl monoethylene ketal(113). To a solution of the aldehyde(41b)(0.65g) and biacetyl monoethylene ketal(113)(0.86g) in ethanol(10 ml) was added a solution of sodium hydroxide(265 mg) in water(1 ml)-ethanol(1 ml) and the mixture was stirred at 15~20°C for 14 hr under nitrogen. The reaction mixture was poured onto ice-water and extracted with ether. The extracts were washed with water and saturated sodium chloride solution and dried($MgSO_4$). Removal of the solvent in vacuo gave a residue, which was chromatographed on silica gel(20g) and eluted with benzene~benzene-ether(19:1) gave a yellowish brown oil(727mg). The residue was rechromatographed on alumina to afford a yellow oil, which crystallized on standing at room temperature. Recrystallization from petroleum ether afforded lemon yellow crystals, 285 mg, mp 63.2~63.7°C; mass spectrum(m/e), 248(M^+); infrared spectrum(KBr), 3250s (C≡CH), 2089w(C≡C), 1701s(C=O), 1597vs(C=C), 1020~1147vs(C-O-C), 999s(trans -CH=CH-) cm^{-1}; n.m.r. spectrum($CDCl_3$) τ 2.05(dd, J=16 and 11Hz, 1H, β-position of ketone), 3.35(d, J=16Hz, 1H, α-position of ketone), 3.47(d, J=11Hz, 1H, γ-position of ketone), 5.88~6.20 (m, 4H, $O-CH_2-$), 6.44(s, 1H, C≡CH), 8.51(s, 3H, $-CH_3$), 8.80(s, 9H, t-Bu).

Found: C, 72.43; H, 8.07 %. Calcd for $C_{15}H_{20}O_3$: C, 72.55; H, 8.12 %.

An attempt to synthesize(110e). To a stirred suspension of sodium hydroxide(2.00g) in liquid ammonia(180 ml) was added a solution of the ketone(108e)(10 mg) in tetrahydrofuran(35 ml) at -34°C over a period of 6 hr. The mixture was stirred at the same temperature for a further 8 hr and then ammonium chloride(4.00g) was added. The ammonia was allowed to evaporate off and the residue was worked up by the usual way to give pale yellow crystals.

The crystals was dissolved in ether and cooled at -60°C under nitrogen. Ether saturated hydrogen chloride was added and subsequently, stannous chloride dihydrate was added. The mixture was stirred for 10 min at the same temperature and then worked up by the usual way. Removal of the solvent in vacuo and chromatographed on alumina to give a annulene-like material; u.v. spectrum $\lambda_{max}^{benzene}$ 343, 454sh, 480, 616, 646 nm.

VIII. SYNTHESIS OF DI-t-BUTYL-DICARBOMETHOXY-DIDEHYDRO-THIA[13]ANNULENE (120).

Preparation of thiadicarboxylic acid derivative(119) by means of the Stobbe condensation of the pentaenyne-aldehyde(41b) with thio-diglycolate(115). To a solution of the aldehyde(41b)(1.00 g, 7.34 mmol) and dimethyl thiodiglycolate(115)(650 mg, 3.65 mmol) in absolute methanol(10 ml) was added 0.5M sodium methoxide solution (29.4 ml, 14.7 mmol) under nitrogen with stirring and ice-cooling. The mixture was stirred at 17~20 °C for a further 4 hr and evaporated *in vacuo*. Cold 3N hydrochloric acid(10 ml) was added to the residue and the mixture was extracted with ether. The organic layer was washed with water and saturated sodium chloride solution and dried($MgSO_4$). Removal of the solvent *in vacuo* to give a yellow residue. The residue was washed with ether-n-hexane to afford (117), 0.30 g(Y: 21 %), as pale yellow crtstals. The washings were evaporated under reduced pressure to give crude (116), *ca.* 1 g.

The dicarboxylic acid(117)(0.30 g, 0.78 mmol) was dissolved in methanol(20 ml), and ether(5 ml) saturated with hydrogen chloride was added at 20 °C. The solution was stirred for 24 hr at room temperature and then poured onto ice-water. The mixture was extracted with ether and the extracts were washed with water, saturated sodium bicarbonate and sodium chloride solutions and dried ($MgSO_4$). Removal of the solvent *in vacuo* and chromatography on silica gel gave (119), 127 mg as a yellow oil; n.m.r. spectrum ($CDCl_3$) τ 2.00(d, J= 11 Hz, 2H, β-position of ester), 2.93(d, J= 11 Hz, 2H, α-position of ester), 6.28(s, 6H, -OMe), 6.45(s, 2H, C-CH), 8.84(s, 18H, t-Bu).

Crude (116) was esterified by the same way as (117). The mixture of crude (116)(ca. 1 g), methanol(30 ml) and ether(10 ml) saturated with hydrogen chloride was stirred at 30 °C for 20 hr and worked up by the usual way. The residue thus obtained was chromatographed on silica gel and elution with benzene ~ ether-benzene(1:20) gave pure (118), 279 mg(Y: 26 %, based on (119)) as a yellow oil; n.m.r. spectrum($CDCl_3$) τ 1.94(d, J= 12 Hz, 1H, β-position of ester, olefinic), 2.94(d, J= 12 Hz, olefinic, α-position of ester), 6.19 (s, 3H, -OMe), 6.37(s, 3H, -OMe), 6.49(s, 1H, C≡CH), 8.77(s, 9H, t-Bu).

Di-t-butyl-dicarbomethoxy-didehydrothia[13]annulene(120).

A mixture of cupric acetate monohydrate(1.00 g) and pyridine(30 ml) was stirred at 45 °C and a solution of thia-diester(119)(127 mg, 0.78 mmol) in tetrahydrofuran (20 ml) was added over a period of 1.5 hr and the mixture was stirred for a further 1 hr and then poured onto ice-cold 3N hydrochloric acid and worked up by the usual way. The solvent was evaporated in vacuo and the residue was chromatographed on silica gel short column. Elution with benzene ~ benzene-ether(4:1) yielded crude (120), which was washed with ether to give pure (120), 50 mg(Y: 40 %), as yellow crystals; n.m.r. spectrum($CDCl_3$) τ 2.02(d, J= 11 Hz, 2H, inner protons), 2.81(d, J= 11 Hz, 2H, outer protons), 6.23(s, 6H, -OMe), 8.74 (s, 18H, t-Bu).

IX. SYNTHESES OF DECADIENDIYNDIALS AND FACILE INTRAMOLECULAR CYCLIZATION OF ALDEHYDES.

Bis(2-formyl-1-cyclohexenyl)-1,3-butadiyne(121). a) Oxidative Coupling in the Presence of Methanol. A solution of (127)(200 mg, 1.49mmol) in pyridine(2ml) was added to a mixture of cupric acetate monohydrate(1.00g, 5.01mmol), pyridine(5ml) and methanol (3ml). After being stirred for 2hr at 16°C, the reaction mixture was poured onto 3N hydrochloric acid(50ml) and extracted with ether(20ml×3). The extract, after being washed and dried, was evaporated under reduced pressure. The crystals thus obtained was chromatographed on alumina. Elution with n-hexane-benzene (1:1) and benzene afforded pure (121), 171mg(86%).

b) Oxidative Coupling in the Absence of Methanol To a mixture of cupric acetate monohydrate(1.00g, 5.01mmol) and pyridine(7ml) was added a solution of (128)(200mg, 1.49mmol) in ether(3ml). After being stirred for 6hr at 16°C, the reaction mixture was worked up to give (121), 183mg(92%), pale yellow crystals, mp 89.0-90.5°C; UV: $\lambda_{max}^{95\%EtOH}$(ε) 205.5(22150), 231*(10050), 238.5 (13470), 258*(12300), 270(14550), 290(15900), 317(15800), 334 (16800), 358(12400) nm, IR(KBr-disk): 1670vs(C=O), 1580m(C=C) cm^{-1}, NMR($CDCl_3$): -0.12(s. 2H, CHO), 7.62(m. 8H, allylic CH_2), 8.32(m. 8H, non-allylic CH_2), Mass(m/e): 266(M^+), 239(M-29).

Found: C, 80.91; H, 6.95%. Calcd for $C_{18}H_{18}O_2$: C, 81.17; H, 6.81%.

The mother liquors were chromatographed on alumina to yield second crop of (121).

3,8-Diphenyl-2,8-decadien-4,6-diyndial(122). To a solution of (44a)(327mg, 1.42mmol) in ether(3ml) was added a mixture of

cupric acetate monohydrate(566mg, 2.83mmol), pyridine(6ml) and ether (2ml). The mixture was stirred at 15°C for 17hr and then poured onto 3N hydrochloric acid(49ml), and extracted with ether(20ml×4). The extract was washed successively with water, saturated solutions of sodium hydrogen carbonate and sodium chloride, and evaporated under reduced pressure. The residue(130) containing water was mixed with 20% aqueous acetic acid(5ml) and the mixture was stirred for 15min at room temperature. The reaction mixture containing light brown crystals was mixed with water(40ml) and extracted with dichloromethane(30ml×4). The extract, after being washed and dried, was concentrated under reduced pressure to yield crystals. Chromatography of the crystals on silica gel followed by elution with carbon tetrachloride containing 10 20% dichloromethane afforded pure (121), yellow crystals, 163mg(74%), mp 119.4-120.3°C, Mass (m/e): 310(M^+), IR(KBr-disk): 2850w, 2740w(CHO), 2135w(-C≡C-), 1688vs(C=O), 1581w, 1560m(C=C) cm^{-1}, NMR($CDCl_3$): -0.27(d, J=8.0 Hz, 2H, CHO), 2.01–2.68(m, 10H, phenyl), 3.07(d, J=8.0 Hz, 2H, olefinic).

Found: C, 84.86; H, 4.57%. Calcd for $C_{22}H_{14}O_2$: C, 85.14; H, 4.55%.

Bis(3-phenyl-2-furanyl)acetylene(128). A solution of (122) (93mg, 0.30mmol) in benzene(4ml) was kept at 50°C for 8hr. The reaction mixture was concentrated under reduced pressure and chromatographed on alumina. Elution with carbon tetrachloride-20% dichloromethane afforded (128), colorless crystals, 81mg(86%), mp 131.5-131.8°C (from benzene-n-hexane), Mass(m/e): 310(M^+), IR(KBr-disk): 3140w, 3215w(furan CH), 892s(furan) cm^{-1}, NMR($CDCl_3$): 2.50 (d, J=2.0 Hz, 2H, α-H of furan), 2.10-2.87(m, 10H, phenyl), 3.76 (d, J=2.0 Hz, 2H, β-H of furan), UV: λ_{max}^{EtOH} (ε) 231.5(32900), 258.5*

(14800), 342.5(17500) nm.

Found: C, 84.84; H, 4.52%. Calcd for $C_{22}H_{14}O_2$: C, 85.14; H, 4.55%.

6-(5-Methoxy-3-phenyl-2-dihydrofuranylidene)-3-phenyl-2-penten-4-ynal(129). a) In the Presence of Pyridine and Methanol A solution of (122)(83mg, 0.26mmol) in pyridine(5ml) and methanol (8ml) was stirred for 2hr at 30°C, and then the mixture was poured onto 3N hydrochloric acid(40ml). The mixture was extracted with dichloromethane(30ml×4). The extract, after being washed and dried, was concentrated under reduced pressure. Brownish oily residue was chromatographed on silica gel and eluted with benzene to yield (129) as pale brown oil, 78mg(85%), Mass(m/e): 342(M^+), IR(neat) 2180s(-C≡C-), 1662vs(C=O), 1620m(C=C) cm^{-1}. The NMR spectrum of (129) showed complex pattern owing to the presence of cis- and trans-isomers.

A solution of 2,4-dinitrophenylhydrazine(97mg, 0.49mmol) and phosphoric acid(1.2ml) in ethanol(0.8ml) was added to a solution of (129)(47mg, 0.13mmol) in ethanol(8ml) and the mixture was stirred for 15hr at room temperature. Red crystals deposited were washed thoroughly with benzene. Red crystals obtained by evaporating the washings under reduced pressure were chromatographed on silica gel. Elution with benzene afforded pure 2,4-dinitrophenylhydrazone of (129) red crystals, mp 208.4°C, 58mg(81%).

Found: C, 66.61; H, 4.22; N, 10.51%. Calcd for $C_{28}H_{28}N_4O_6$: C, 66.66; H, 4.24; N, 10.27%.

b) In the Absence of Pyridine A solution of (122)(108mg, 0.34mmol) in methanol(10ml) and ether(5ml) was stirred for 28hr at 30°C. Brown oily residue obtained by evaporating the solvent

was chromatographed on silica gel, and eluted with benzene. (128) (39mg, 36%) was obtained from early fractions and the following fractions afforded (122)(28mg, 26%) and then (129)(35mg, 29%).

Oxidative Coupling of Phenylpentenynal(41a). a) In the Presence of Methanol. A solution of (41a)(1.00g, 6.4mmol) in pyridine(10ml) and methanol(10ml) was added to a mixture of cupric acetate monohydrate(5.00g, 0.025mol), pyridine(30ml) and methanol (10ml). After being stirred for 30min at room temperature, the mixture was poured onto 3N hydrochloric acid(200ml) and extracted with benzene. The extract was washed successively with water, saturated sodium hydrogen carbonate and sodium chloride solutions and dried. Chromatography of the residue obtained by evaporating the extract afforded (128), 127mg(13%) and (129), 449mg(41%).

b) In the Absence of Methanol. To an ice-cooled solution of cupric acetate monohydrate(2.00g, 0.010mol) in pyridine(20ml) was added a solution of (41a)(1.00g, 0.0064mol) in ether(15ml). After the mixture had been stirred for 12hr at 15-20°C, ice-cooled 3N hydrochloric acid(100ml) was added and the mixture was extracted with dichloromethane(30ml×3). The extract, after being washed and dried, was concentrated under reduced pressure. The residue was chromatographed on alumina. The fractions eluted with carbon tetrachloride containing 10-20% of dichloromethane afforded (128) (303mg, 30.5%).

3,8-Di-t-butyl-2,8- decadien-4,6-diyndial(123). a) From (41b). A solution of (41b)(945mg, 6.94mmol) in ether(12ml) was added to a mixture of cupric acetate monohydrate(2.10g, 10.5mmol) and pyridine(20ml) and the mixture was stirred for 24hr at 15-20°C. The reaction mixture was poured onto 3N hydrochloric acid(110ml)

and extracted with ether(40ml×3). The extract was worked up by the usual way. Crude crystals obtained were chromatographed on alumina. Elution with benzene yielded pure (123), mp 83.3-84.5°C (from benzene-n-hexane), pale yellow needles, 765mg(80%), Mass (m/e): 270(M^+), IR(KBr-disk): 2115vw(-C≡C-), 1681vs(C=O), 1574m (C=C) cm^{-1}, NMR($CDCl_3$): -0.09(d, J=7.5 Hz, 2H, CHO), 3.61(d, J=7.5 Hz, 2H, olefinic), 8.74(s, 18H, t-Bu), UV: $\lambda_{max}^{EtOH}(\varepsilon)$ 224.5*(13200), 232.0(14400), 253.5(13200), 264.5(14300), 280.0(14100), 303.5* (10500), 322.0(12200), 343.5(8300) nm.

Found: C, 80.14; H, 8.20%. Calcd for $C_{18}H_{22}O_2$: C, 79.96; H, 8.20%.

b) From (44b) To a stirred mixture of cupric acetate monohydrate(50g) and pyridine(300ml) was added a solution of (44b)(9.50g, 0.045mol) in pyridine(50ml) at 50°C and the mixture was stirred for 2hr at the same temperature. The cooled reaction mixture was poured onto a mixture of cracked ice and dilute hydrochloric acid, and extracted with ether. The extract, after being washed and dried, was concentrated under reduced pressure to give crude (132) [NMR(CCl_4): 3.19(d, J=7.0 Hz, 2H, olefinic), 4.86(d, J=7.0 Hz, acetal), 6.44(q, J=7.0 Hz, 4H, CH_2), 6.49(q, J=7.0 Hz, 4H, CH_2), 8.82(t, J=7.0 Hz, 12H, CH_3), 8.82(s, 18H, t-Bu)]. Crude (132) was mixed with acetic acid(250ml) and water(80ml). After being stirred for 30min, the mixture was worked up by the usual way and chromatographed on alumina to yield pure (123), 6.6g(55% based on (44b)),

Oxidative Coupling of (41b) in the Presence of Methanol. A mixture of (41b)(500mg, 3.64mmol), cupric acetate monohydrate (1.706g, 8.45mmol), pyridine(15ml) and methanol(11ml) was stirred for 22hr at room temperature. The reaction mixture was worked up

by the usual way to give brownish crystals. The crystals were chromatographed on alumina and eluted with benzene. A mixture of (123) and 6-(5-methoxy-3-t-butyl-2-dihydrofuranylidene)-3-t-2-penten-4-ynal(131) was obtained by evaporating the benzene eluate. The approximate composition of the mixture could be estimated to be (123), 250mg(50%) and (131), 70-75mg(10-15%) by an NMR spectroscopy.

Bis(3-t-butyl-2-furanyl)acetylene(136). a) Thermal Cyclization in the Absence of Pyridine. A solution of (123) (82mg, 0.3mmol) in benzene(4ml) was stirred for 20hr at 60°C. Concentration of the reaction mixture under reduced pressure afforded yellow crystals(81mg) which were chromatographed on alumina and eluted with n-hexane containing 20-30% of benzene. Evaporation of the eluate yielded (136), pale yellow crystals, 68mg(82%), mp 42.0-42.6°C(from ether-n-hexane), Mass(m/e): 270 (M^+), IR(KBr-disk): 3130w(furan C-H), 1585w(C=C), 890s(furan) cm^{-1}, NMR($CDCl_3$): 2.69(d, J=2.0 Hz, 2H, α-H of furan), 3.62 (d, J=2.0 Hz, 2H, β-H of furan), 8.64(s, 18H, t-Bu), UV: λ_{max}^{EtOH} (ε) 253.0(16200), 296.0*(19700), 300.5(20100), 318.5*(12600) nm.

Found: C, 80.20; H, 8.27%. Calcd for $C_{18}H_{22}O_2$: C, 79.96; H, 8.20%.

Bis(3,4-tetramethylene-2-furanyl)acetylene(137). a) Cyclization at 120°C. A solution of (121)(112mg) in p-xylene (5ml) was kept at 120°C for 5hr. Crystals obtained by removing the solvent under reduced pressure was chromatographed on alumina(5g). Elution with n-hexane-benzene(1:1) afforded (137), colorless crystals, mp 146-147°C(from benzine), 64mg(57%), Mass (m/e): 266(M^+, base peak), IR(KBr-disk): 2170vw(-C≡C-), 1547m (C=C), 1505w(C=C) cm^{-1}, NMR($CDCl_3$): 2.87(s, 2H, α-H of furan),

7.43(m, 8H, allylic CH_2), 8.29(m, 8H, non-allylic CH_2).

Found: C, 81.02; H, 6.88%. Calcd for $C_{18}H_{18}O_2$: C, 81.17; H, 6.81%.

b) Cyclization at 60°C. A solution of (121)(104.5mg) in benzene(5ml) was heated to 60°C for 2hr. Chromatography on alumina(3g) of the reaction mixture yielded (137), 1.9mg(1.8%) and recovered (121), 76.9mg(73.6%).

Cyclization of (123) in the Presence of Cupric Acetate and Pyridine. To a mixture of cupric acetate monohydrate(184mg, 0.92mmol) and pyridine(4ml) maintained at 60±2°C was added a solution of (123)(198mg, 0.73mmol) in benzene(10ml). The mixture was stirred in nitrogen atmosphere at the same temperature for 5hr, then poured onto 3N hydrochloric acid(30ml) and extracted with ether(30ml×3). The extract was washed and dried. A mixture of light brown crystals and liquid obtained by evaporating the extract was chromatographed on alumina and eluted with n-hexane containing 20% of benzene to yield (136), 91mg(46%). The results of reactions performed under different conditions are summarized in Table 13.

Table 13. Formation of (136) in the Presence of Cupric Acetate

Temp. °C	(122) (mg)	$Cu(OAc)_2 \cdot H_2O$ (mg)	Solvent (ml)	Reaction time(hr)	(136) (mg)(%)
40	221	250	pyridine 4 +benzene 10	24	92(41)
50	193	409	pyridine 4 + ether 3	24	109(56)

cis- and trans-1-(2-Formylcyclohexenyl)-3-(3,4-tetramethylene-5-methoxy-2-dihydrofuranylidene)-1-propyne (140) and (141).

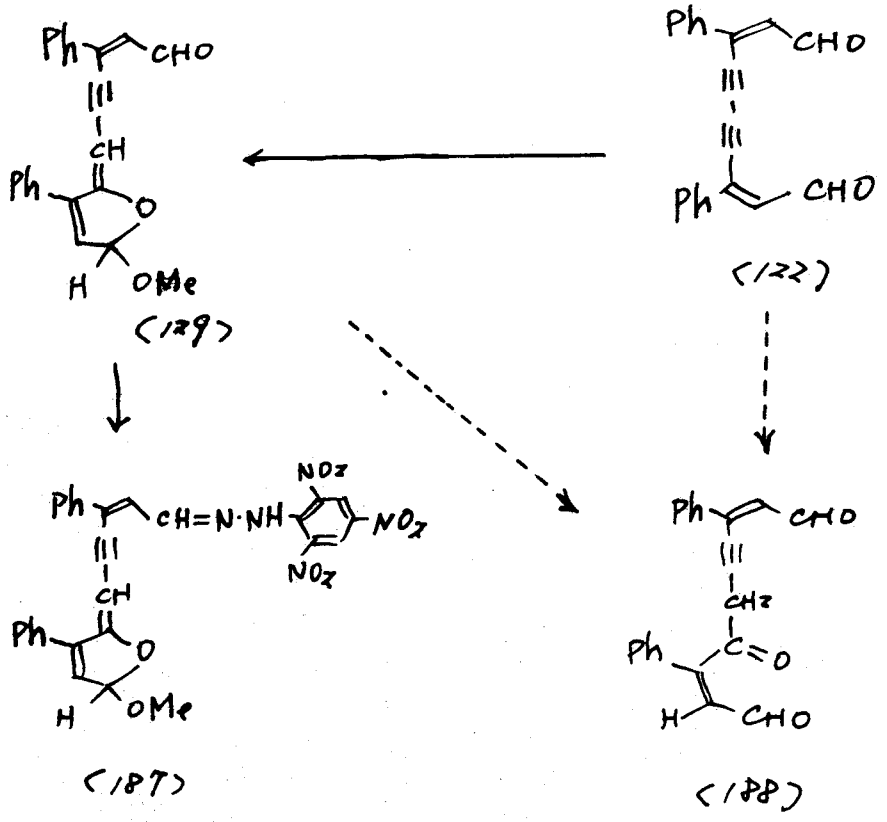
To an ice-cooled solution of (121)(186mg, 0.698mmol) in ether(10 ml) was added 1N solution of sodium methoxide in methanol(2ml). After being stirred for 30min at the same temperature, the mixture was mixed with 3N hydrochloric acid(1ml) and extracted with ether (20ml). The extract, after being washed and dried, was concentrated under reduced pressure. Brownish yellow oily residue was chromatographed on silica gel to yield a mixture of (140) and (141) (187mg, 90%). The mixture was re-chromatographed on silica gel. Elution with benzene resulted in the separation of isomers. (140) was obtained from early fractions, yellow crystals, mp 115.6-116.2°C (from benzene-methanol), Mass(m/e): 298(M^+), 267(M-31), 266(M-32), IR(KBr-disk): 2160s(-C≡C-), 1670vs(C=O), 1626s(C=C), 1580vs(C=C) cm^{-1}, NMR($CDCl_3$): -0.10(s, 1H, CHO), 4.26(s, 1H, hemiacetal), 4.80 (s, 1H, olefinic), 6.58(s, 3H, OCH_3), 7.25-8.00(m, 8H, allylic CH_2), 8.29(m, 8H, non-allylic CH_2), UV: λ_{max}^{EtOH}(ε) 249*(10900), 256(11200), 286.5(8750), 360(20500) nm.

Found: C, 76.33; H, 7.44%. Calcd for $C_{19}H_{22}O_3$: C, 76.48; H, 7.43%.

Evaporation of the following benzene eluates afforded (141), yellow crystals, mp 91.5-93.0°C(from methanol), Mass(m/e): 298(M^+), IR(KBr-disk): 2175m(-C≡C-), 1663vs(C=O), 1626s(C=C), 1578m(C=C) cm^{-1}, NMR($CDCl_3$): -0.27(s, 1H, CHO), 4.18(s, 1H, hemiacetal), 5.33(s, 1H, olefinic), 6.50(s, 3H, OCH_3), 7.40-8.00(m, 8H, allylic CH_2), 8.29(m, 8H, non-allylic CH_2).

Found: C, 75.86; H, 7.42%. Calcd for $C_{19}H_{22}O_3$: C, 76.48; H, 7.43%.

(140) and (141) showed closely related mass, IR and UV spectra. However, marked difference of chemical shifts of olefinic protons between (140)(4.80) and (141)(5.33) was observed. The structure of (140) was assigned to the isomer with low -value, because the olefinic proton in (140) is deshielded by the magnetic anisotropy of oxygen atom of dihydrofuran ring.



Scheme XXVII

We attempted to convert the hemiacetal(129) into keto-aldehyde (188). However, hydrolysis of (129) gave a mixture of decomposition products, which did not contain the keto-aldehyde(188). The hemiacetal(129) hardly hydrolyzed with aq. acetic acid at room temperature but rapidly decomposition occured by heating the solution.

We also attempted to convert the dialdehyde(122) into the keto-aldehyde(188). The dialdehyde(122) decomposed at room temperature by treatment in a very weak alkaline solution. This reaction gave a black material like coal-tar, which showed no peak in the measurement of n.m.r. spectrum.

X. SYNTHESIS OF DINAPHTHO[2,1-f:2',1'-m]-3,10-DI-t-BUTYL-1,8-DIDEHYDRO[14]ANNULENE(178).

2-Hydroxymethylene-1-tetralone(161). To a stirred suspension of sodium methoxide(18.5 g, 0.342 mol) in dry benzene (200 ml) was added a solution of α-tetrarone(10.0 g, 0.0684 mol) and ethyl formate(25.3 g, 0.342 mol) in dry benzene(50 mol) at room temperature under nitrogen. The temperature of the mixture rose slowly to 50°C and dropped. The color turned reddish brown and stirring of the mixture became increasingly difficult. After being stirred for 15hr, icewater(100 ml) was added and the aqueous layer was separated. The organic layer was extracted with 5 %sodium hydroxide solution and the combined aqueous layer was washed with benzene, acidified with conc hydrochloric acid (pH 1~2) and extracted with ether. The extracts were washed with water and saturated sodium chloride solution and dried ($MgSO_4$). Removal of the solvent in vacuo and distillation yielded(161), 10.6 g(Y:88.6 %), as a pale yellow liquid, bp 102~106°C/0.5 mmHg; infrared spectrum(film), 3680~2500brm(-OH), 1750~1550s(C=O, C=C) cm^{-1}; n.m.r. spectrum($CDCl_3$)τ0.42(br s, 1H, -OH) disappeared on shaking with D_2O, 1.83(s, 1H, -O-CH=), 1.98~2.14(m, 1H, aromatic H_8), 2.47~2.92(m, 3H, aromatic H_5, H_6, H_7), 7.28(m A_2B_2, 4H, $-CH_2-$); u.v. spectrum, $\lambda_{max}^{95\%EtOH}$(ε), 260,5 (8,890), 327(9,700), 299*(8,640) nm.

Found: C, 75.62 ; H, 5.76 %. Calcd for $C_{11}H_{10}O_2$: C, 75.84 ; H,5.79 %.

2-Isopropyloxomethylene-1-tetralone(162) from α-tetralone (160). To a stirred suspension of sodium methoxide(18.5 g, 0.342 mol) in dry benzene(400 ml) was added a solution of α-tetralone(25.0 g, 0.171 mol) and ethyl formate(25.3 g, 0.342 mol) in dry benzene(100 ml) with stirring and cooling in an ice-bath under nitrogen. After being stirred at 0°C for 3hr and at 30°C for 15hr, the reaction mixture was chilled in an ice-bath and 3N hydrochloric acid(150 ml) was added slowly. The organic layer was separated and the aqueous layer was extracted with ether. The combined organic layer was washed with water and saturated sodium chloride solution and dried($MgSO_4$). Removal of the solvent and distillation gave crude(161), 25.38 g(containing α-tetralone on the basis of n.m.r.spectrum).

Crude hydroxymethylenetetralone(161) (25.38 g) was added dropwise to a suspension of potassium carbonate 30.0 g in acetone (150 ml) at room temperature under nitrogen. To the mixture was added isopropyl iodide(30.0 g) and the mixture was warmed at 50°C for 12hr. Evaporation of the solvent in vacuo afforded a residue, which was extracted with dichloromethane. The extract was evaporated and distilled to give(162), 14.13 g(Y: 38 %) as a pale yellow liquid, bp 126~133°C/0.048 mmHg. Recovered α-tetralone was obtained as the forerunner, 7.68 g.

The spectral data of (162) was as follows: infrared spectrum (film), 1673vs, 1606vs; n.m.r.spectrum ($CDCl_3$), τ 1.99(m, 1H, H_8), 2.37(m, 1H, m), 2.53~2.95(m, 3H, aromatic H_5~H_7), 5.75(septet, J=6.0Hz, 1H, -O-CH=), 7.21(m, 4H, $-CH_2-$), 8.69(d, J=6.0Hz, 6H, CH_3).

2-n-Butylthiomethylene-1-tetralone(165). A mixture of(161) (10.25 g, 0.0588 mol), n-butylmercaptan(5.84 g. 0.0647 mol) and a catalytic amount of p-toluenesulfonic acid in benzene(150 ml) was refluxed in a system equipped with a water separator. After 20hr the mixture was cooled and washed with saturated sodium bicarbonate and sodium chloride solutions and dried($MgSO_4$). Evaporation of the solvent *in vacuo* and distillation yielded (165), 14.45 g(Y: 99.7 %), as a yellow liquid, bp 167~172°C / 0.009mmHg;mass spectrum(m/e), 246(M^+); infrared spectrum(film), 1660s(C=O , 1604s(C=C),cm^{-1}; n.m.r. spectrum($CDCl_3$), τ 1.98~2.13(m, 1H, aromatic H_8), 2.45 (s, 1H, S-CH=), 2.65~2.83(m, 3H, aromatic H_5,H_6,H_7), 6.95~7.47 (m, 6H, S-CH_2-; methylene of 3,4-position), 8.08~8.85(m, 4H, S-C-CH_2-CH_2-), 9.07(m, 3H, -CH_3).

Found: C, 73.16 ; H, 7.38 ; S, 12.85 %. Calcd for $C_{15}H_{18}OS$: C, 73.13 ; H, 7.36 ; S, 13.01 %.

4-Ethynyl-1,2-dihydro-3-naphthaldehyde di-n-butylthioacetal (167). Absolute tetrahydrofuran(60 ml) was saturated with acetylene. Lithium acetylide-ethylenediamine(2.00g, 21.7 mmol) was added and then a solution of the ketone(165)(2.30g, 9.34mmol) in absolute tetrahydrofuran(20 ml) was added dropwise with stirring and passing a steady stream of acetylene, and stirred for a further 4.5 hr at room temperature. The mixture was cooled in ice-bath and water was added. The organic layer was separated and the aqueous layer was extracted with ether. The combined organic layer was washed with water and dried($MgSO_4$). Evaporation of the solvent *in vacuo* gave a reddish brown oil(homogeneous on t.l.c., Rf=0.5 developed with benzene).

p-Toluenesulfonic acid(3.11 g, 16.2 mmol) was added to a solution of crude(166) and n-butylmercaptan(1.46 g, 16.2 mmol) in benzene(30 ml) and the mixture was stirred for 1.5 hr at room temperature. The reaction mixture was chilled in an ice-bath and 0.75N-sodium hydroxide(100 ml) was added. The organic layer was separated and the aqueous layer was extracted with ether. The combined organic layer was washed with water and dried($MgSO_4$) and evaporated under reduced pressure. Chromatography on alumina(80 g) and elution with n-hexane-benzene(1:1) gave (167), 3.11 g(Y:96.7%), as a yellow liquid; mass spectrum(m/e), 344(M^+); infrared spectrum (film), 3300 m, 3280 m(≡CH), 2100 vw(C-C≡C-), 1600 w(C=C) cm-; n.m.r. spectrum($CDCl_3$) τ 2.28-2.50(m, 1H, H_5), 2.68-2.93(m, 3H, H_6,H_7,H_8), 4.53(s, 1H, thioacetal), 6.59(s, 1H, C≡CH), 7.17-7/50(m, 8H, H_1,H_2, S-CH_2-), 8.24-8.77(m, 8H, S-CH_2-CH_2-), 9.13(m, 6H, -CH_3).

Hydrolysis of (166) with 4N-sulfuric acid. Absolute tetrahydrofuran(30 ml) was saturated with acetylene and lithium acetylide-ethylenediamine(1.00 g, 10.9 mmol) was added. To the mixture a solution of the ketone(165)(1.00 g, 4.06mmol) in absolute tetrahydrofuran(10 ml) was added dropwise with stirring and passing a stream of acetylene, and stirred for a further 1hr at 30°C. The mixture was cooled in an ice-bath and water was added. The organic layer was separated and the aqueous layer was extracted with ether. The combined organic layer was washed successively with water and saturated sodium chloride solution and dried($MgSO_4$). Removal of solvent in vacuo gave crude(166), (homogeneous on t.l.c.).

A solution of ethynyl glycol(166) in dioxane was added to 4N-sulfuric acid(50 ml) at 25°C and the mixture was vigorously stirred for 2 hr. The reaction mixture was extracted with ether, and extracts were

washed with saturated sodium bicarbonate and sodium chloride solutions and dried($MgSO_4$). Evaporation of the solvent under reduced pressure yielded a oily residue, which was chromatographed on silica gel. Elution with n-hexane-benzene(1:1) gave thioacetal (167), 639 mg (Y:49.5%) and elution with benzene-ether-benzene(1:19) gave aldehyde (164), which was washed with n-hexane to afford pure (167), 246 mg (Y:33.3%). The analytical sample of (167) was recrystallized from n-hexane-ether to give pale yellow crystals, mp 71.6-72.2°C; mass spectrum (m/e): 182(M^+); infrared spectrum (KBr), 3250 m(≡CH), 2090 vw(-C≡C-), 1662 s (-CHO), 1600 m (C=C) cm^-; n.m.r.spectrum ($CDCl_3$), τ -0.31 (s, 1H, -CHO), 2.13-2.35 (m, 1H, H_8), 2.58-2.98 (m, 3H, H_6,H_7, H_8), 6.33 (s, 1H, C≡CH), 7.32 (m, A_2B_2, 4H, $-CH_2-$, H_1,H_2); U.v.spectrum $\lambda_{max}^{99\%EtOH}$ (ε), 243.4(11.500), 315(14.100) nm.

Found: C, 85.76 ; H, 5.55 %. Calcd for $C_{13}H_{10}O$: C, 85.69; H, 5.53 %.

1-Ethynyl-2-naphthaldehyde(173). A solution of the thioacetal (174) (1.50 g, 4.35 mmol), DDQ (2.30 g, 10.1 mmol) in dry benzene (50 ml) was warmed at 55°C for 24 hr. Dichlorodicyanohydroquinone was precipitated from the solution. The mixture was cooled and filtered off. The crystals were washed with water, 2% sodium hydroxide solution and saturated sodium chloride solution and dried ($MgSO_4$). Removal of the solvent in vacuo to give crude (175).

To a solution of crude (175) in acetonitrile were added water (20 ml) and methyl iodide (10 ml), and the mixture was warmed at 50°C for 15 hr under nitrogen. Benzene (50 ml) was added and the mixture was poured onto water (100 ml). The organic layer was separated and the aqueous layer was extracted with ether. The combined organic layer was washed with water, 2% sodium thiosulfate solution and

saturated sodium chloride solution and dried($MgSO_4$). Evaporation of the solvent in vacuo gave a crystalline residue, which was chromatographed on silica gel (eluent; n-hexane—benzene) to yield pure aldehyde(173), 290mg(Y; 37%). The sample for analysis was recrystallized from n-hexane—carbon tetrachloride(1:1) to give the yellow plates, mp 139.4~140.3°C; mass spectrum(m/e), 180(M^+); infrared spectrum(KBr), 3250m(≡CH), 2850w(CHO), 2100vw(-C≡C-), 1673vs(C=O) cm^{-1}; n.m.r. spectrum($CDCl_3$) τ -0.66(s, 1H, CHO), 1.53(m, 1H, H_8), 1.99~2.80(m, 5H, H_3~H_7), 6.15(s, 1H, C≡CH).

Found: C, 86.53 ; H, 4.53%, Calcd for $C_{13}H_8O$: C, 86.65 ; H, 4.48%.

Aldol condensation of (173) with pinacolone. To a stirred solution of the aldehyde(173)(184mg, 1.02mmol) and pinacolone(153mg, 1.53mmol) in ethanol(50ml) was added a solution of sodium hydroxide (123mg, 3.06mmol) in ethanol(1ml)-water(0.5ml) at 20°C under nitrogen. After being stirred at room temperature for 2 days, the solvent was evaporated under reduced pressure. Water was added and the mixture was extracted with ether. The organic layer was washed successively with water, saturated sodium bicarbonate and sodium chloride solutions and dried($MgSO_4$). Removal of the solvent gave a residue, which was chromatographed on silica gel(n-hexane—benzene) to afford(176), 105mg (Y: 39.2%). The analytical sample was recrystallized from ether—n-hexane to give pale yellow crystals, mp 114.7~115.3°C; mass spectrum (m/e) 262(M^+); infrared spectrum(KBr), 3225m(≡CH), 2090vw(-C≡C-), 1678vs(C=O), 1599vs(C=C)cm^{-1}; n.m.r. spectrum($CDCl_3$) τ 1.51(d, J=16Hz, 1H, β-position of ketone), 1.48~1.69(m, 1H, H_8), 2.08~2.60(m, 5H, naphthalene H_3~H_7), 2.70(d, J=16Hz, 1H, α-position of ketone),

6.10(s, 1H, C≡CH), 8.74(s, 9H, t-Bu).

Found: C, 86.78; H, 6.81%. Calcd for $C_{19}H_{18}O$: C, 86.98; H, 6.91%.

Dinaphtho[1,2-d:1',2'-k]-1,8-di-t-butyl-cyclotetradeca-6,13-dien-2,9-diyn-1,8-diol(177). To a suspension of finely powdered potassium hydroxide(2.00g, 35.7mmol) in liquid ammonia(200ml) was added very slowly a solution of the ketone(176)(104mg, 0.396mmol) in absolute tetrahydrofuran(15ml) at -34°C for 10 hr. After being stirred for 5 hr at -34°C, ammonium chloride(5.00g, 93.5mmol) was added and the ammonia was allowed to evaporate off and the residue was treated with water and ether(20ml). The aqueous layer was then further extracted with ether(15ml×2). The combined organic layer was washed successively with water and saturated sodium chloride solution. Drying($MgSO_4$), evaporation under reduced pressure yielded a crystalline solid, which was chromatographed on alumina(30g) and eluted with benzene—tetrahydrofuran(4:1~1:1). The crystals thus obtained were washed with n-hexane to give pure(177), 94mg(Y: 90%). The analytical sample was recrystallized from benzene-tetrahydrofuran to afford colorless crystals, mp 279.0~279.5°C(dec.); mass spectrum(m/e), 524(M^+); infrared spectrum(KBr), 3550s(-OH), 2215vw (-C≡C-) cm^{-1}; n.m.r. spectrum(THF-d_8) τ 1.34(m, 2H, H_8), 1.62(d, J=16Hz, 2H, internal olefinic H of the ring), 2.07~2.27(m, 3H, naphthalene), 2.36~2.64(m, 2H, naphthalene), 3.14(d, J=16Hz, 2H, external olefinic H of the ring), 4.75(s, 2H, OH), 8.76(s, 18H, t-Bu).

Found: C, 87.05; H, 6.86%. Calcd for $C_{38}H_{36}O_2$: C, 86.98; H, 6.91%.

Dinaphtho[2,1-f:2',1'-m]-3,10-di-t-butyl-1,8-didehydro[14]-annulene(178). Since dinaphtho-didehydro[14]annulene(178) was very sensitive to oxygen even at -78°C, all solvents used this reaction was degassed with argon.

N.m.r. spectrum of (178) was measured as described belw. The mixture of the cyclic glycol(177)(2 mg, 0.003_8 mmol) and deuteriotetrahydrofuran(0.25 ml) was placed in n.m.r. tube under argon and cooled at -78°C. Cold deuteriotetrahydrofuran(0.15 ml) saturated with deuterium chloride(-15°C) and stannous chloride dihydrate (3 mg, 0.01_3 mmol) was added and the mixture was shaken at -30°C for 5 min. The resulting blue-violet solution was used for the measurment of 100 MHz n.m.r. spectrum at -54°C, see Fig. 15 (p. 73). N.m.r. spectrum($CDCl_3$) τ -0.22(d, J= 15 Hz, 2H, outer protons), 0.29 (d, J= 8 Hz, 2H, H_8 of naphthalene), 0.46(d, J= 10 Hz, 2H, H_3 of naphthalene), 1.73(d, J= 10 Hz, H_4 of naphthalene), ca. 2.00(m, H_7 of naphthalene), 7.89(s, 18H, t-Bu), 13.45(d, J= 15 Hz, inner protons), see also Fig. 24(apparatus Fig. 23).

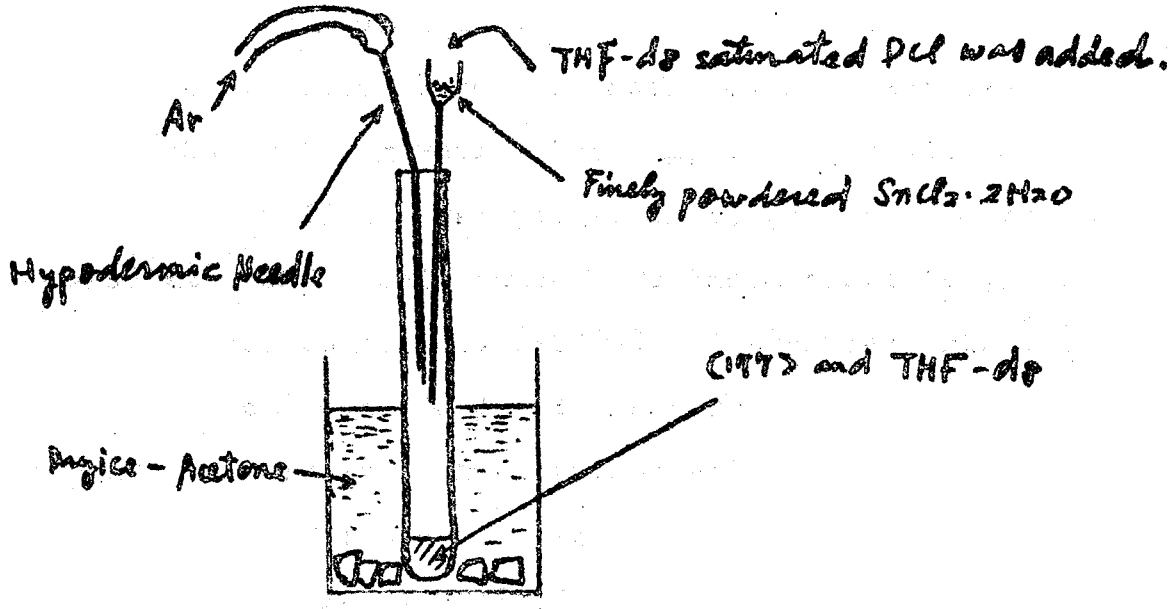


Fig. 23.

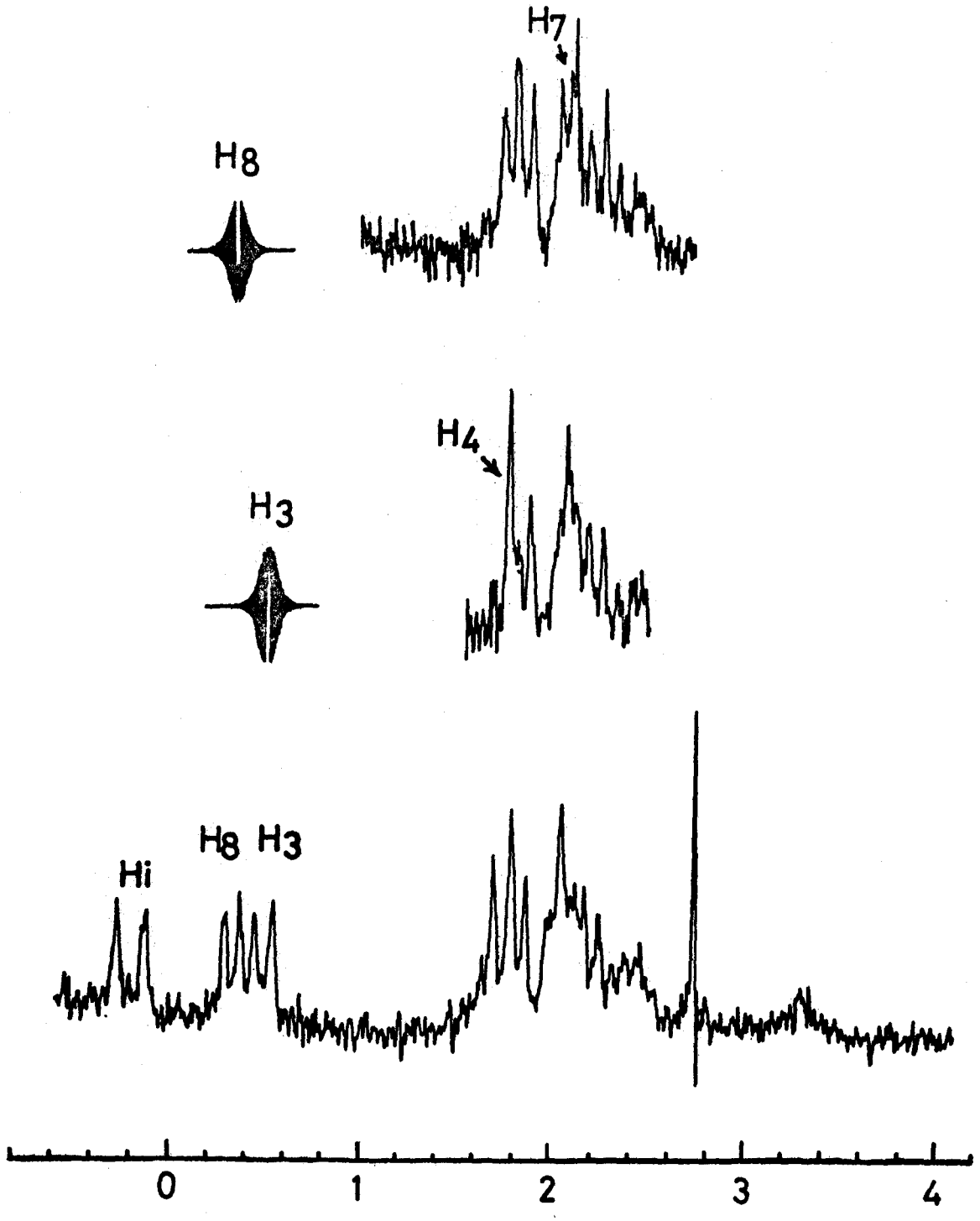


Fig. 24. N.m.r. spectrum of (178)(100 MHz, THF-d_8, -54°C).

Electronic spectrum of (178) was measured as described below. The mixture of the glycol(0.165 mg), stannous chloride dihydrate (2.2 mg) and tetrahydrofuran(0.5 ml) was cooled at -20°C under argon. Cold tetrahydrofuran(1 ml) saturated with hydrogen chloride (-20°C) was added and the mixture was stirred at -20°C for 5 min. The resulting blue-violet solution was cooled to -78°C and tetrahydrofuran was added to make the volume of the solution up to 5ml. The resulting solution was used for the electronic spectrum. The same condition of the reaction was carried out in order to obtain more diluted solution(0.00955 mg of the glycol(177) was used). U.v. spectrum λ_{max}^{THF}(ε) at -78°C, 385(34,700), 405.5(191,000), 506* (1,700), 541.5(4,770), 580.5(12,500), 621(1,430), 680(2,000), see Fig. 25. The ε-values of (178) were calculated assuming quantitative conversion of (177) into (178). see Fig. 14 and Fig. 25.

(apparatus Fig. 26)

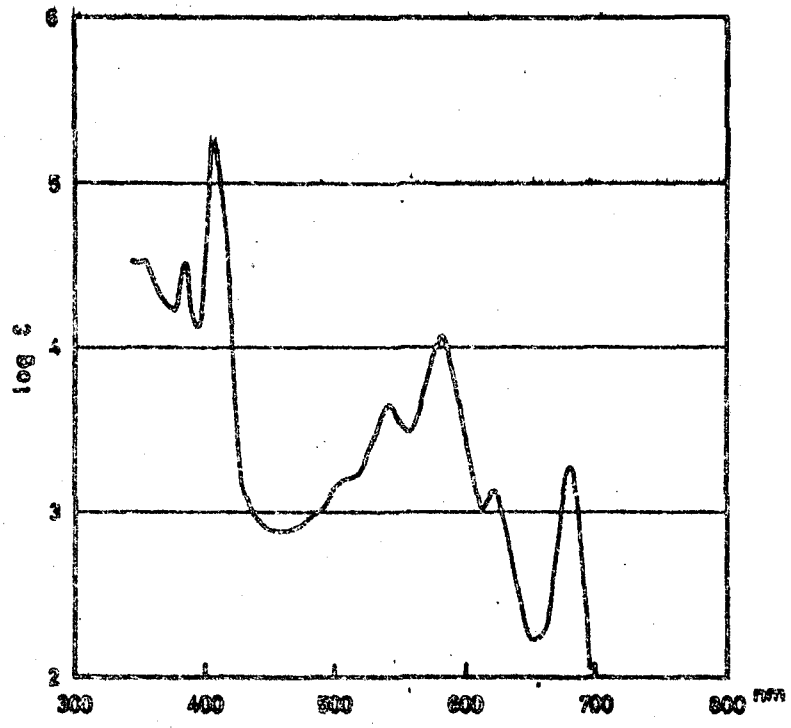


Fig. 25. Electronic spectrum of (178).

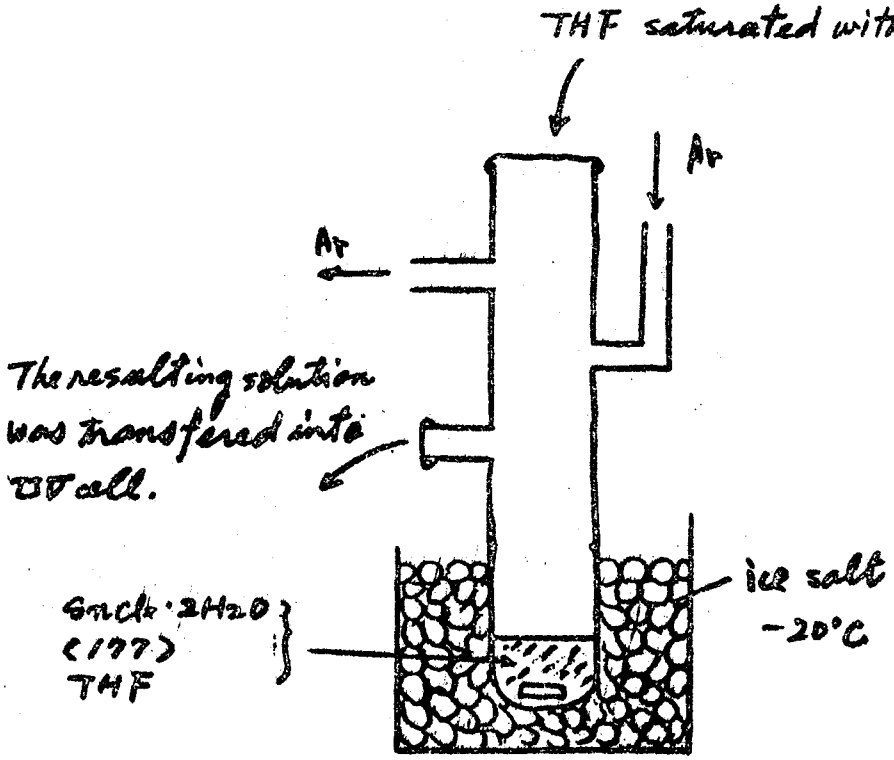


Fig. 26. Apparatus using the measurment of electronic spectrum of (178).

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メトキシブタジエンの製法 (P133 参照)

100 mlのフラスコを用い Fig. 25のような装置を組み立てる。30gの1,1,3-トリメトキシブタン をフラスコに入れ還流させる(bath 170°C)。この中に 100 mgの H_3PO_4 を 40gのトリメトキシブタンに溶かした溶液 をゆっくり滴下する。滴下すると共に MeOH, メトキシブタジエンが生成してくる。フラスコ内の液量を常に 50 mlにしながらトリメトキシブタンを追加する。このようにして 約15時間 反応後、220 mlの液体を得た。このうちの 110 mlを次の方法で精製した。

n-Pentane 30 mlを追加し、有機層は水洗、飽和食塩で洗浄後、無水 $CaCl_2$ で乾燥した。分留管をつけ蒸留することによりメトキシブタジエンを得た。

bp 78°C

21.73g

(文献 bp 91~92°C)

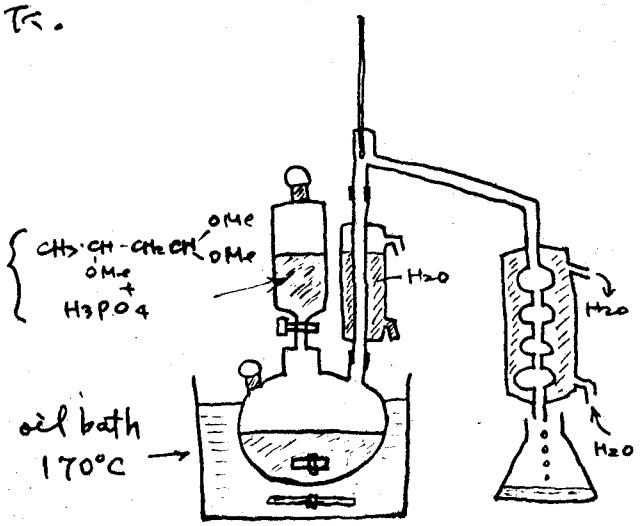
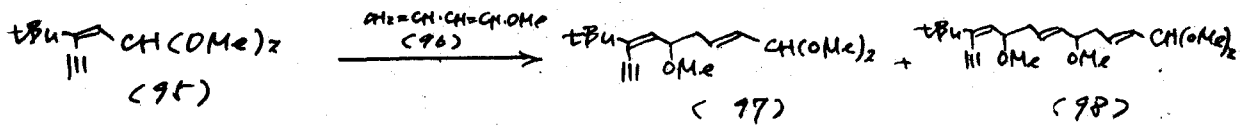


Fig. 25

アセタール(95)とメトキシブタジエン(96)の $BF_3 \cdot OEt_2$ 触媒下の反応。



アセタール(95), 25.37g(0.139モル)のベンゼン溶液(40ml)に 25°C で $BF_3 \cdot OEt_2$ を3滴加えた後、(96) 4.68g(0.47g)のベンゼン溶液(10ml)を 25°C ~ 30°C に保ちながら滴下する。滴下後 20分 25°C で撹拌し、K_2CO_3 粉末 5.00g を加えて BF_3 を分解させる。K_2CO_3 を沪過し、ベンゼン

層を減圧濃縮し蒸留することにより次の fraction を得た。

f1　bp 63～64°C/4mmHg　回収(94) 18.84g

f2　bp 116～118°C/3mmHg　(97)　5.56g(Y:55%)

f3　bp 89～92°C/0.007mmHg (98)　2.22g(Y:22%).

テトラ-t-ブチル ジデヒドロ[30]アヌレンのスペクトルデータ(P140, P141参照)

注1). Mass スペクトルについて.

Massの機械の内部で200～250°Cの温度をかけて測定するので分解している可能性もある。Massのパターンは テトラ-t-ブチル ジデヒドロ[14], [18], [22], [26]アヌレンと同じである。

注2). NMR スペクトルについて.

ジデヒドロ[30]アヌレン(91)は非常に不安定で難溶性である。(91)は $CDCl_3$ 5mlに約5mg溶けるが この溶液は −40°Cでも徐々に分解していく。分解物は(91)よりさらに難溶性の黒紫色の固体で溶液は暗緑色をしている。分解物のNMRスペクトルは $CDCl_3$ 中, −40°Cで で δ3.40～4.00 m と δ4.05～4.60 m にシグナルを示す。NMR スペクトルは $CDCl_3$ 中で −40°C, −20°Cでも測定したが大きな変化はなかった。t-Bu基はほとんどの場合 broad singlet であったが 最初の測定(−20°C)では sharp singlet であった。これについては, sharp singlet が正しいのか, 分解物のt-Bu基と[30]アヌレン(91)のt-Bu基が重なって broadになっているのか, F-T法による長時間の測定であるのでドリフトの影響がでたのかはっきりしない。

注3). 電子スペクトルについて.

スペクトルの測定には(91)[1.4mgの(1.05b)から作った]を THF 50mlに溶かした溶液とそれを1/10にした溶液を用いて測定した。非常に希薄な溶液では安定でスペクトルの時間変化はなかった。室温にして1晩置くと完全に分解し黄色の溶液となった。この溶液は 450nm以上に吸収極大を示さず 吸収強度も全体に弱くなる。

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