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Synthesis and Photochemistry of Some Bridged Bicyclic Systems

Yoshikazu Sugihara

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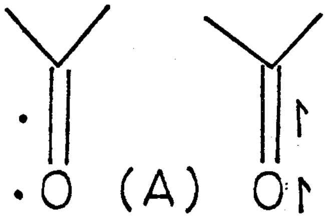
CHAPTER I Introduction

Since 1948 when W. A. Noyes, Jr., and V. Boekelheide1) reviewed the techniques used in the study of photochemical reactions, organic photochemistry has undergone very rapid development and, today, it takes an indisputable position in organic chemistry. Many types of photoreactions were found out and they were often applied to the syntheses of interesting molicules. Among the various compounds studied, photochemistry of compounds containing a carbonyl group has especially received much attention, because the difference in the nature of an electronically excited state (multiplicity and/or $n\pi^*$, $\pi\pi^*$) causes the different type of reactions.2) Thus, hydrogen atom abstraction is ascribed to the $n\pi^*$ character of a carbonyl group and the formula (A) best represents the $n\pi^*$ triplet state of a carbonyl group.

Intramolecular (1,3)- and (1,2)3)-acyl shifts of this group, which take place by way of singlet and triplet state, respectively, have been also studied with acute interest and qualitative interpretations based



(A)

on spin density[4] and MO theory[5] have recently been presented.

On the other hand, geometrical isomerization, bond reorganization and cycloaddition of unsaturated hydrocarbons[6] are also extensively studied and it was proved that the several concepts for ground state reactions can hold in these excited state reactions. For the purpose of a satisfactory understanding of a light-induced reaction, following questions have to be answered. Such questions involve i) nature of the reactive state ii) mechanism of the nonradiative deactivation iii) rate of all reactions including emission process iv) quantum yield of a given process.[7]

However, with such considerations as the relationship between emission spectra of the reactive state, the difinition and characterization of $n\pi^*$ and $\pi\pi^*$ states, and the determination of the energy levels by spectroscopic methods, the mechanistic questions identical with those asked for the ground state reactions (structural variation and reactivity relationship) will be, in some cases, reasonable for the excited state reactions. The concepts obtained by this study, corresponding to classical organic electronic theory for ground state reactions, will be useful for the synthetic design to many compounds which is not readily accessible through the ground state reactions.

This dissertation describes the syntheses and the photochemical reactions of some new bridged bicyclic compounds with i) di-π-methane system, ii) α,β-unsaturated carbonyl system iii) β,γ-unsaturated carbonyl system iv) exocyclic methylene system, v) aromatic annelated system.

1) W. A. Noyes, Jr., and V. Boekelheide : Photochemical Reactions In : Technique of Organic Chemistry, ed. by A. Weissberger, Vol 2. New York : Interscience 1948, pp 79-141

2) A. A. Lamola and N. J. Turro, "Energy Transfer and Organic Photochemistry" John Wiley and Sons, New York (1969).

3) R. S. Givens and W. F. Oettle, J. Amer. Chem. Soc., 93, 3963 (1971).

4) D. I. Schuster, G. R. Underwood and T. P. Knudsen, J. Amer. Chem. Soc., 93, 4304 (1971).

5) K. N. Houk, D. J. Northington and R. E. Duke, Jr., J. Amer. Chem. Soc., 94, 6233 (1972).

6) A. Schönberg, "Preparative Organic Photochemistry" Springer-Verlag, New York (1968).

7) P. J. Wagner, Accounts Chem. Res. 4, 168 (1971).

CHAPTER II

Section I. Introduction

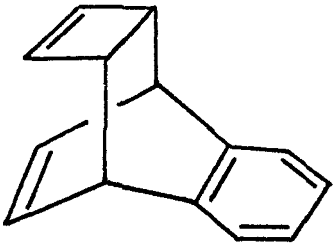
In a last decade, a part of the hydrocarbon chemistry dealing with the isomers consisted of only methine units has been studied extensively.1) The synthetic challenge to these molecules as well as the propensity for thermal and photochemical interconversions which are frequently subject to the conservation of orbital symmetry control2) seems to be the reason for the active investigations.

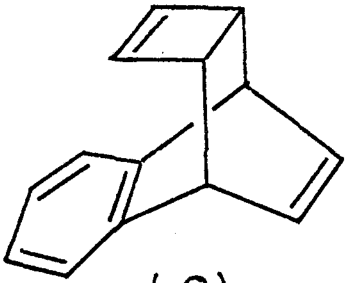
Among the $(CH)_n$ hydrocarbons studied, a number of $(CH)_{10}$3) hydrocarbons are known and become of great interest not only in the stability of the individual compounds but also in their interconversion and degenerate isomerization suggested by the orbital symmetry consideration.4)

In contrast to the wide researches in the parent $(CH)_{10}$ hydrocarbons an effect of the annelation with benzenoid ring to the one of the π-bonds in such molecules seems relatively not to have received so much attention.

In 1970, E. Vedjes,5) after his first paper on a cycloaddition of benzyne to cyclooctatetraene, reported the synthesis of anti-7,8-benzotricyclo[4.2.2.$0^{2,5}$]deca-3,7,9-triene (1), a

first member of the benzo $(CH)_{10}$ hydrocarbon, in low yield. This cycloaddition reaction appears to be a good entry into the synthesis of benzo $(CH)_{10}$ series, because of the potential lability of this molecule to irradiation and pyrolysis.
In view of a photochemistry, hydrocarbon (1), in which three π-bond are closely located and mutually exerted an influence each other, has a possibility of some rearrangements beginning with different initial steps. These expectations prompted us to examine the chemistry of (1). Moreover, syn-7,8-benzotricyclo[4.2.2.$0^{2,5}$]deca-3,7,9-triene (2) in which a cyclobutene ring has a syn-configuration respect to the benzene ring, has not been synthesized yet. The difference in the configuration of a cyclobutene ring may be able to, sufficiently, alter the bond reorganization pathway. Furthermore, synthesis of compounds involving a cyclobutene ring are relatively so unaccessible that new preparative method of cyclobutene ring is considered to be available to settle pending


(1)


(2)

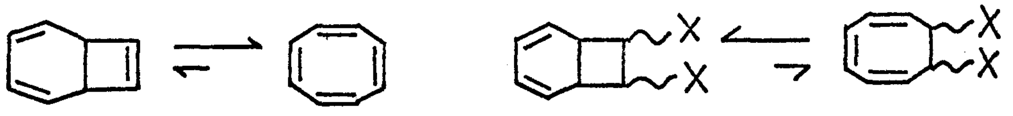
problems of the cyclobutene chemistry.

In this chapter, we will describe the convenient synthesis of anti-7,8-benzotricyclo[4.2.2.$0^{2,5}$]deca-3,7,9-triene (1) as well as the successful preparation of hitherto unknown benzo $(CH)_{10}$ isomer, syn-7,8-benzotricyclo[4.2.2.$0^{2,5}$]deca-3,7,9-triene (2) and some of their chemistry.

SECTION 2 Synthesis and Photochemistry

To start with the synthesis of (1), cyclooctatetraene dibromide (5) was chosen as the starting material because, as FIG 1 shows, the equilibrium of cyclooctatetraene so favors a monocyclic isomer under an usual condition that highly active reagents such as benzyne are considered to react mostly with the monocyclic isomer (4) to yield several kinds of adducts, while in cyclooctatetraene dibromide (5) the equilibrium between the valence isomers, (5) and (6), is shifted preferentially to the bicyclic isomer (5) in which four 2p orbitals lie perpendicularly in the plane of six-membered ring, one side of the diene moiety in (5) being sterically shielded by the fused cyclobutane ring. Therefore, compound (5) is considered to be a suitable substrate for the stereoselective Diels-Alder reaction.

FIG 1



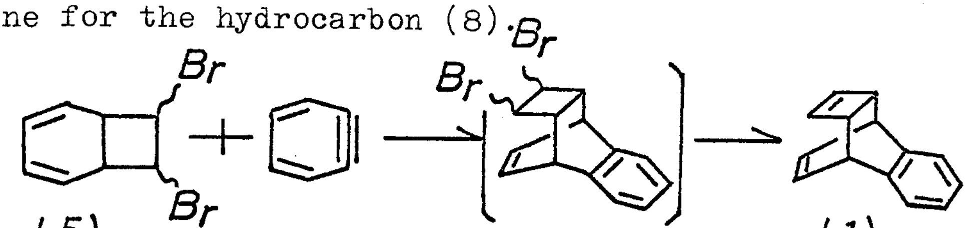
(3) (4) (5) X=Br (6)

=Cl

Dibromide (5)[6] was treated with isoamyl nitrite and anthranilic acid and the adduct was, without isolation, debrominated with Zn-Cu powder.7) Chromatography over silica gel afforded compound (1) as colorless needles (1), mp 56-57°, in 46% yield.

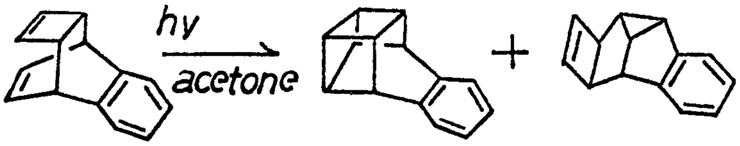
The anti-configuration of the resulting cyclobutene ring with respect to benzene ring was confirmed by the photolysis of (1) and synthesis of syn-isomer (2).

Acetone-sensitized photolysis of (1) through Pyrex filter proceeds to afford (8) (mp 51-52°) and (9) (oil) in 32% and 46% yield, respectively. The nmr spectrum of (8) bears a striking resemblance to that of basketene (10),8) indicating benzobasketene for the hydrocarbon (8).

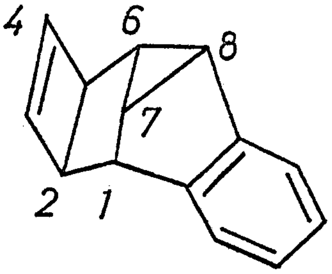


(5) (1)

Structure of the rearranged product (9) was assigned as a benzosemibullvalene derivative by means of nmr measurement. Nmr spectrum (100 MHz, $CDCl_3$, δ) of (9) displays three cyclopropyl proton signals at 1.97 (dd, J=6.4 and 8.0 Hz, 1H), 2.35 (dd, J=6.4 and 8.0 Hz, 1H) and 2.69 (ddt, J=1.0, 5.0, 8.0 and 8.0, 1H), two cyclobutyl proton signals at 2.99 (m, 1H) and 3.10 (m, 1H), one benzylic proton signal at 3.55 (d, J=5.0, 1H), two cyclobutenyl proton signals at 5.96 (ddd, J=2.8, 2.2, 0.8, 1H) and 6.21 (d, J=2.8, 1H) and four aromatic proton signals centered at 7.06 (m, 4H). The absorption peak at 2.35 was assigned to H_8 by means of double resonance techniques, namely irradiation at the area of 7.06 increased the height of the peak at 2.35. The small coupling constant between H_1 and H_2 (≃0 Hz) indicates the exo-configuration of the cyclobutene ring. This is also supported by the consideration of the chemical shift values assigned to H_3 and H_4. If the cyclobutene were in the endo configuration, H_1 would be coupled additionally to H_2, and H_3 and H_4 would experience shielding by the proximate aromatic ring. In order to determine the bond reorganization pathway, vinyl deuterated compound (1-d) was prepared. Treatment of (1) with N,N-dideuteriocyclohexyamine-lithium N-deuteriocyclohexlamide9) exchanged the sp^2-bound hydrogens, leaving the bridgehead positions alone bearing hydrogens. After one such treatment, nmr analysis revealed that there was 66.6% deuteration in vinyl positions, this quantity being derived by assuming no deuterated bridgehead carbon atoms.

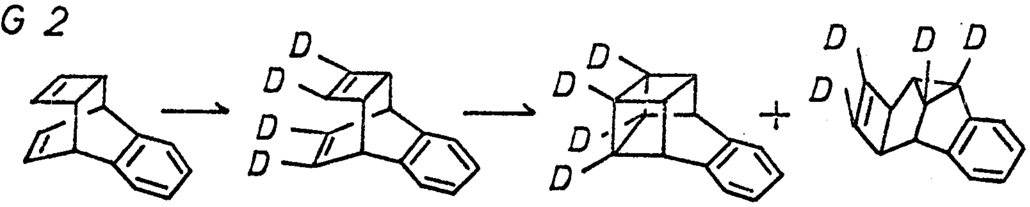


(1) (8) (9)



Deuterated compound (1-d) was photolyzed in acetone and the resulting mixture was chromatographed over silica gel to yield deuterated benzobasketene (8-d) and rearranged product (9-d). Nmr analysis revealed that (9-d) was exclusively deuterated at C_7 and C_8 along with at cyclobutenyl carbons.

FIG 2



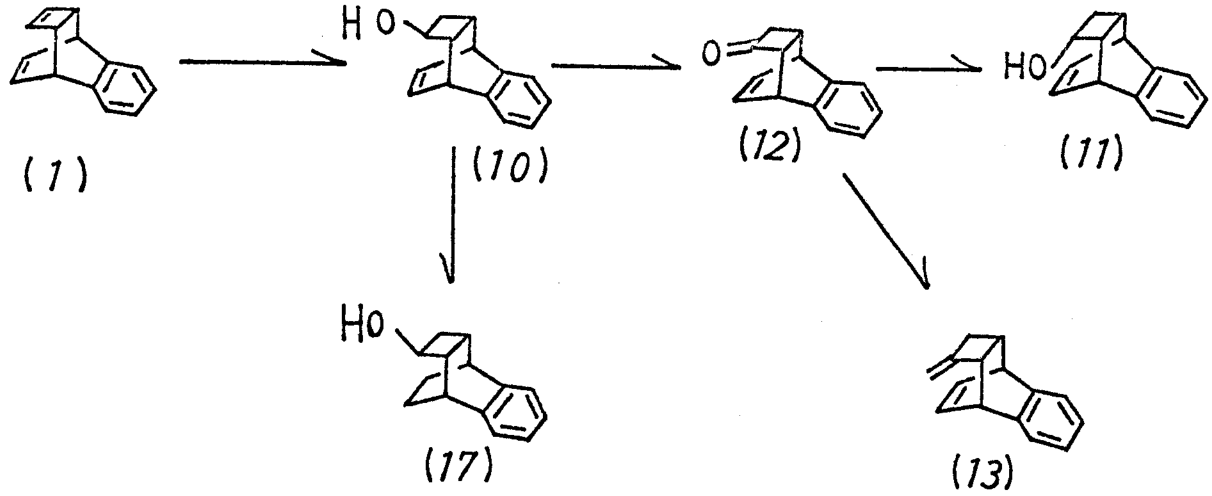
(1) (1-d) (8-d) (9-d)

No deuterium scrambling was observed on the four membered ring of (9) and the deuterium distribution in (8) was consistent with symmetry allowed $\pi 2s+\pi 2s$ addition mechanism.

In order to clarify the effect of substituent at C_3 of (1) on the photorearrangement, the epimeric exo- and end-alcoholes ((10) and (11), mp 86-87° and 118-119°, respectively) and exo-methylene derivative (13) (mp 67-68°) were prepared, as illustrated in FIG 3.

Oxymercuration of (1) with mercuric acetate followed by demercuration with sodium borohydride gave (10) in 61% yield. Compound(10) was oxidized with chromic anhydride in pyridine to the ketone (12) which on reduction with sodium borohydride in methanol gave 92% of the epimeric alcohol (11).

FIG 3

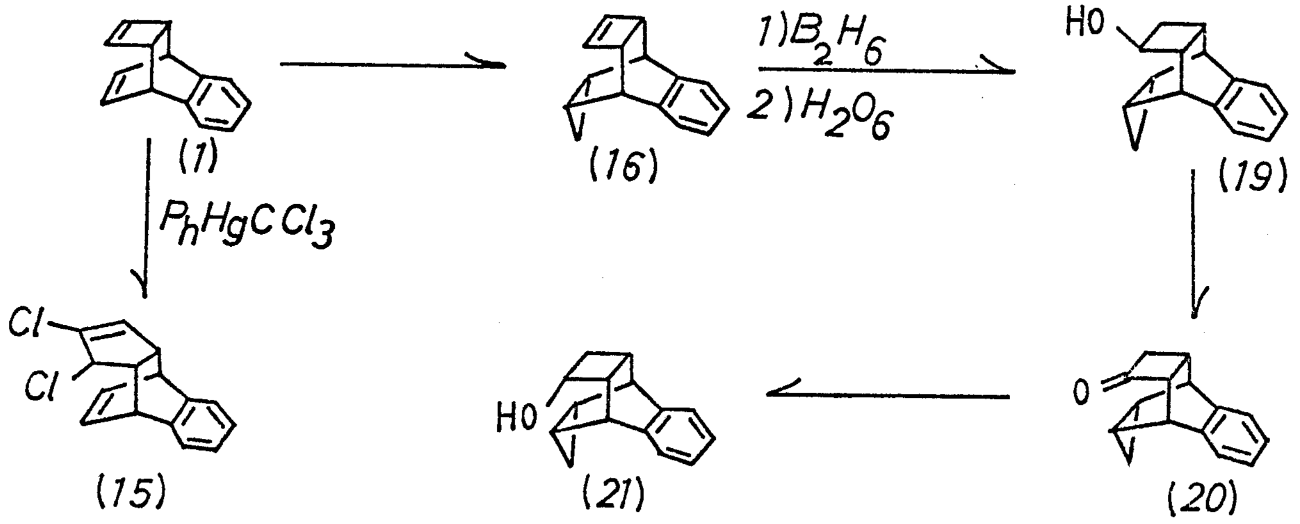


The configuration of the epimeric hydroxyl groups is readily understood by the reaction sequence and the comparison of the chemical shifts of vinyl protons. (6.45 for (10) and 6.67 for (11))

Here, it is noteworthy to refer to some derivatives of (1). Thus, cyclopropanation of (1) by Simmons-Smith[11] reaction afforded (16) (mp 57°) while the treatment of (1) with phenyl trichloromethylmercury resulted in the expansion of the four membered ring to give (15). Interestingly, the less hindered double bond of the cyclobutene ring was inert to Simmons-Smith reaction. Though oxymercuration of (16) resulted in the recovery of the starting material (16), introduction of the exo- and endo-hydroxyl groups at C_3 was effected by way of hydroboration[12] as depicted in FIG 4.

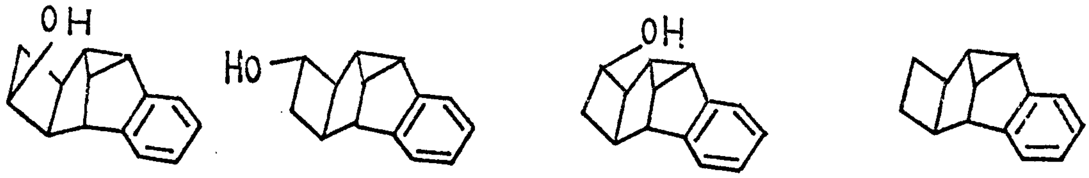
Compounds (10), (19) (mp 190°) and (17) (mp 113°), all of which have the exo-hydroxyl group on the four membered ring, serve as good model compounds for the solvolytic study. Actually, the values of chemical shift of the hydrogens at C$_3$ suggest the remote participation of the bond closely located to the carbon bearing the hydroxyl group (δ 3.95, 4.53, 4.58, respectively).

FIG 4



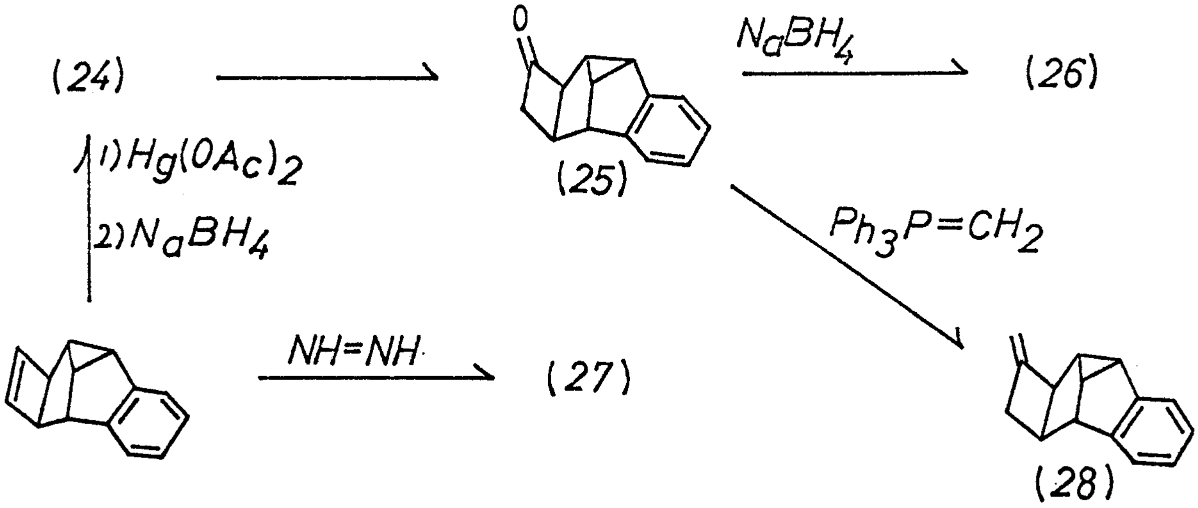
Compound (11) was photolyzed in pet. ether-acetone mixture (4/6 v/v) through Pyrex filter for 6 hr afforded rearranged alcohol (22) in 35% yield. On the contrary, exo-isomer (10) gave a complex mixture of polymeric products and no definite photoproduct could be separated. The structural assignment to (22) follows convincingly from: (a) its nmr spectrum in CDCl$_3$ which displays a four proton multiplet at 7.0 (aryl), a multiplet of area 1 at 4.21 for the hydrogen attached to carbon bearing the hydroxyl group (H_3) and a one proton doublet at 3.73 (J=5.8 Hz) for the benzylic hydrogen (H_1); (b) oxidation of (22) with chromic anhydride in pyridine gives the cyclobutanone (23), ir (film) 1770 cm^{-1}, which is isomeric but not identical with the cyclobutanone (25) obtained from the alcohol (24) [See FIG 6]; (c) comparison of the values of the chemical shift of benzylic hydrogen of (22) with those of the model compound (24), (26) and (27) [See FIG 5]. These model compounds are easily derived from the hydrocarbon (9) as illustrated in FIG 6. The hydroxyl group in (22) is very probably on C_3 with β-configuration since the shift of benzylic proton peak to a lower field clearly reflects the increasing proximity of this hydrogen to the hydroxyl group in (22).

FIG 5



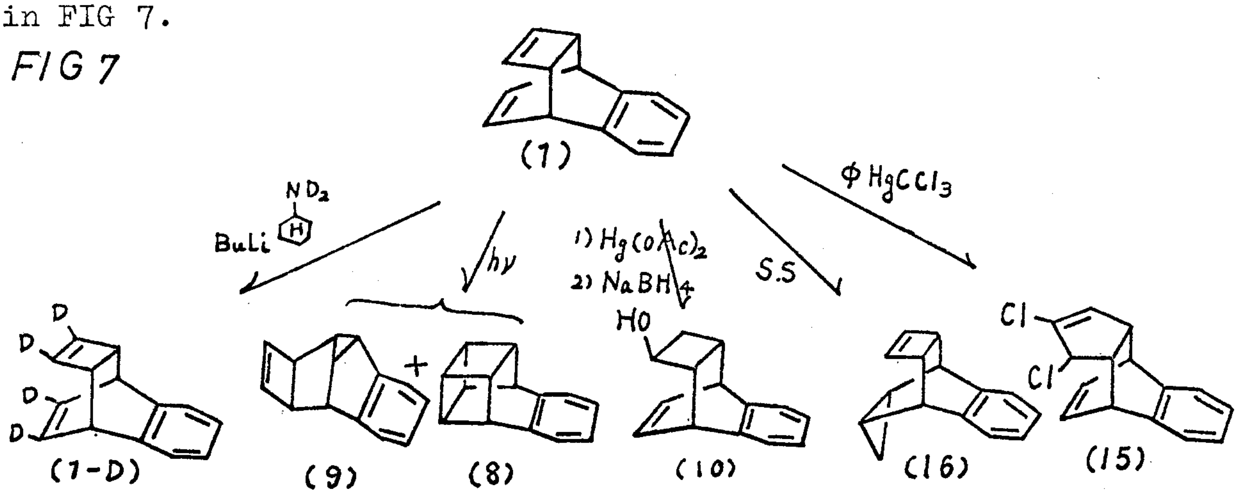
	(22)	(24)	(26)	(27)
δ benzyl	3.73	3.38	3.45	3.38
mp	100-102°	86-87.5°	97-98°	oil

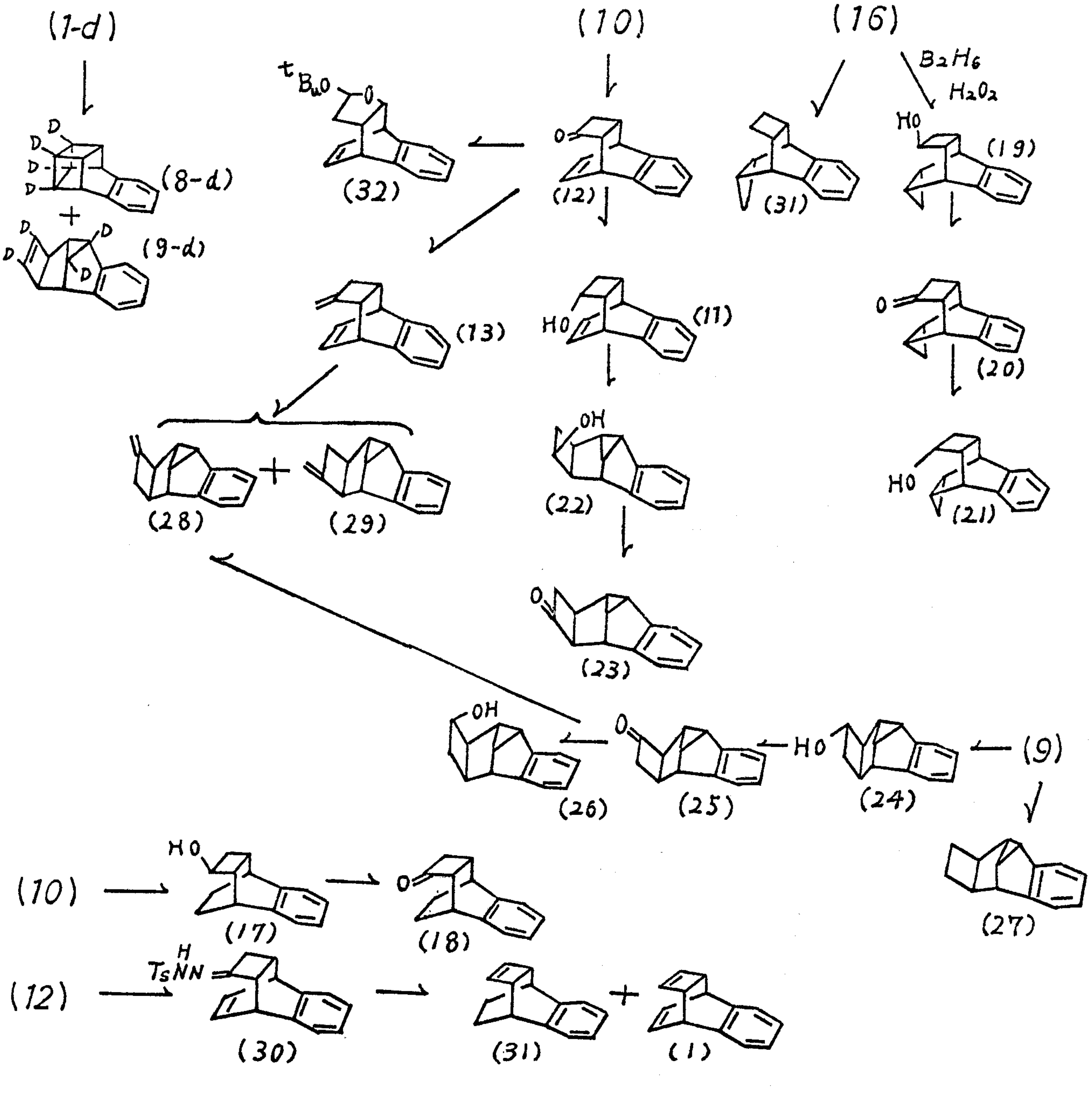
FIG 6



Sensitized photolysis of an acetone solution of (13) resulted in rapid disappearance of (13) with concomitant formation of two isomeric products in 6:4 ratio. Independent synthesis indicates structure (28) for the minor photoproduct. Reaction of the ketone (25) (mp 92.5-94) with methylenetriphenylphosphorane afforded (28). The major product is, therefore, assigned to structure (29). These reactions are summarized in FIG 7.

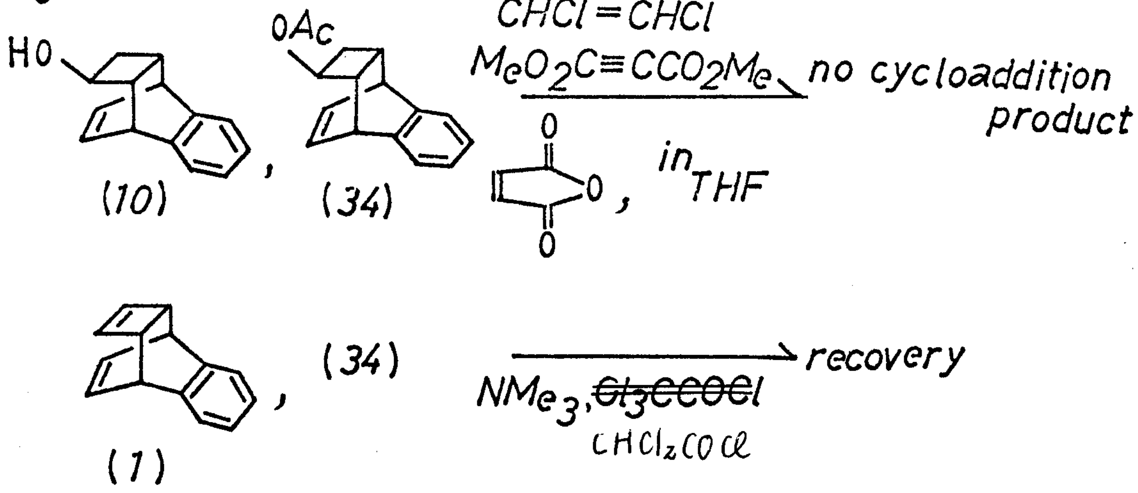
FIG 7




(1-d)
D
D
D
D
(8-d)
+
D
D
D
D
(9-d)
tBuO
O
(32)
(10)
O
(12)
(16)
B2H6
H2O2
(31)
HO
(19)
(13)
HO
(11)
O
(20)
OH
(28)
+
(29)
(22)
HO
(21)
O
(23)
OH
(26)
O
(25)
HO
(24)
(9)
(27)
(10)
HO
(17)
O
(18)
(12)
H
TsNN
(30)
(31)
+
(1)

Photocycloaddition of (10) and (34) with maleic anhydride, dichloroethylene and dimethyl acetylenedicarboxylate were unsuccessful. Treatment of (1) and (34) with dichloroketene also resulted in the recovery of the starting materials (1) and (34).

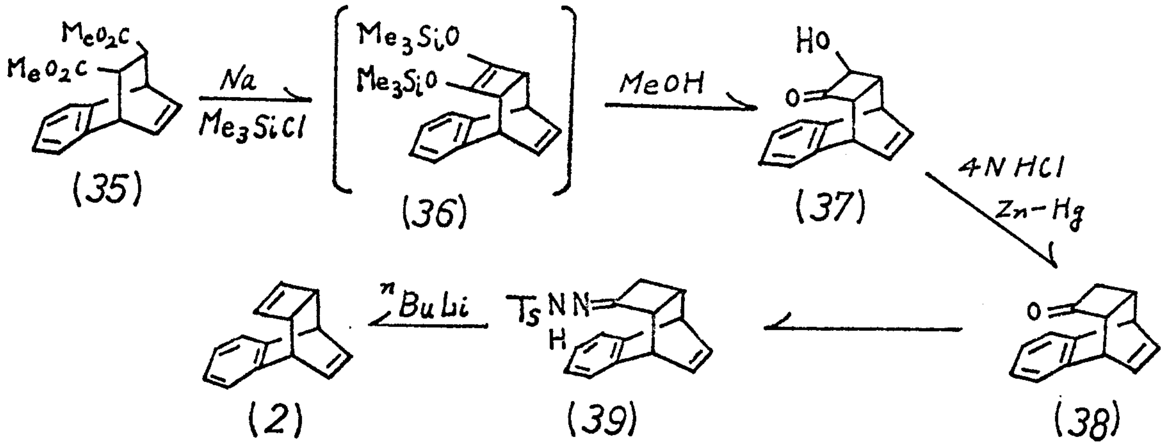
FIG 8



Starting material for our synthesis of (2), dimethyl syn-5,6-benzobicyclo[2.2.2]oct-2-ene-7,8-dicarboxylate (35),[13] preserving the syn configuration of the two methoxycarbonyl groups to the aromatic moiety, was treated with sodium dispersion in refluxing xylene in the presence of trimethylchlorosilane under nitrogen for 6 hr.[14] Hydrolysis of the bistrimethysilyl ether of the intermediate enediol (36) by methanol gave the acyloin

(37) (mp 148-9°, ir (KBr) 3530, 1775 cm^{-1}) in 62% yield.

FIG 9



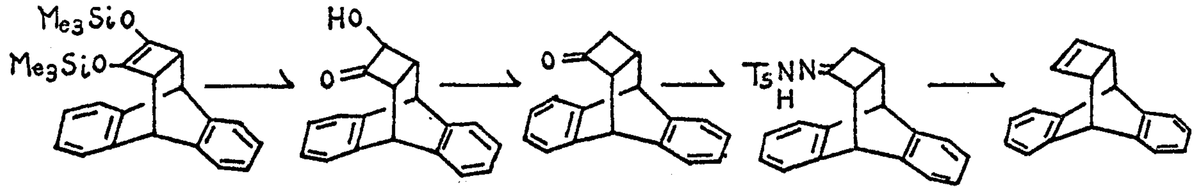
The acyloin (37), dissolved in toluene, was reduced with amalgamated zinc in 4N hydrochloric acid by 1.5 hr refluxing to produce the ketone (38) (mp. 69-70° ir (KBr) 1770 cm^{-1}) in 73% yield. The ketone (38) was converted into its p-toluenesulfonylhydrazone (39) (mp. 189-190°), which, in a typical experiment, was treated with three mole equivalents of n-butyllithium in diglyme at 60° for 3 hr.15) After filtration of the resulting lithium p-toluene sulfinate, most of the diglyme was removed under reduced pressure. The silica gel column chromatography of the benzene extract of the residue with pet. ether afforded colorless needles (mp. 43°) in 40% yield. The structure was assigned as the desired (2) based on the following evidences: (a) Mass spectrum of (2) shows a parent peak at m/e 180 ($C_{14}H_{12}^{+}$,100%); (b) the nmr spectrum (CCl_4) of (2) reveals four proton singlet at 7.00 (aryl), two proton multiplet at 6.52 (olefinic), two proton singlet at 5.82 (cyclobutenyl), two proton multiplet at 3.65- 3.90 (diallylic methine) and two proton multiplet at 2.70 (methine) and exhibits a striking resembalance to that of the anti-isomer(1) except for the values of chemical shift of vinyl protons. Thus the cyclobutene formed by the aforementioned reaction can be confidently assigned as the syn configuration to the benzene ring on the basis of this nmr spectrum in which cyclobutenyl proton singlet appears 0.23 ppm upfield than that of (1) due to the shielding effect of the proximate benzene ring, whereas the olefinic proton multiplet emerges o.3 ppm downfield than that of (1) due to the lack of the proximate cyclobutenyl double bond.

This synthetic procedure was applied to the preparation of 7,8:9,10-dibenzotricyclo[4.2.2.$0^{2,5}$]deca-3,7,9-triene (45) which has already been synthesized by way of the Diels-Alder reaction of 9,10-dibromoanthracene with cis-3,4-dichlorocyclobutene followed by treatment with lithium-amalgam.16)

Our preparation of (45) began with readily available 3,4-bistrimethylsiloxy-7,8-9,10-dibenzotricyclo[4.2.2.$0^{2,5}$]deca-

3,7,9-triene (41).(17) Hydrolysis with ethanol converted the siloxy derivative (41) into acyloin (42) (mp 195-197°, ir (KBr) 3550, 3460, 3350, 1775 cm^{-1}), which then smoothly reduced in refluxing toluene with amalgamated zinc and 4N-hydrochloric acid to give the cyclobutanone (43) (mp 167-168° ir (KBr) 1775 cm^{-1}) in 83% yield. This was converted to p-toluenesulfonylhydrazone (44) (mp 228-229°), which was subjected to the reaction in diglyme with excess n-butyllithium at 120° to give the anticipated cyclobutene (45) (mp 138-139°, lit.(16) 137°) in 43% yield. The ir and uv spectra of (45) were identical with those of the reported values. In the nmr spectrum (60 MHz, $CDCl_3$), the cyclobutenyl protons appear as a singlet at 5.87, denoting the presence of the same structural moiety with (2).

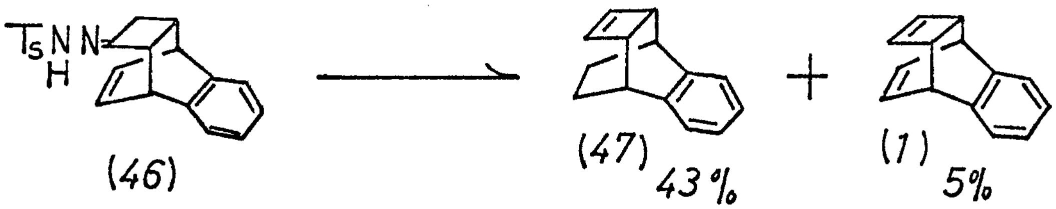
FIG 10



(41) (42) (43) (44) (45)

The method described here are quite useful for the synthesis of these fused cyclobutenes. But there remains some disturbing matters in this procedure. Thus treatment of p-toluenesulfonylhydrozone (46), isomer of (39) under the similar condition resulted in the reduction of the double bond located closely to the reaction site, to afford the dihydrocompound (47) (mp 35°) in 43%, the desired compound (1) being a minor product.

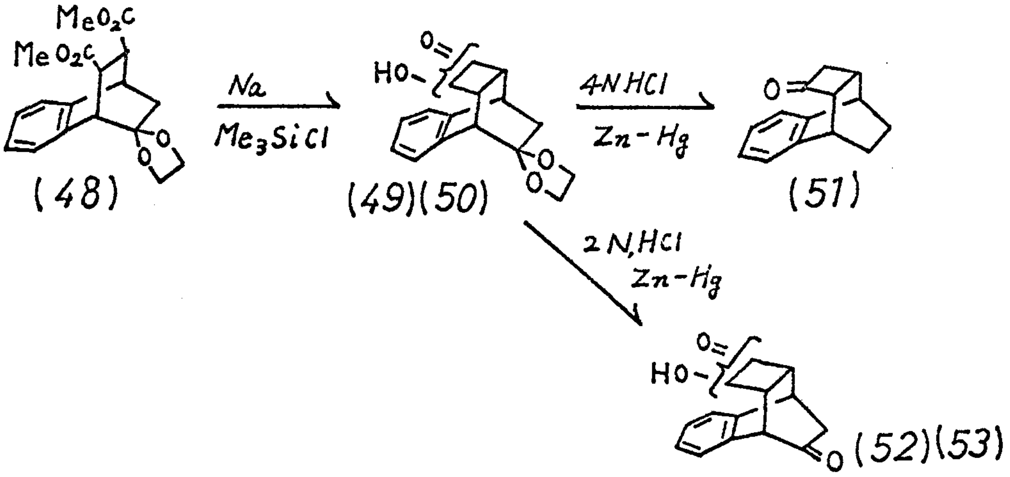
FIG 11



The hydrocarbon (47) gave the symmetical nmr spectrum, in which there appear four proton singlet at 7.08, two proton singlet at 6.46, two proton multiplet at 3.08, two proton multiplet at 2.64, two proton multiplet centered at 2.00 and two proton multiplet centered at 1.10. The upfield shift of benzylic proton signal (0.6 ppm, compared with (1)) supports the structural assignment. The study on this mechanism is in progress.

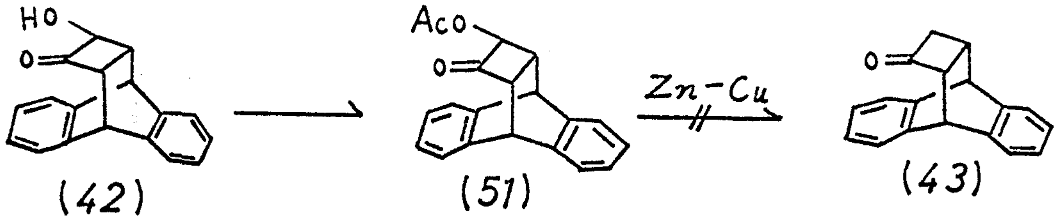
Acid catalyzed reduction with amalgamated zinc used in the conversion of acyloins to cyclobutanones are impractical for the compounds bearing a functional group sensitive to an acidic condition. Actually, acyloins (49) and (50), prepared from the compound (48)[18] in 30% yield, were reduced to (51) under the aforementioned condition and the similar treatment in the presence of 2N-hydrochloric acid only resulted in deketalization.

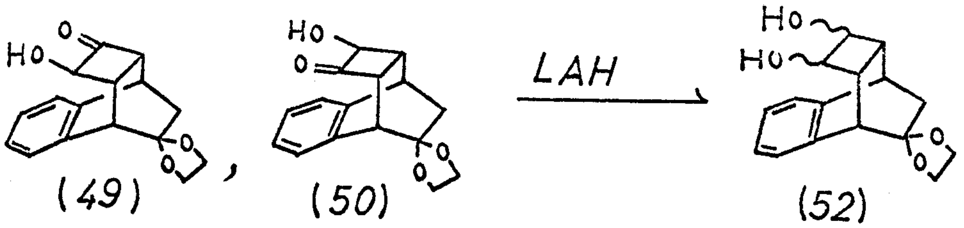
FIG 12

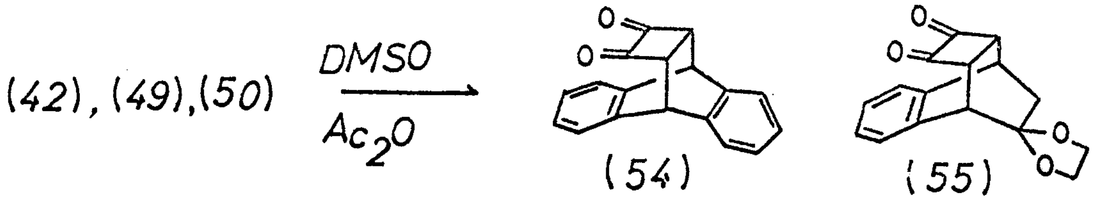


In order to investigate the route from an acyloin to a cyclobutene, some reactions were attempted (FIG 13): a) acetylation of the acyloin (42) followed by treatment with Zn-Cu under the neutral condition; b) reduction of the acyloins (49) and (50) with lithium aluminum hydride and c) oxidation of acyloin (42) (49) and (50) with acetic anhydride-dimethylsulfoxide to diketones. The reaction of (a) resulted in the recovery of acetate (51)

FIG 13





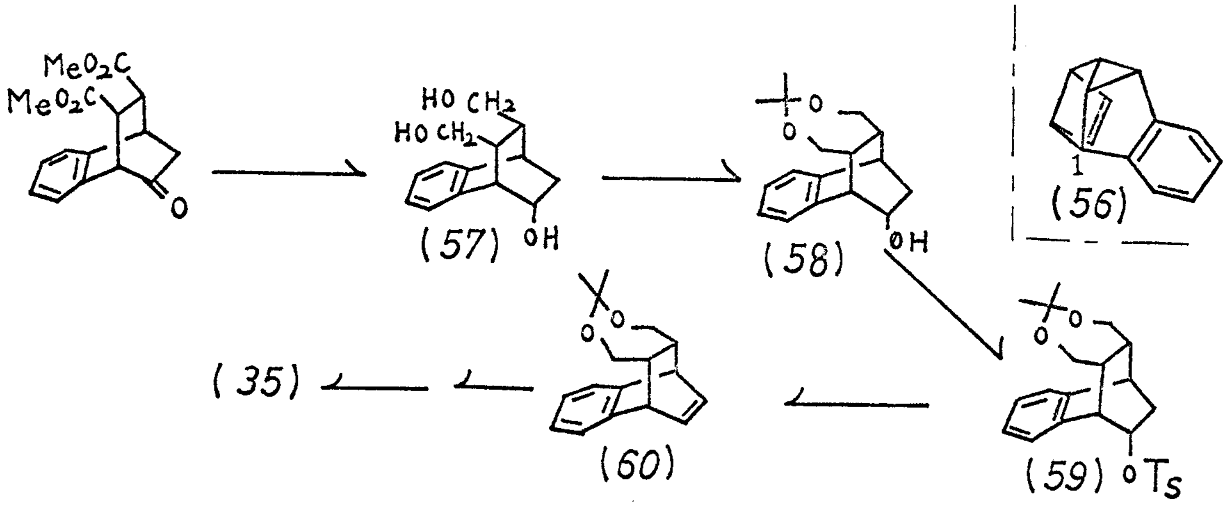


Reduction of acyloins with lithium aluminum hydride, even in pyridine,[19] was unsuccessful and α-diketone (54) and (55) could be prepared in fairly good yield, however, these are too unstable to be well suited for the intermediate to cyclobutenes.

Photolysis of (2) in acetone was carried out with 450W Hg lamp through Pyrex filter and the disappearance of (2) was checked on tlc. After 30 minutes, the spot of (40) disappeared and a new single spot appeared on tlc. Evaporation of the solvent followed by chromatography on silica gel with pet. ether, afforded oil (56) in about 20% yield, whose nmr spectrum (CCl_4) shows aromatic proton signals centered at 7.0, a vinyl proton signal at 5.58 ($J \sim 2$Hz), a vinyl proton signal at 5.24 ($J \sim 2$Hz), and signals of the proton bonded to sp^3 carbon atoms, in which one proton triplet ($J \sim 5$Hz) assigned to benzylic proton H_1 was observed. Signals due to the impurities prevents the full assignment of all peaks but the data is, seemigly, sufficient to assign (56) to the product.

Finally, the poor yield of Diels-Alder reaction of naphthalene with maleic anhydride requires another route to the adduct (35). The work along with this line is under way (FIG 14).

FIG 14



Photoreduction occured, upon photolysis of (45) in acetone, to yield (61) in 48% yield. Photolysis in benzene resulted in the recovery of the starting material, acompanied by a trace of unidentified hydrocarbons.

SECTION 3 Discussion

Although several types of bond reorganization pathway of (1) are expected, only two products were, interestingly, produced in a fairly good yield. As shown in the previous section, product (8) is regarded to be formed by ($\pi 2s + \pi 2s$) reaction, revealed by the deuterium labeling study.

In case of (9), there is a priori possibility of two fundamentally different mechanisms (FIG 15); (C_1-C_2 or C_1-C_8 bond migration). As the photoylsis of several compounds (FIG 16) exemplified, total energy available in the excited state of (1) (E_T) is sufficient to break the C_1-C_2 bond.[20) If the C_1-C_2 bond fission and the C_2-C_9 or C_2-C_{10} bond formation ((1,2) or (1,3)-shift, respectively) are occured in a concerted manner, triplet state favors (1,2)-shift whereas (1,3)-shift is predominant in singlet state, according to the generalized postulate suggested by K. Fukui (FIG 17).[21)Nevertheless, the experimental finding is not consistent with photochemically allowed concerted ($\pi 2a + \pi 2a$) cycloaddition of C_1-C_2 and C_9-C_{10} bonds, but with that of C_1-C_8 bond and C_9-C_{10} bond, in which the fission of the stronger bond (C_1-C_8 bond) takes place, indicating the participation of p orbitals of benzene ring during the di-π-methane rearrangement.

The concerted (1,2)-shift along a cyclobutene ring (FIG 18) is worthnoting. To best of out knowledge, this type of reactions extremely rare in the literature[22] because of the hard availability of the suitable model compounds. Thus, in such a molecule as (1), (1,2)-shift on the six membered ring takes precedence over that on the cyclobutene ring, because of the high strain energy required to form a bicyclobutane system. If the molecule is so designed as to restrain the (1,3)-shift, (1,2)-shift would be feasible even on cyclobutene ring. The study along the line seems interesting. As to path (d),[23] (FIG 15 and 16), no evidence for the formation of (2) and(61) was gained by means of TLC analysis. These facts indicate the very facile di-π-methane rearrangement of (1).

FIG 15

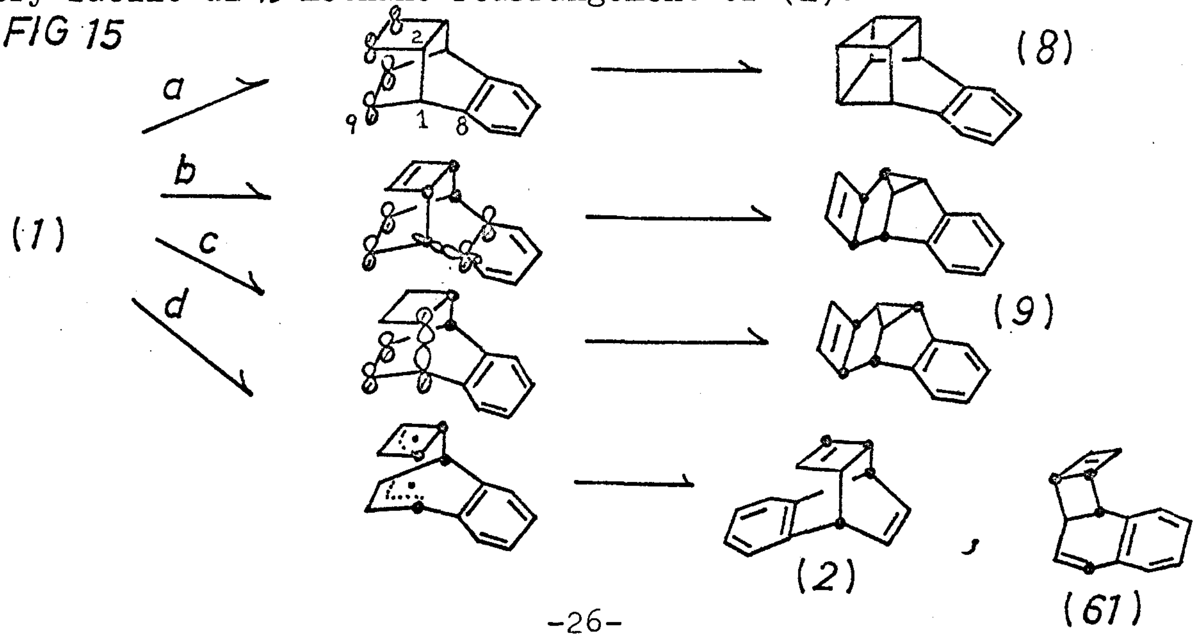


FIG 16

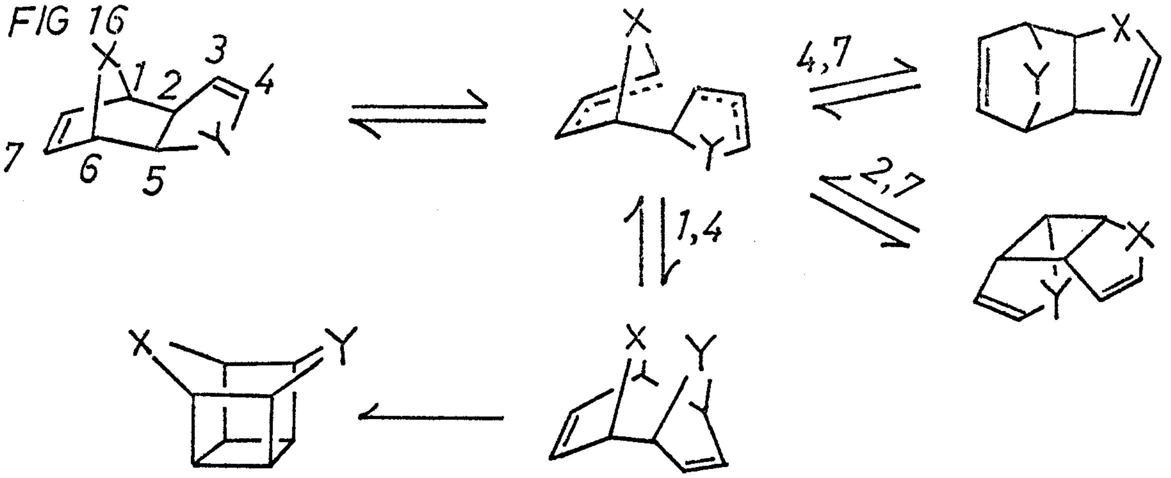


FIG 17

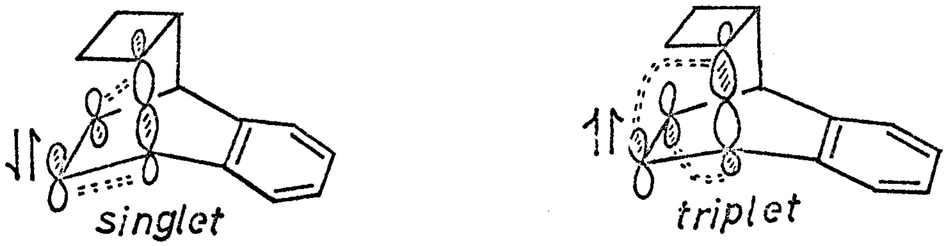
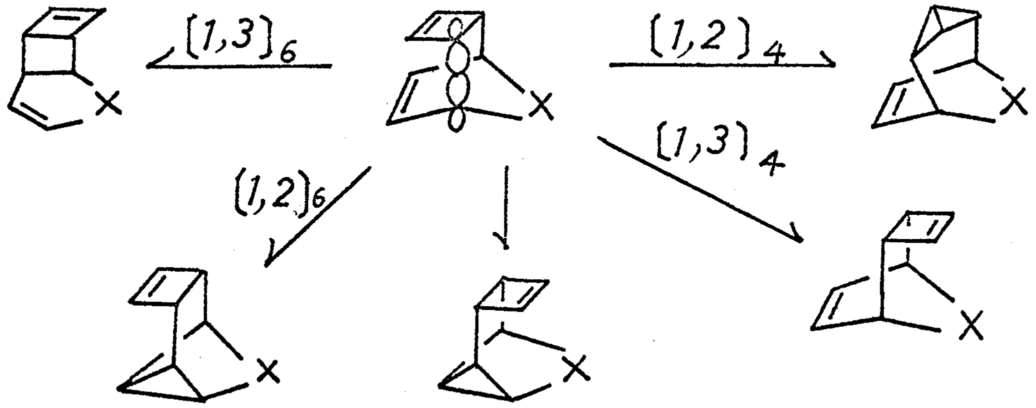
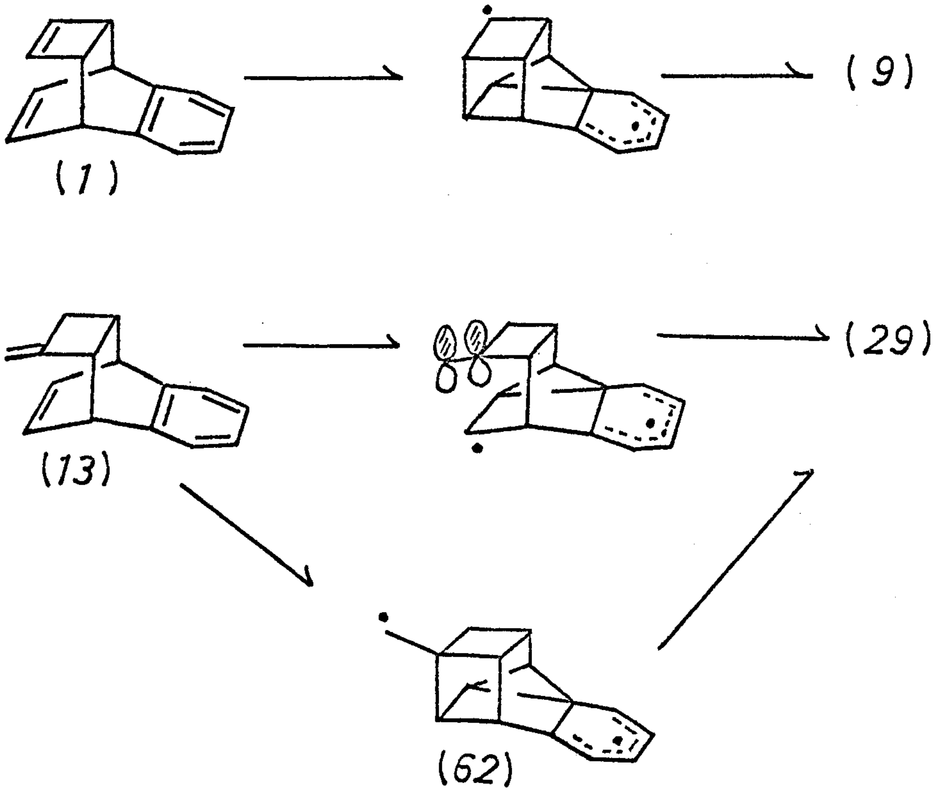


FIG 18

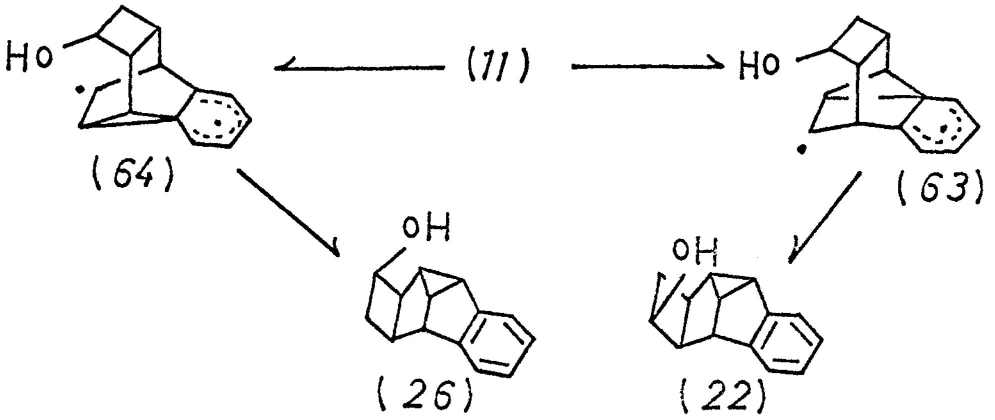


The extent of which p orbital of a four membered ring participates in the pathway of this rearrangement cannot be inferred at the present stage. The lack of regiospecificity in a rearrangement of (13), however, seemingly excludes a possibility of remote radical stabilization effect of the p orbital, and an intermediate or a point of potential surface such as (62) (FIG 19).

FIG 19



The regiospecificity observed for the photolysis of endo-alcohol (11) apparently suggests a larger preference for (63) over (64).



This is partially due to the factors which involve hydrogen bonding or charge transfer interaction between a developing redical and the oxygen, as indicated by H. Hart.[24] However, other explanations cannot be also excluded. Actually, despite the stability of product (22), the yield of (22) is dependent on purity of solvent and temperature. In order to clarify the regiospecificity we must await the structural analysis of the unidentified products.

Photoreduction of compound (16) and (45) can be easily understood according to the energetic argument proposed to rationalize the selectivity of bridging in benzobarrelene.[25] Thus E_{T1} value of ethylene (82 kcal) is lower than that of benzene (85 kcal), and the substitution and strain also lower the value of ethylene. Accordingly, it is apparent that the cyclobutenyl double bond in (45) is an active site under the sensitized condition. Another example of such a ready photoreduction of a strained double bond is well known in the literature.26)

SECTION 4 Experimental

Anti-7,8-benzotricyclo[4.2.2.$0^{2,5}$]deca-3,7,9-triene (1)

Cyclooctatetraene dibromide, which was prepared from 8.32 g of cyclooctatetraene (COT) and 12.8 g of bromine in ice-salt cooled dichloromethane, and 14.0 g of i-amylnitrite were dissolved in a mixture of tetrahydrofuran and dichloromethane (880 ml, 2:9 v/v). To the mixture maintained at 50°, 16.40 g of anthranilic acid dissolved in 480 ml of tetrahydrofuran was added dropwise over a period of 10 hr. Dark reddish brown residue obtained by evaporation of solvent was treated with 35 g of Zn-Cu couple in 350 ml of refluxing tetrahydrofuran for 3 hr. After removal of the solvent, ether was added to precipitate a yellow solid which was filtered off and the filtrate was concentrated in vacuo. This procedure was repeated several times till no more precipitate was yielded. The filtrate was concentrated to give a viscous brown oil, which was chromatographed over silica gel and eluted with pet. ether to afford crystals (6.7 g, 46%). Recrystalization from pet. ether gave colorless needles, mp. 56-57°; ν_{max}^{KBr} 1460, 1448, 1288, 965, 802, 740 and 700 cm^{-1}; δ^{CDCl_3} 2.58 (m, 2H), 3.63 (m, 2H), 5.96 (s, 2H), 6.09 (m, 2H) and

7.00 (m, 4H); Anal. Calcd. for $C_{14}H_{12}$: C, 93.29; H, 6.71. Found: C, 92.89; H, 6.78.

Photolysis of the hydrocarbon (1)

A solution of the hydrocarbon (1) (1.8 g) in dry acetone (1 liter) was irradiated for 4 hr through Pyrex filter with a 450-w high-pressure mercury lamp. Evaporation of acetone afforded a yellow oil which was chromatographed over silica gel (450 g) and eluted with pet. ether. The first fraction contained 576 mg of benzobasketene (8) (32%), and from the next fraction 829 mg of the hydrocarbon (9) (46%) was obtained as a colorless oil. benzobasketene (8): mp 51-52°; ν_{max}^{KBr} 2970, 1480, 1458, 1256 and 740 cm^{-1}; δ^{CDCl_3} 3.0 (m, 4H), 3.40 (m, 2H), 4.16 (m, 2H) and 7.30 (s, 4H); Anal. Calcd. for $C_{14}H_{12}$: C, 93.29; H, 6.71. Found: C, 93.24; H, 6.68. the hydrocarbon (9): ν_{max}^{NaCl} 3040, 2920, 1470, 1280, 782, 735 and 6.72 cm^{-1}; Anal. Calcd. for $C_{14}H_{12}$: C, 93.92; H, 6.71. Found: C, 93.00; H, 6.82.

The exo-alcohol (10)

Hydrocarbon (1) (360 mg) was added to a yellow suspension of 636 mg of mercuric acetate in a mixture of water and tetrahydrofuran (20 cc, 1:1 v/v). After yellow color disappeared (ca. 3 hr, r.t.) 10 ml of 3M sodium hydroxide was added to colorless solution, followed by reduction with 10 ml of 0.5M sodium borohydride in 3M sodium hydroxide. The mercury was allowed to settle. Extraction with ether, followed by removal of a solvent, gave colorless oil, which was chromatographed over silica gel. The first fraction eluted with dichloromethane contained the starting material (28%). Hydroxy compound (10) was obtained as a colorless oil, which was crystallized by standing overnight. Recrystalization from dichloromethane yielded needles (61%), mp 87-88°; ν_{max}^{NaCl} 3350, 2940, 1462, 1080 and 745 cm^{-1}; δ^{CDCl_3} 1.90 (m, 2H), 2.31 (m, 2H), 2.53 (m, 1H, -O$\underline{H}$), 3.95 (m, 3H), 6.45 (m, 2H) and 7.16 (m, 4H); Anal. Calcd. for $C_{14}H_{14}O$: C, 84.81; H, 7.12. Found: C, 84.25; H, 7.19.

Deuteration of the hydrocarbon (1)

To a mixture of N,N-dideuteriocyclohexylamine (20 ml) and (10 ml) of hexane solution of n-butyl lithium (n-BuBr, 1.37 g; Li, 175 mg), 540 mg of the hydrocarbon (1) was added. The solution was heated at 70° for 50 hr under dry nitrogen atmosphere to become a dark orange solution, which was quenched with 6 ml of D_2O. The precipitate was removed by filtration and the filtrate was extrated with ether. The organic phase was washed several times with water, followed by desiccation over $MgSO_4$. Removal of a solvent afforded yellow oil, which was chromatographed over silica gel and eluted with pet. ether. Crystals (420 mg) was obtained. Nmr analysis revealed that there was 66.6% deuteration in vinyl positions; ν_{max}^{KBr} 3000, 2900, 1448, 1158, 960, 860, 750 and 670 cm^{-1}; δ^{CDCl_3} 2.58 (m, 2H), 3.63 (m, 2H), 5.96 (s, 0.7H), 6.09 (m, 0.7H) and 7H (m, 4H).

Photolysis of the deuterated compound (1-d)

The deuterated hydrocarbon (8-d) and (9-d) were obtained by the same procedure as nondeuterated hydrocarbon (8) and (9) were prepared; the hydrocarbon (8-d): δ^{CDCl_3} 3.0 (m, 2.7H), 3.40 (m, 0.7H), 4.16 (m, 2H) and 7.20 (m, 4H): the hydrocarbon (9-d): δ^{CDCl_3} 1.97 (m, 1H), 2.35 (m, 0.4H), 2.69 (m, 0.4H), 2.99 (m, 1H), 3.10 (m, 1H), 3.55 (m, 1H), 5.96 (s, 0.4H), 6.21 (s, 0.4H) and 7.06 (m, 4H).

Simmons-Smith reaction of (1)

500 mg of Cu-Zu couple prepared according to H. E. Simmons was placed in 10 ml of abs. ether. A crystal of iodine was added and the mixture was stirred till the brown color has

disappeared. A mixture of 1.6 g of CH_2I_2 and 500 mg of hydrocarbon (1) in 5 ml of abs. ether was added in one portion. The mixture was refluxed overnight. Ether solution was decanted from the couple, which was washed several times with ether. Combined ether layer was washed with dil. HCl solution and dried over Na_2SO_4. Evaporation of a solvent gave a pale yellow oil, which was chromatographed over silica gel and eluted with pet. ether. First fraction yielded crystals, which was recrystallized from pet. ether (42%); mp 57-58°C. Second fraction contained the starting material (50%). ν_{max}^{KBr} 3025, 2900, 1475, 752 and 730 cm^{-1}; δ^{CDCl_3} -0.83 (td., J=4.0, 4.0 and 5.5 Hz, 1H), -0.05 (td., J=7.5, 7.5 and 5.5 Hz, 1H), 1.20 (m, 2H), 2.70 (m, 2H), 3.40 (m, 2H), 6.50 (s, 2H) and 7.20 (m, 4H); Anal. Calcd. for $C_{15}H_{14}$: C, 92.74; H, 7.26. Found: C, 92.77; H, 7.31.

The ketone (12)

The exo-alcohol (10) was oxidized with chromic anhydride in pyridine to the ketone (12), mp. 141°; ν_{max}^{KBr} 2950, 1762, 1463, 1380, 760 and 715 cm^{-1} ; δ^{CDCl_3} 2.30-3.06 (m, 3H), 3.50 (m, 1H), 4.30 (m, 2H), 6.63 (m, 2H) and 7.33 (m, 4H); Anal. Calcd. for $C_{14}H_{12}O$: C, 85.68; H, 6.16. Found: C, 85.43, H, 6.19.

The endo-alcohol (11)

The ketone (12) was reduced with sodium borohydride in methanol to give the endo-alcohol (11), mp. 118-119°; 92%; ν_{max}^{KBr} 3280, 2900, 1458, 1445, 1080, 755, 740 and 700 cm^{-1}; δ^{CDCl_3} 1.2-2.8 (m, 4H), 3.8-4.4 (m, 3H), 6.67 (m, 2H) and 7.10 (m, 4H); Anal. Calcd. for $C_{14}H_{14}O$: C, 84.81; H, 7.12. Found: C, 84.91; H, 7.20.

Witting reaction of the ketone (12)

10 ml of ethereal solution of n-butyl lithium (n-BuBr, 411 mg; Li, 51.7 mg) was added to 15 ml of anhydrous tetrahydrofuran. To the solution, 714 mg of triphenylmethylphosphonium bromide was added cautiously, and the mixture was allowed to stand at r.t. for 5 hours with stirring. 240 mg of the ketone (12) was then added carefully, and the solution was heated under reflux overnight and allowed to cool to r.t. White precipitate was removed by filtration. Organic phase was washed with H_2O and dried over $MgSO_4$. Removal of the solvent gave a viscous oil, which was chromatographed over silica gel and eluted with benzene-pet. ether (1:1 v/v). The product was recrystallized from hexane (52%), mp. 67-68°, ν_{max}^{KBr} 3050, 2950, 2900, 1465, 872, 862, 808, 750, 708 and 692 cm^{-1} ; δ^{CDCl_3} 2.0-2.6 (m, 3H), 2.7-3.1 (m, 1H), 4.0 (m, 2H),

4.83 (m, 2H), 6.53 (m, 2H) and 7.2 (m, 4H); Anal. Calcd. for $C_{15}H_{14}$: C, 92,74; H, 7.26, Found: C, 92.51; H, 7.30.

The alcohol (19)

The apparatus utilized were constructed according to H. C. Brown and G. Zweifel.[27)] Diborane was generated by the dropwise addition of 2.4 ml of 0.5M sodium borohydride in diglyme to the stirred solution of BF_3 in diglyme (0.34 g in 2.5 ml). The gas was passed into the 10 ml of tetrahydrofuran containing 388 mg of the compound (16) by applying a slight flow of dry nitrogen through the generator. During the reaction the solution of starting material was kept at 20°. After completion of the addition of sodium borohydride, the generater was heated for 1 hr. at 75°, the nitrogen flow being maintained to ensure the complete transfer of B_2H_6 to the hydroboration flask. The excess B_2H_6 was decomposed by dropwise addition of 0.5 ml of H_2O. The organoborane is oxidized at 43° by the addition of 0.3 ml of 3N-NaOH, followed by dropwise addition of 0.3 ml of 30% H_2O_2. After the addtion of Et_2O, organic phase was separated, the aqueous phase was saturated with sodium chloride and then extracted twice. The combined extracts were washed and dried over $MgSO_4$. The oil obtained after evaporation of the solvent, was chromatographed over silica gel. The first fraction eluted with benzene contained the starting material and the second fraction gave a hydroxyl compound (19), which was recrystallized with CH_2Cl_2 (69%), mp. 190-191°; ν_{max}^{KBr} 3200, 3000, 2920, 1420, 1080 and 748 cm^{-1}; δ^{CDCl_3} 0.83 (td., J=4.0, 4.0 and 5.5 Hz, 1H), 0.00 (7.5, 7.5 and 5.5 Hz, 1H), 1.30 (m, 2H), 1.8-2.6 (m, 5H), 3.23 (m, 1H), 3.50 (m, 1H), 4.53 (m, 1H) and 7.20 (m, 4H); Anal. Calcd. for $C_{15}H_{16}O$: C, 84.87; H, 7.60. Found: C, 84.76; H, 7.55.

The ketone (20)

The compound (19) was oxidized with chromic anhydride in pyridine to the ketone (20), mp. 136°, ν_{max}^{KBr} 3000, 2900, 1760, 1432, 1080, 1040 and 748 cm^{-1}; δ^{CDCl_3} -0.70 (td., J=5.5, 3.8 and 3.8 Hz, 1H), 0.13 (td., 7.0, 7.0 and 5.5 Hz, 1H), 1.36 (m, 2H), 2.60 (m, 1H), 3.0-3.4 (m, 3H), 3.56 (m, 2H) and 7.13 (m, 4H); Anal. Calcd. for $C_{15}H_{14}O$: C, 85.68; H, 6.71. Found: C, 85.80; H, 6.70.

The alcohol (21)

The ketone (20) was reduced with sodium borohydride in methanol to the endo-alcohol (21), mp. 123-124°; ν_{max}^{KBr} 3200, 2920, 1425, 1102, 1097, 1038, 1019 and 750 cm^{-1};

δ^{CDCl_3} -0.8 (td., J=4.0, 4.0 and 5.5 Hz, 1H), 0.06 (td., J=8.0, 8.0 and 5.5 Hz, 1H), 1.56 (m, 2H), 2.0-2.7 (m, 4H), 3.24 (t, J=4.0 Hz, 1H), 3.51 (t, J=3.1 Hz, 1H), 4.48 (m, 1H) and 7.06 (m, 4H); Anal. Calcd. for $C_{15}H_{16}O$: C, 84.87; H, 7.60. Found: C, 84.49; H, 7.65.

Photolysis of the endo-alcohol (11)

Irradiation of the alcohol (11) in pet. ether containing 40% acetone with 450-w high-pressure Hg lamp for 6 hr, followed by chromatography over silica gel with benzene, afforded the rearranged alcohol (22) in 35% yield, mp. 100-102°; ν_{max}^{KBr} 3250, 3000, 2920, 1432, 1088, 760 and 742 cm^{-1}; δ^{CDCl_3} 1.4-2.1 (m, 2H), 2.24 (t, J=6.8 Hz, 1H), 2.40-2.83 (m, 3H), 3.03 (td., J= 6.8, 6.8 and 5.0 Hz, 1H), 3.73 (d, J=5.0 Hz, 1H), 4.21 (m, 1H) and 7.0 (m, 4H); Anal. Calcd. for $C_{14}H_{14}O$: C, 84.81; H, 7.12. Found: C, 84.11; H, 7.37.

The alcohol (24)

The alcohol (24) was prepared by oxymercuration of the hydrocarbon (9) with mercuric acetate, followed by demercuration with sodium borohydride in 72% yield, mp. 86-87.5°; δ^{CDCl_3} 1.61 (dd, J=8.0 and 6.0), 1.4-2.0 (m, 1H), 2.0-2.4 (m, 3H), 2.5-3.0 (m, 2H), 3.38 (d, J=5.1 Hz, 1H), 3.86 (dd, J=4.3 and 1.8 Hz, 1H) and 7.0 (m, 4H); Anal. Calcd. for $C_{14}H_{14}O$: C, 84.81; H, 7.12. Found: C, 84.97; H, 7.15.

The ketone (25)

The alcohol (24) was oxidized with chromic anhydride in pyridine to the ketone (25), mp. 92.5-94°; ν_{max}^{KBr} 3050, 3020, 2960, 2910, 1775, 1473, 1455, 1100, 800, 770, 750 and 745 cm^{-1}; δ^{CDCl_3} 2.00 (dd., J=6.0 and 8.0 Hz, 1H), 2.2-2.75 (m, 2H), 2.75-3.45 (m, 4H), 3.72 (d, J=5.0 Hz, 1H) and 7.02 (m, 4H); Anal. Calcd. for $C_{14}H_{12}O$: C, 85.68; H, 6.16. Found: C, 85.40, H, 6.18.

The alcohol (26)

The ketone (25) was reduced with sodium borohydride in methanol to the alcohol (26), mp. 97-98°; δ^{CDCl_3} 1.8-2.75 (m, 6H), 2.93 (td., J=5.5, 6.2 and 6.2 Hz, 1H), 3.45 (d, J=4.8 Hz, 1H), 4.16 (m, 1H) and 7.03 (m, 4H); Anal. Calcd. for $C_{14}H_{14}O$: C, 84.98; H, 7.27. Found: C, 84.81; H, 7.12.

Diimide reduction of the alcohol (10)

Treatment of 2 g of azodicarbonamide with 5 ml of 50% aq. KOH solution, which was filtered before use, gave yellow solid. After desiccation on filter paper, the solid was added to a solution of the alcohol (10) (200 mg) in 15 ml of methanol. Acetic acid in methanol (1:5 v/v) was added to the yellow suspension, till the yellow color disappeared. Excess acetic acid was neutralized with saturated aq. $NaHCO_3$ solution and the mixture was extracted several times with ether.
The combined organic phase was concentrated to give a colorless powder, which was recrystallized from ether (98%), mp. 113-114° ; δ^{CDCl_3} 1.2-1.5 (m, 2H), 2.0-2.6 (m, 6H), 2.8-3.2 (m, 2H), 4.58 (m, 1H) and 7.15 (m, 4H); Anal. Calcd. for $C_{14}H_{16}O$: C, 83.96; H, 8.05. Found: C, 83.98; H, 7.99.

The ketone (18)

The alcohol (17) was oxidized with chromic anhydride in pyridine to the ketone (18), mp.135°; ν_{max}^{KBr} 1770 and 758 cm^{-1}; Anal. Calcd. for $C_{14}H_{14}O$: C, 84.81; H, 7.12. Found: C, 84.75; H, 7.10.

Photolysis of the ketone (18) in tert.-butanol

The ketone (18) in tert.-butanol was irradiated with 450-w high pressure Hg lamp. Among the many products only the product (32) could be isolated by chromatography over silica gel in 32% yield, mp. 83-85°; δ^{CDCl_3} 1.20 (s, 9H), 2.80 (m, 1H), 3.06 (m, 1H), 4.10 (dd., J=10.0 and 4.0 Hz, 1H), 5.57(m, 1H) and 7.06 (m, 4H); Anal. Calcd. for $C_{18}H_{24}O_2$: C, 79.37; H, 8.88. Found: C, 79.06; H, 8.73.

Photolysis of the hydrocarbon (13) and the structure assignment of the product (28) and (29)

The hydrocarbon (13) in acetone was irradiated through Pyrex filter with 450-w high-pressure Hg lamp for 3 hours. After removal of acetone chromatography over silica gel gave the mixture of the hydrocarbon (29) and (28) (6:4, based on nmr measurement) in 80% yield. Nmr spectrum of the mixture shows the signals at 3.53 (d, J=4.8 Hz, 0.4H), 3.70 (d, J=4.8 Hz, 0.6H), 4.67 (m, 0.4H) and 4.95 (m, 0.6H). Nmr spectrum of the compound (28), prepared from the ketone (25) by treatment with methylenetriphenylphosphorane in abs. tetrahydrofuran, displays the signals at 3.53 (d, J=4.8 Hz, 1H) and 4.67 (m, 1H), which are ascribed to the benzylic (H_3) and exo-methylene protons, respectively, indicating the structure (28) for the minor product.

The compound (15)

The hydrocarbon (1) and pheny trichloromethylmercury (1.2 equ.) were warmed in refluxing benzene for 4 hours under the nitrogen atmosphere. After cooling, the solution was filtered. Concentration of the filtrate, followed by chromatography over silica gel, afforded the product (15) in 82% yield, mp. 144-145.5°; δ^{CDCl_3} 2.6-3.2 (m, 2H), 3.85 (m, 1H), 4.13 (m, 1H), 4.43 (m, 1H), 5.76 (broad s. 1H), 6.37 (m, 2H) and 7.10 (m, 4H); Anal. Calcd. for $C_{15}H_{12}Cl_2$: C, 68.45; H, 4.59. Found: C, 68.41; H, 4.73.

The acyloin (37)

In a three necked flask, trimethylchlorosilane (3.926 g) and sodium (0.836 g) were placed under nitrogen. Then dimethyl ester (35) (2.054 g) in 12 ml of abs. xylene was added dropwise with stirring. After refluxing for 6 hours at 110-120°, the resulting precipitate was filtered off and washed several times with abs. xylene. The combined filtrate was concentrated in vacuo to afford a brown oil. Treatment of the oil with methanol for 1 hour yielded acyloin (37) as colorless precipitate (0.508 g). After filtration, the filtrate was concentrated and chromatographed over silica gel to give an additional amount of acyloin (37) (0.487 g), mp. 148-149°, 62%; ν_{max}^{KBr} 3530 and 1775 cm^{-1} ; δ^{CDCl_3} 1.50 (s, 1H, -O$\underline{H}$), 3.00 (m, 1H), 3.43 (m, 1H), 4.26 (m, 3H), 6.70 (m, 2H) and 7.17 (m, 4H); Anal. Calcd. for $C_{14}H_{12}O_2$: C, 79,22; H, 5.70. Found: C, 78.95; H, 5.67.

The ketone (38)

To a solution of 322 mg of acyloin (37) in 7.7 ml of toluene, 16.8 ml of 4N-hydrochloric acid and 3.61 g of amalgamated zinc were added. After refluxing for 1.5 hours with stirring, amalgamated zinc was filtered and washed with benzene. The combined filtrate was neutralized with aq. sodium bicarbonate and extracted with benzene. The organic layer was dried over $MgSO_4$. Removal of the solvent, followed by chromatography over silica gel, gave the ketone (38) in 72.7% yield, mp. 69-70°C; ν_{max}^{KBr} 1770 cm^{-1}; δ^{CDCl_3} 1.55-1.95 (m, 2H), 2.30-2.80 (m, 2H), 3.43 (m, 1H), 4.05 (m, 1H), 4.15 (m, 1H), 6.63 (m, 2H) and 7.09 (m, 4H); Anal. Calcd. for $C_{14}H_{12}O$: C, 85.68; H, 6.16. Found: C, 85.92; H, 6.11.

The tosylhydrazone (39)

The ketone (38) (210 mg) and p-toluenesulfonylhydrazide (289 mg) were dissolved in 20 ml of methanol. After addition of one drop of conc. hydrochloric acid, the mixture was stirred for 6.5 hours at room temperature. The mixture was extracted with benzene and dried over $MgSO_4$. Evaporation of benzene, followed by treatment of small amount of methanol afforded (39) as colorless crystals, mp. 189-190°, 80.6%; ν_{max}^{KBr} 3190, 1600 and 1165 cm^{-1}; Anal. Calcd. for $C_{21}H_{20}O_2N_2S$: C, 69.14; H, 5.53; N, 7.68. Found: C, 68.38; H, 5.69; N, 7.44.

Syn-7,8-benzotricyclo[4.2.2.$0^{2,5}$]deca-3,7,9-triene (2)

Three mole equivalents of n-butyllithium was added to a solution of tosylhydrazone (39) (262.4 mg) in 25 ml of diglyme. The mixture was stirred at 60° for 3 hours. After treatment with aq. benzene, lithium sulfinate was filtered off. Removal of the organic solvent gave a viscous residue, which was extracted with benzene, washed several times with water and dried over $MgSO_4$. After evaporation of benzene, chromatography over silica gel afforded crystals, mp. 43°, 40%; ν_{max}^{KBr} 3025 and 740 cm^{-1}; δ^{CDCl_3} 2.70 (m, 2H), 3.65-3.90 (m, 2H), 5.82 (s, 2H), 6.52 (m., 2H) and 7.00 (m, 4H); Mass. m/e: 180(M^+), 128, 52; Anal. Calcd. for $C_{14}H_{12}$: C, 93.29; H, 6.71.

Found: C, 93.26; H, 6.75.

The acyloin (42)

3,4-bistrimethylsiloxy-7,8:9,10-dibenzotricyclo[4.2.2.$0^{2,5}$]deca-3,7,9-triene (41) was prepared according to the same procedure as in the case of the acyloin (37). After filtration of the resulting precipitate, most of the solvent was removed in vacuo to yield a brown residue, which was treated with ethanol in an icebox overnight. After filtration of the acyloin (42), the filtrate was concentrated and chromatographed over silica gel to give the additional amount of the acyloin, mp. 195-197°, 13%; ν_{max}^{KBr} 3550, 3460, 3350 and 1775 cm^{-1}; $\delta^{pyridine\text{-}d_5}$ 3.02 (dt., J=9.0 and 3.9 Hz, 1H), 3.58 (m, 1H), 4.60 (d, J=5.0 Hz, 1H), 4.78 (d, J=3.9 Hz, 1H), 4.90 (d., J=3.9 Hz, 1H), 5.95 (s, 1H, -O<u>H</u>) and 6.90-7.65 (m, 8H); Anal. Calcd. for $C_{18}H_{14}O_2$: C, 82.42; H, 5.38. Found: C, 82.21; H, 5.44.

The ketone (43)

The acyloin (42) (1.6 g) was reduced in refluxing toluene with amalgamated zinc (15 g) and 4N-hydrochloric acid (70 cc) to the cyclobutanone in 83% yield, mp. 167-168°; ν_{max}^{KBr} 1770 cm^{-1}; δ^{CDCl_3} 1.60-2.20 (m, 1H), 2.40-3.00 (m, 2H), 3.55 (m, 1H), 4.43 (d, J=3.9 Hz, 1H), 4.50 (d, J=4.0 Hz, 1H) and 7.15 (m, 8H); Anal. Calcd. for $C_{18}H_{14}O$: C, 87.77; H, 5.73. Found: C, 87.83; H, 5.78.

The tosylhydrazone (44)

The compound (44) was prepared in the usual way in 78% yield, mp. 228-229°; ν_{max}^{KBr} 3200, 1600 and 1160 cm^{-1}; Anal. Calcd. for $C_{25}H_{22}O_2N_2S$: C, 72.19; H, 5.35. Found: C, 72.16; H, 5.46.

The hydrocarbon (45)

The tosylhydrazone (44) (1.44 g) in 120 ml of diglyme was treated with excess n-butyllithium at 120° to give the hydrocarbon (45) in 43% yield, mp. 138-139°; δ^{CDCl_3} 2.95(m, 2H), 4.23 (m, 2H), 5.87 (s, 2H) and 6.9-7.4 (m, 8H); Mass. m/e: 230 (M^+) 178 and 52; Anal. Calcd. for $C_{18}H_{14}$: C, 93.87; H, 6.13. Found C, 93.13; H, 6.22.

The hydrocarbon (47)

Treatment of tosylhydrazone (46) with n-butyllithium in the similar manner gave the hydrocarbon (1) and (47) in 5% and 43% yield, respectively. Nmr spectrum of the product (47) displays signals at 1.00-1.40 (m, 2H), 1.80-2.20 (m, 2H), 2.60 (broad s, 2H), 3.08 (broad s, 2H), 6.43 (s, 2H) and 7.06 (m, 4H), indicating the structure (47) for the major product.

Photolysis of the compound (2)

A solution of the hydrocarbon (2) (42.3 mg) in 42 ml of abs. acetone was bubbled with nitrogen for 1 hour. The mixture was irradiated through Pyrex filter with 450-w high-pressure mercury lamp for 30 minutes. Removal of the solvent, followed by chromatography over silica gel, gave the compound (56) as a colorless oil in 23% yield.

Photolysis of the compound (45)

The compound (45) was photolyzed in acetone for 1 hour with 450-w high-pressure Hg lamp to afford the hydrocarbon (61) in 48% yield, mp. 164°. Nmr spectrum of the product (61) shows the resembalance to that of the diimide-reduction product of the compound (45), indicating the structure (61) for the photolysis-product. δ^{CDCl_3} 0.90 (m, 2H), 1.80 (m, 2H), 2.57 (m, 2H), 4.13 (broad s, 2H) and 7.20 (m, 8H).

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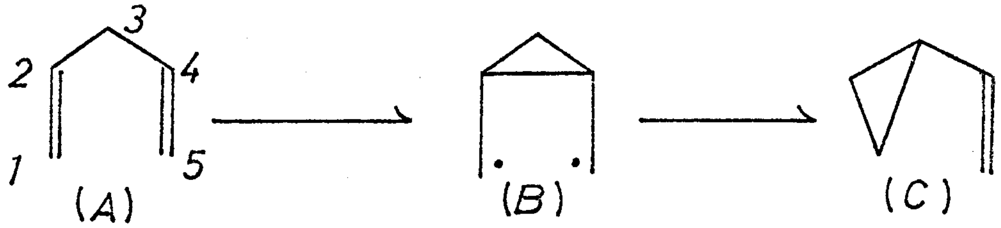
CHAPTER III

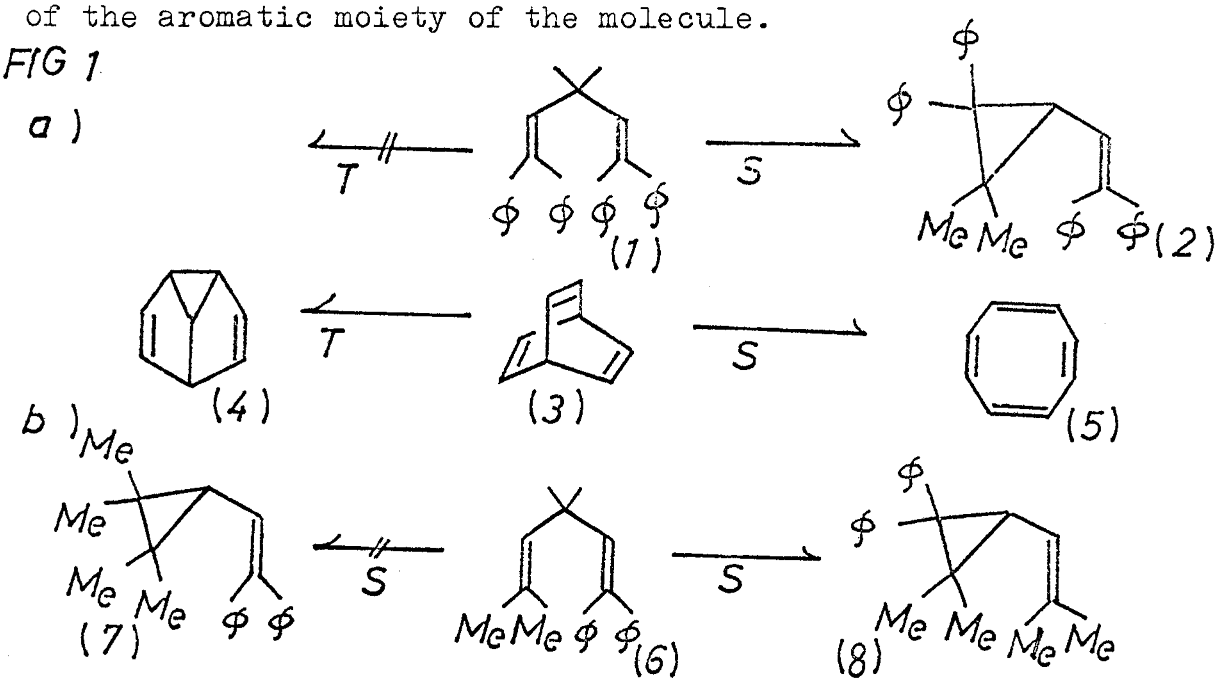
SECTION I Introduction

The recognition of di-π-methane to vinycyclopropane transformation as a general photochemical rearrangement by H.E. Zimmerman1) has been followed by intense interest and the photoreactions reported, which can be classified in this category, are great many, establishing its generality and synthetic usefulness.

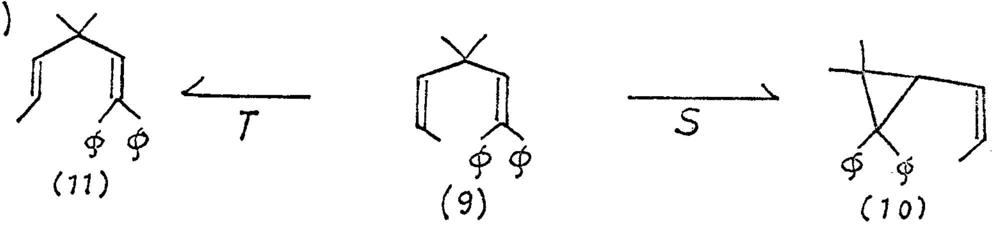


The mechanistic studies have also been investigated extensively with H.E. Zimmerman as a leader in the discussion and several useful findings are obtained (FIG 1) as follows: a) the acyclic di-π-methanes rearrange by way of the singlet excited states while the bicyclics utilize the triplet:2) b) the direction of the di-π-methane rearrangement is controlled by demand of the excited state for retention of maximum electron delocalization during the rearrangement;3) c) the stereochemistry of the double bond in the starting acyclic compound is retained during the singlet state rearrangement while the sensitized re~~du~~action results in geometrical isomerization of the starting material;4) d) the lack of triplet reactivity in case of monocyclic compounds bearing an exocyclic methylene group is ascribed to a free rotar effect wherein twisting of this group leads to rapid radiationless decay of the triplet;5) e) central methyl substitution at C-3 position in an acyclic compound (27) is required for the facile di-π-methane rearrangment and in this case vinyl-vinyl bridging in the excited singlet is rate-limiting;6) and f) energetic argument used in the benzobarrelene study to rationalize the selectivity of bridging holds in the reaction of naphthobarrelenes.7) Thus an aromatic-vinyl bridging process is enforced by lowering the triplet excitation energy of the aromatic moiety of the molecule.

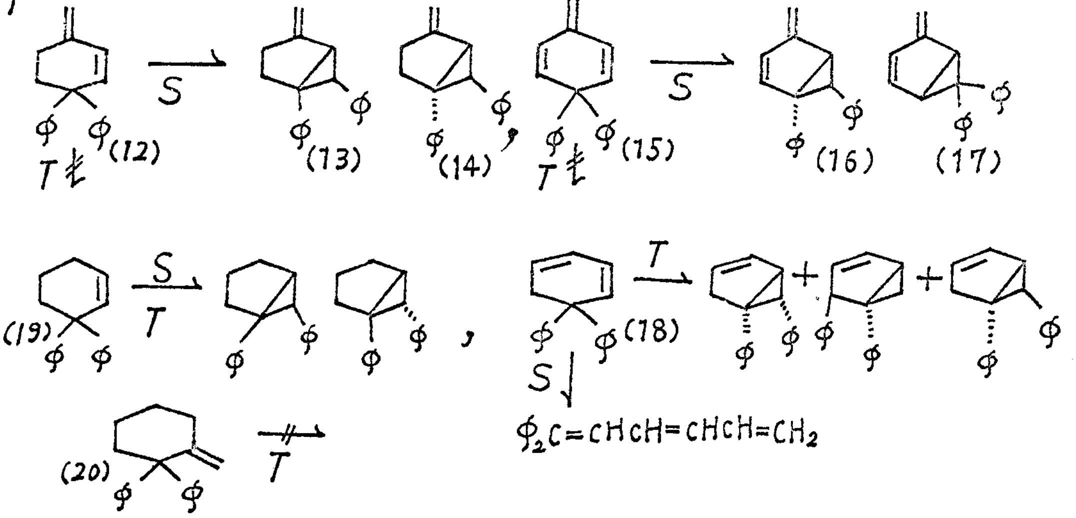
FIG 1



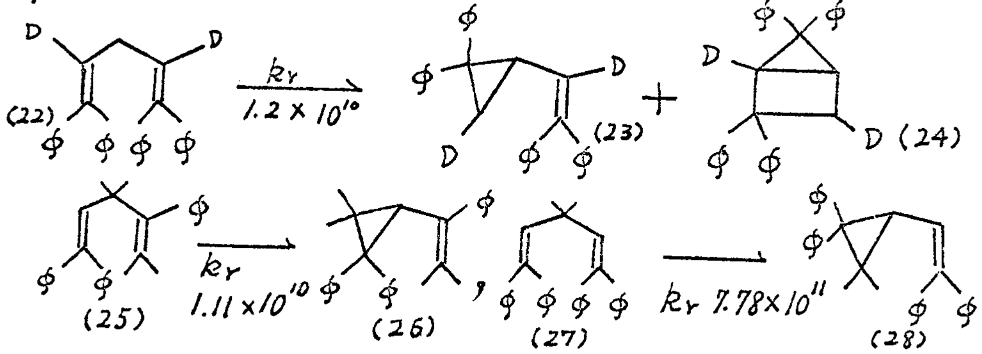
c)



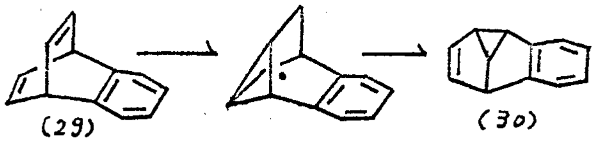
d)



e)

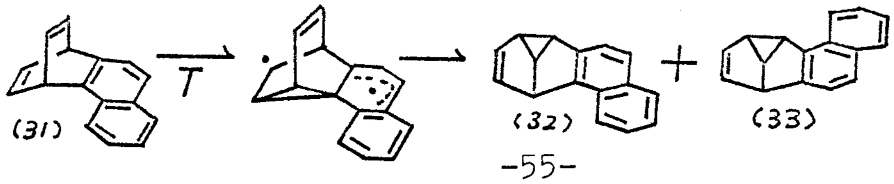


f)



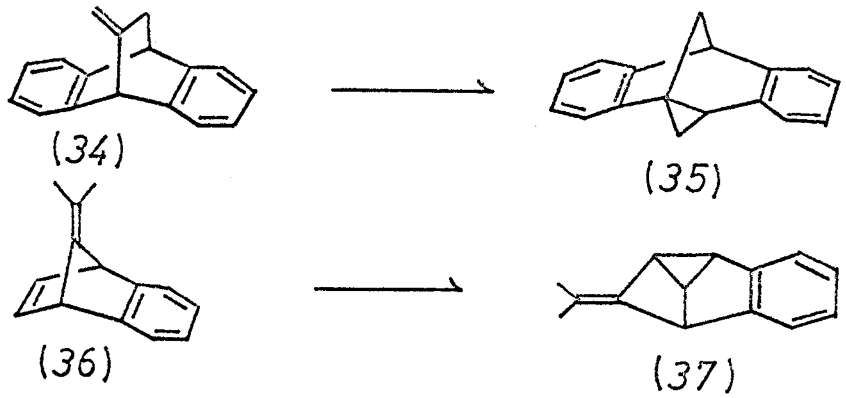
E_T (styrene) 61.8 Kcal

E_T (cyclohexadiene) 53.5 Kcal



Free rotar hypothesis, a useful postulate in designing the synthesis, has the definite applicability both in the acyclic and the monocyclic compounds. However, the photochemistry of bicyclic compound containing an exocyclic methylene group, to the best of my knowledge, seems to scarcely be known. Recently, it was group reported that compound (34) rearranges to photolabile (35) under the sensitized irradiation (FIG 2).8) In contrast to the photoreaction of (36), this reaction seems interesting because of the following points of view; a) the lowest E_T among three chromophores in this molecule corresponds to that of the dialkyl ethylene, and b) vinyl-benzo bridging is, even if at any stage of the reaction, necessary to produce (35).

FIG 2

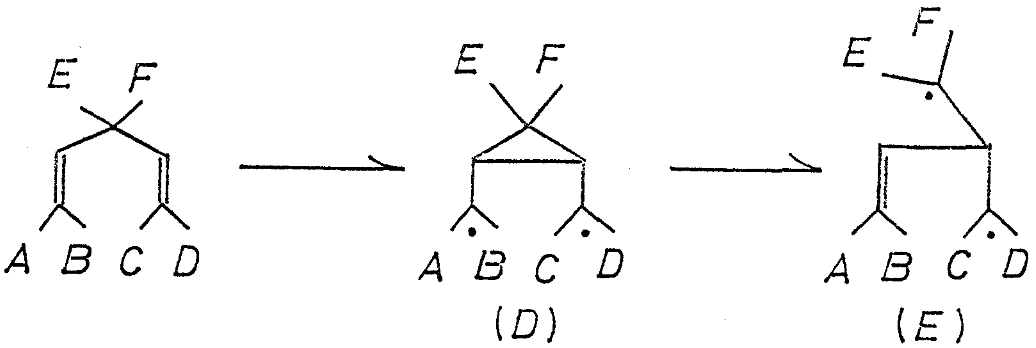


Generally, lower energy in triplet state, as compared to that in singlet state, causes the increase of the selectivity in photoreaction. Actually hydrocarbon (34) yielded a fairly amount of by-products, accompanied with polymeric materials under direct irradiation. Furthermore, di-π-methane rearrangement in general affords the product which shows similar but somewhat shorter wavelength absorption in UV spectrum than that of the starting material. The fact, experimentally, prefers to the sensitized condition for this rearrangement, when the product is photochemically and thermally sensitive. For these reasons photochemistry of bicyclic compounds bearing exocyclic methylene group drew my attention.

As to the generalization (b) and (e), several points are worth noting. Thus, in the step from biradical-like intermediate (D) to (E), which correspond to the point on a potential surface of an excited state reaction, a driving force for this bond breaking step is necessary (FIG 3). Consequently, radical character on C_1 and C_5, and the stabilization effect of the substituents at C-3 on the developing radical at this site play an important role in this step.

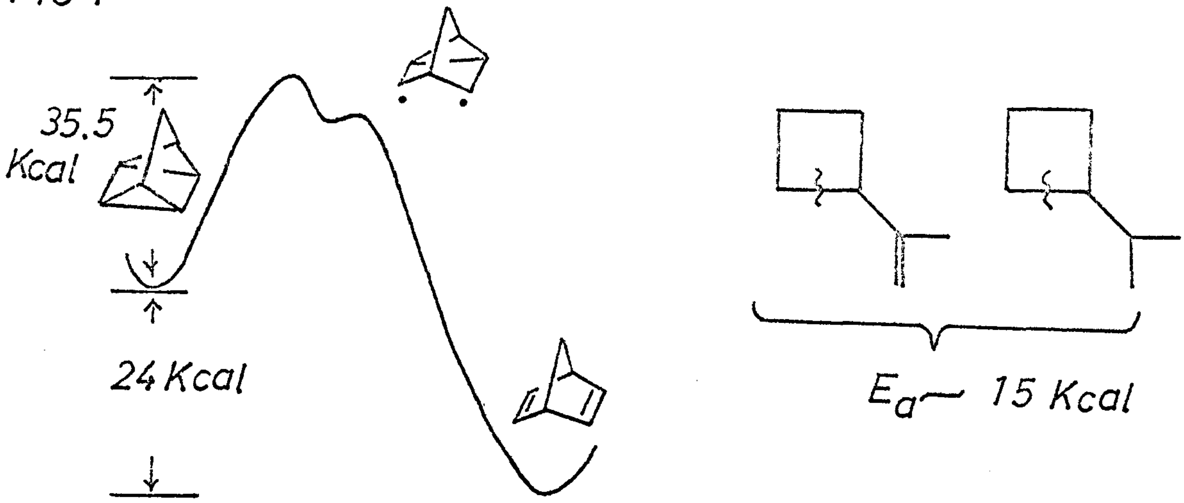
In bicyclic compounds fused with naphthalene ring, the total energy available for the rearrangement is about 50-60 Kcal (E_T). If the energetic arguement discussed by J. R. Edman 9) is valid, the value (– 60 Kcal) seems close to the energy boundary for this reaction to occur and the allylic resonance energy (– 15 Kcal) 10) due to the double bond attached on C_3 effectively contributes to the course of this reaction. (FIG 4).

FIG 3



In this chapter, photolysis of some bicyclic compounds containing exocyclic methylene and ketone groups, and also naphtho-annelated analogs are described.

FIG 4



SECTION 3 Synthesis and Photochemistry

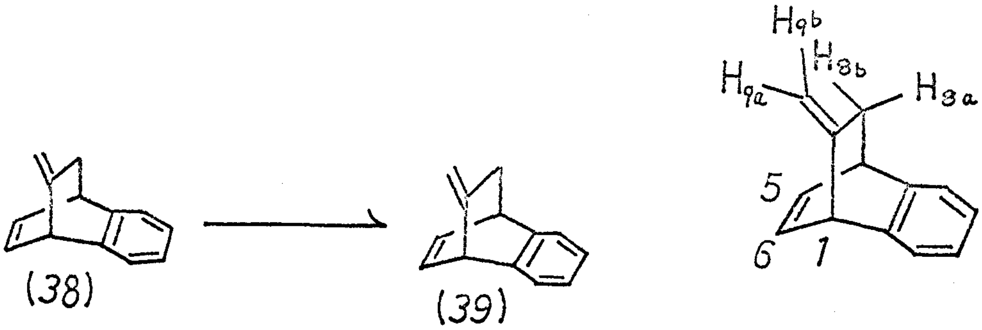
Hydrocarbon (39), (42), (45), (48) and (51) are studied to examine the validity of the free rotar hypothesis in bicyclic systems.

FIG 5


(39) (42) (45) (48) (51)

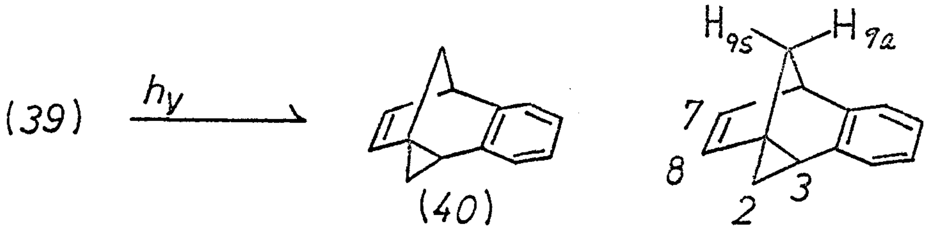
Treatment of readily available enone (38)[11] with methylenetriphenylphosphorane in ether afforded 7-methylene-5,6-benzobicyclo[2.2.2]octa-2,5-diene (39) in 38.7% yield, whose nmr spectrum reveals one proton triple doublets (J=15.2, 2 and 0.8 Hz) at 2.11, one proton triple doublets (J=15.2, 2 and 0.8 Hz, H_{8b}) at 2.32, one proton multiplet at 3.95 (H_4) one proton double doublets (J=4.0 and 3.6 Hz, H_1) at 4.28, one proton double doublets (J=3.4 and 0.8 Hz, H_{9b}) at 4.63, one proton broad singlet (H_{9a}) at 4.97, one proton triple doublets (J=6.4, 4.0 and 3.6 Hz, H_3) at 6.53, one proton triple doublets (J=6.4, 4.0 and 3.6 Hz, H_2) at 6.65, and four aromatic protons multiplet at 7.10. Ir spectrum of (39) shows absorption due to the exocyclic methylene group at 875 cm^{-1}.

FIG 6



Hydrocarbon (39) was irradiated in acetone through Pyrex filter and the progress of the reaction was checked on tlc. After 20 minutes, a new spot of less polar product appeared and the starting material gradually disappeared. After irradiation for 6 hr, the solvent was evaporated in vacuo and the residue was chromatographed over silica gel with pet. ether to give an unstable colorless oil in 2.3% yield.

FIG 7



This oily product (40) displays nmr signals (δ, $CDCl_3$) at 0.71 (dd., J=8.0 and 6.8 Hz, H_2), 0.83 (d, J=10 Hz, H_{9s}), 1.70

(dd., J=6.8 and 6.0 Hz, H_2), 2.03 (dd., J=8.0 and 6.0 Hz, H_3), 2.74 (dd., J=10 and 4.0 Hz, H_{9a}), 3.22 (dd., J=4.0 and 3.6 Hz, H_6), 5.86 (dd., J=5.4 and 3.6 Hz, H_7), 6.33 (d, J=5.4 Hz, H_8) and 7.18 (m. aromatic). This spectrum shows the resembalance to that of (35) except for the appearance of the new signals at 5.86 and 6.33 and the coupling pattern of the signal at 3.22, indicating the sturcture (40) for this compound. Actually, double resonance study supports the aforementioned signal assignment, namely, saturation of the signals due to H_3 and H_6 respectively, exhibits the change of signals summerized in Table 1:

Table 1

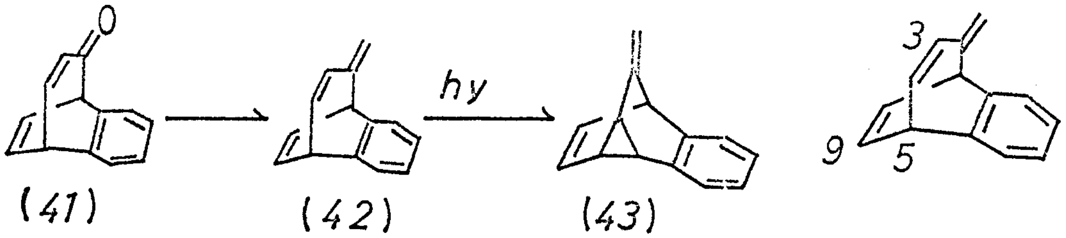
proton (irradiated),	normal	after irradiation
H_3 (δ 2.03)	H_2 (δ 0.71) dd, J=6.8 and 8.0 Hz	d, J=6.8 Hz
H_6 (δ 3.19)	H_{9a} (δ 2.71) dd, J=4.0 and 10.0 Hz	d, J=10.0 Hz
	H_7 (δ 5.86) dd, J=5.4 and 3.6 Hz	d, J=5.4 Hz

The shift of H_{9s} signal to higher field, as compared to H_{9a} proton signal, is ascribed to the anisotropy effect of a cyclopropyl ring. The reaction is regarded to involve an initial triplet state. Although direct irradiation of (39) afforded only polymeric products, it is not clear whether hydrocarbon (40) was formed or not, because compound (40) was considerably unstable under the condition studied. The low yield of (40) under acetone sensitized condition is, also, attributable to the instability of (40), not to the slow rate of the conversion from (39) to (40).

Photochemistry of (42) is attractive in view of the following points: a) this hydrocarbon has butadienoid moiety and the energy is considered to be concentrated on this moiety; b) monocyclic compounds, bearing the butadienoid moiety have extensively been studied.[12)] [13)]

Wittig reaction of enone (41) in THF gave hydrocarbon (42), mp 43° C, in 32.8% yield; nmr ($CDCl_3$) 3.8 (ddd, J=8.0, 6.0 and 1.5 Hz, H_5), 4.14 (dt, J=6.0, 1.5 and 1.5 Hz, H_1), 4.65 (d, J=1.5 Hz, H_{10}), 5.11 (t, J=1.5 and 1.5 Hz, H_{10}), 5.50 (d, J= 10 Hz, H_3) 6.10 (dd, J=8.0 and 1.5 Hz, H_9) and 7.10 (aromatic); ir (KBr) 880 cm^{-1}:

FIG 8



Further support for the structure (42) was obtained by means of double resonance study (See Table 2).

Table 2

proton (irradiated)	normal	after irradiation
H_1 (δ4.14)	H_8 (δ 6.41) ddd, J=8.0, 6.0 and 1.5Hz	dd, J=8.0 and 1.5Hz
	H_9 (δ 6.69) ddd, J=8.0, 6.0 and 1.5Hz	dd, J=8.0 and 6.0Hz
H_3 (δ 5.50)	H_4 (δ 6.10) dd, J=10.0 and 8.0Hz	d, J=8.0Hz
H_5 (δ 3.83)	H_4 (δ 6.10) dd, J=10.0 and 8.0Hz	d, J=10.0Hz
	H_9 (δ 6.69) ddd, J=8.0, 6.0 and 1.5Hz	dd, J=8.0 and 1.5Hz

Photolysis of (42) in acetone using Hanovia 450-w Hg lamp through Pyrex filter for 6 hr, followed by chromatography on silica gel, afforded coloreless oil (43) in 65% yield, accompanied with a concomitant formation of a trace of unidentified products. Spectroscopic data indicates that the oil is 9-methylene-3,4-benzotricyclo[3.3.1.0^{2,8}]nona-3,6-diene. Thus the nmr spectrum of (43) showed three cyclopropyl proton signals at δ 2.25 (ddt., J=7.6, 7.6, 6.0 and 1.8 Hz, H_8), 2.71 (dt., J=7.6, 7.6 and 2.0 Hz, H_1) and 2.82 (d, J=7.6 Hz, H_2), one benzylic proton signal at δ 3.68 (dd., J=6.8 and 2.0 Hz, H_5), two exocyclic methylene proton signals at δ 4.84 (d, J= 2.0 Hz) and 4.97 (d, J=2.0 Hz), one vinyl proton signal at δ 5.61 (dd., J=9.0 and 6.0 Hz, H_7), one vinyl proton signal at 5.91 (ddd., J=9.0, 6.8 and 1.8 Hz, H_6), and ir spectrum reveals the absorption peak due to exocyclic methylene group at 875 cm^{-1}. The structural assignment was also confirmed by means of double resonance techniques (See Table 3):

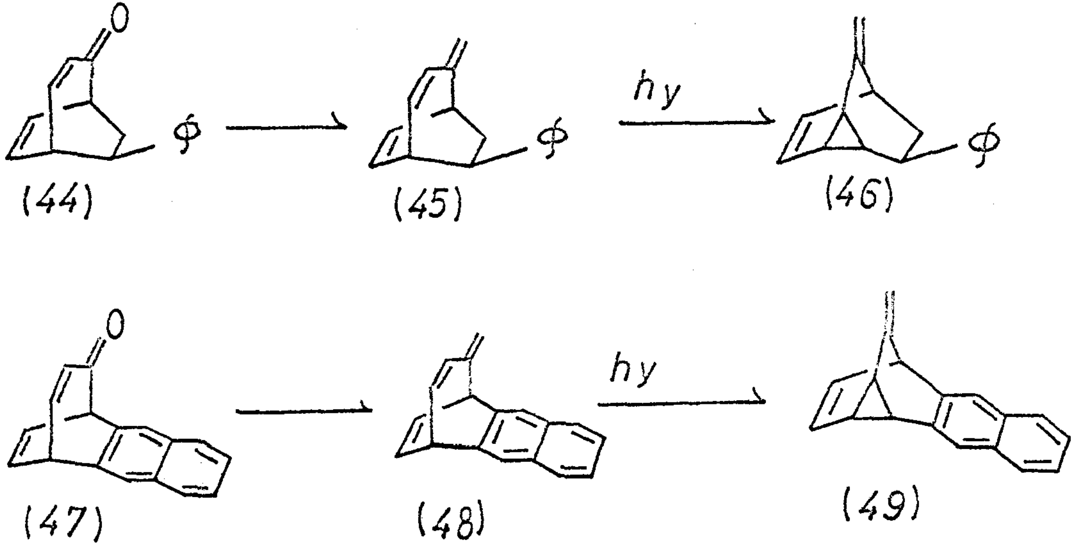
In order to examine the direct photolysis, hydrocarbon (42) was irradiated in THF through quartz filter for 9.5 hr. Formation of several products was indicated by means of tlc analysis and nmr measurment showed hydrocarbon (43) was a major product. In the presence of 1,3-cyclohexadiene (3×10^{-1} M), the reaction also took place, suggesting that, at least, a part of (43) arized from singlet state of (42) under this condition.

Table 3

proton (irradiated),	normal,	after irradiation,
H_5 (δ 3.68)	H_6 (δ5.91)	
	ddd, J=9.0, 6.8 and 1.8Hz	dd, J=9.0 and 1.8Hz
	H_1 (δ 2.71)	
	dt, J=7.6, 7.6 and 2.0Hz	t, J=7.6 and 7.6Hz
H_8 (δ 2.25)	H_6(δ 5.91)	
	ddd, J=9.0, 6.8 and 1.8Hz	dd, J=9.0 and 6.8H
	H_7 (δ 5.61)	
	dd, J=9.0 and 6.0Hz	d, J=9.0Hz
H_6 (δ 5.91) H_7 (δ 5.61)	H_5 (δ 3.68)	
	dd, J=6.8 and 2.0Hz	d, J=2.0Hz
	H_8 (δ 2.25)	
	ddt, J=7.6, 7.6, 6.0 and 1.8Hz	t, J=7.6Hz

Hydrocarbon (45) (mp. 65.5-67°) and (48) (mp. 102-103°), which are regarded to be constructed by replacement of the annelated benzene ring in (42) with phenyl ethano bridge or naphthalene ring, were also prepared by Wittig reaction of corresponding ketone (44) and (47) in 62 and 68% yield, respectively.

FIG 9



Spectroscopic data unequivocally indicate the structure (45) and (48) for the products. Upon both sensitized and direct photolysis hydrocarbon (45) and (48) converted to (46) and (49) respectively. In case of hydrocarbon (45), as well as hydrocarbon (42), the rearrangement took place less rapidly under the direct photolysis, accompanied with formation of secondary products and a fairly amount of polymeric materials.

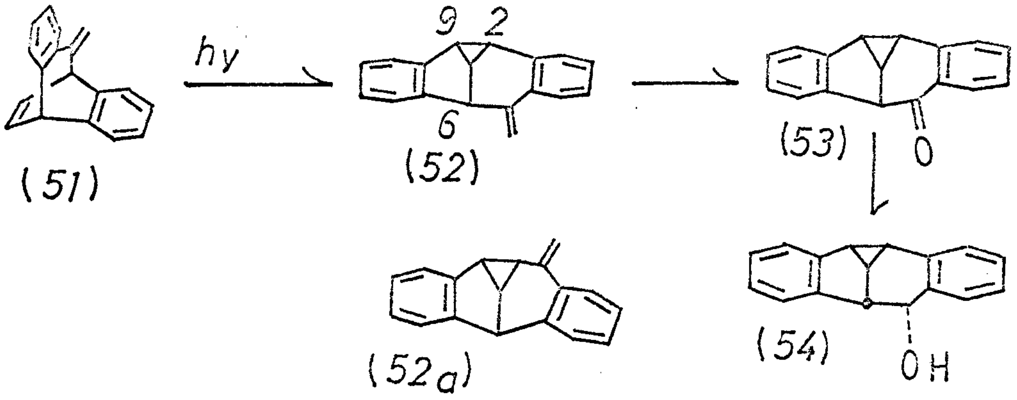
Apparently, this rearrangement prefers to the triplet route over the singlet one. Facile photoconversion, (45) to (46), indicates the driving force for bond breaking due to the radical stabilization effect of π bonds attached at C_3 is not necessarily required. Rearrangement of (48) is so rapid that there observed no preference between the direct and sensitized photolysis on the view point of the synthesis of (49).

In order to obtain further example of triplet state rearrangement of a compound bearing exocyclic methylene group, photolysis of hydrocarbon (51) was studied. Treatment of ketonic adduct (50), mp 104-105°, prepared from 2,3-benzotropone and benzyne, with methylene triphenylphosphorane, followed by chromatography over silica gel, afforded coloreless oil (51) in 85% yield; nmr ($CDCl_3$ δ): 4.29 (2H dd., J=6.5 and 2 Hz bridge-head), 5.13, 5.44 (2H, methylene, s, each), 6.46, 6.77 (2H, olefin, td., each, J=6.5 and 2 Hz) and 7.0-7.8 (8H, m, aromatic), ir (film): 882 cm^{-1}. Direct irradiation of a 0.3% solution of the hydrocarbon (51) in THF resulted in rapid consumption of (51) (after 4 hr) with formation of an isomeric product (52) (mp 124°), in almost quantitative yield.

The ir spectrum of (52) exhibits strong absorption at 885 cm^{-1} attributable to an exocyclic methylene group. Compound (52) displays nmr signals ($CDCl_3$, 100 MHz, δ) at 2.33 (t, J=6.8 and

6.8 Hz, H_9), 2.57 (td., J=6.8, 6.8 and 5.9 Hz, H_1), 2.75 (dd., J=6.8 and 5.9 Hz, H_2), 4.26 (d, J=6.8 Hz, H_6), 5.16 (d, J=0.2 H, H_{10s}), 5.25 (d, J=0.2 Hz, H_{10a}) and 6.9-7.4 (8H, m, aromatic). NOE measurement gave the information about the site of methylene group. Thus a small but distince increase (4.4%) and decrease (6.4%) in the integrated intensities of the H-10s and H-10a signals, respectively, caused by saturation of the H-6 signal indicate that the methylene group is located on C-5. The alternative possibility (52a) can be ruled out by these observations. A final structure proof was obtained by chemical degradation. Treatment of (52) with osmium tetroxide followed by potassium periodate gave a 60% yield of the ketone (53), mp 181-182°C, ν 1680 cm^{-1} (C=O), δ (in $CDCl_3$), 2.56 (1H, t, 7.9 Hz), 2.90 (1H, td., 7.9, 7.0 Hz), 3.17 (1H, t, 7.9 Hz), 4.25 (1H, d, 7.0 Hz), 6.9-7.7 (8H, m.). Reduction of (53) with lithium aluminum hydride in tetrahydrofuran readily gave rise to the alcohol (54), mp 208-209°C (from dichloromethane). Its nmr spectrum showed a doublet of doublets at δ 4.00 (J=6.3, 4.2 Hz) due to a bridgehead hydrogen (H-6) and a doublet at 5.50 (J=4.2 Hz) due to a hydrogen attached to carbon atom bearing hydroxyl group, along with the cyclopropyl hydrogens at 2.20-2.99 (m, 3H) and the aromatic hydrogens at 6.9-7.4 (m, 8H).

FIG 10



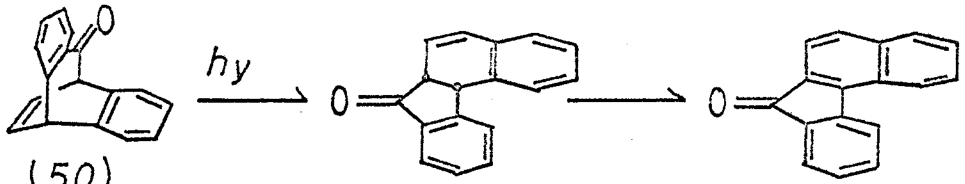
Irradiation at δ 4.00 (H-6) collapsed the doublet at δ 5.50 attributed to H-5 into a singlet and the doublet of doublets at δ 4.00 becomes a doublet by irradiating at δ 5.50.
Thus ascertaining the ralationship between the benzylic and the methylene groups as proposed in the structure shown (52).

Although the sensitized photolysis of (51) in acetone also afforded photoisomer (52) in 50% yield, sensitized photoisomerization took place much slower [18 hr] than the direct reaction. The remaining 50% was a mixture of starting material plus resinous product. In contrast with the photolysis of (42), the present compound (51) containing two annelated benzene rings isomerises preferentially by way of a singlet excited state.

In any cases bicyclic compounds studied here rearrange by way of triplet state. This fact is in striking contrast to the photoinertness of monocyclic compounds bearing an exocyclic methylene group.

Photochemistry of ketone (50) is also worth noting. Irradiation of 0.0002-0.02 M solution of (50) in acetone under nitrogen atmosphere with a 450-w mercury lamp with Pyrex filter for 45 min gave a single product (55), mp 104-105°C, in quantitative yield. Compound (55) had the same molecular formula as the starting material and its structure was proved to be 3,4-benzo-4a,9a-dihydrofluorenone through ir and nmr spectra. Ir (KBr): 1710 cm^{-1} (C=O). NMR ($CDCl_3$, 60 MHz, δ-values): 7.89 (m, 1H, aromatic H-8), 7.60-7.02 (m, 7H, aromatic), 6.41 (dd., 1H, $J_{2,1}$=10 Hz, $J_{2,9a}$=2 Hz, H-2), 5.86 (dd., 1H, $J_{1,2}$=10 Hz, $J_{1,9a}$=3 Hz, H-1), 4.60 (d, 1H, $J_{4a,9a}$ =8 Hz, H-4a), 3.84 (dt., 1H, $J_{9a,4a}$=8 Hz, $J_{9a,1}$=$J_{9a,2}$=3 Hz, H-9a). Chemical evidence for structure (55) was provided by its ready dehydrogenation in benzene with dichlorodicyano-p-benzoquinone to afford the known 3,4-benzofluorenone (56) as yellow prisms, mp 159-159.5°C [lit. mp 160°C].[14] Ir 1702 cm^{-1} (C=O).

FIG 11



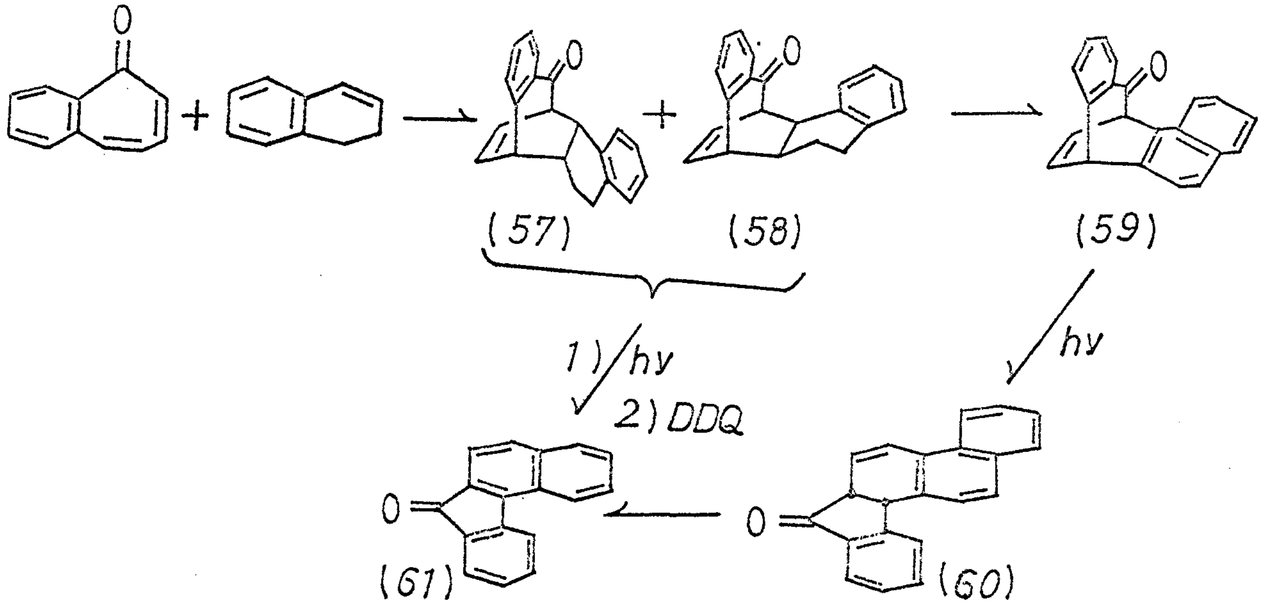
(50) (55) (56)

It is presumed that the acetone sensitized photoconversion (50) to (55) involves an initial triplet state since the irradiation even in dilute acetone solution (2 x 10^{-4} M) unequivocally demonstrates that photosensitization is observed. Interestingly, despite the fact that the triplet sensitized photolysis of δ,γ-unsaturated ketone generally proceeds by (1,2)-acyl migration, the present ketone (50) proceeds exclusively by (1,3)-shift of acyl group.[15)]

The direct irradiation of (50) in tetrahydrofuran with a 450-w mercury lamp through Pyrex was examined and was found to give rise to a same photoproduct (55). Although the effect of added piperylene as a possible triplet quencher on this photoreaction was examined, no effective quenching was observed over a concentration range of 0.5 to 5 M. The fact, together with the presence of an acetophenone moiety in this molecule indicates the rearrangement begins with the initial Norrish type-I reaction, followed by (1,3)migration.

In order to examine the synthetic utility of this facile photorearrangement, the following experiment was carried out. A mixture of 2,3-benzotropone and 1,2-dihydronaphthalene was heated in an autoclave at 70° for 2 days. After chromatography over silica gel, adducts ((57) oil, (58) mp 44-45°) were

FIG 12



obtained in 59% yield (4:6 on tlc). The stereochemistry of adducts is not clear, but nmr spectrum of the crystalline product shows one proton doublet of triplet at 4.32 (J=6.5, 6.5 and 2.0 Hz), suggesting the structure (58) for this compound.

Dehydrogenation of (57) and (58) with dichlorodicyano-p-benzoquinone in benzene yielded a single product (59) (mp 129-130°), whose nmr spectrum shows an absorption peak at 4.65 (dd., J=6.5 and 1.5 Hz), 5.60 (dd., J=6.5 and 1.2 Hz), 6.60 (td., J=7.8, 7.8 and 1.5 Hz), 7.06 (td., J=7.8, 7.8 and 1.2 Hz), 7.08-8.08 (m. 9H) and 8.24 (m. 1H).

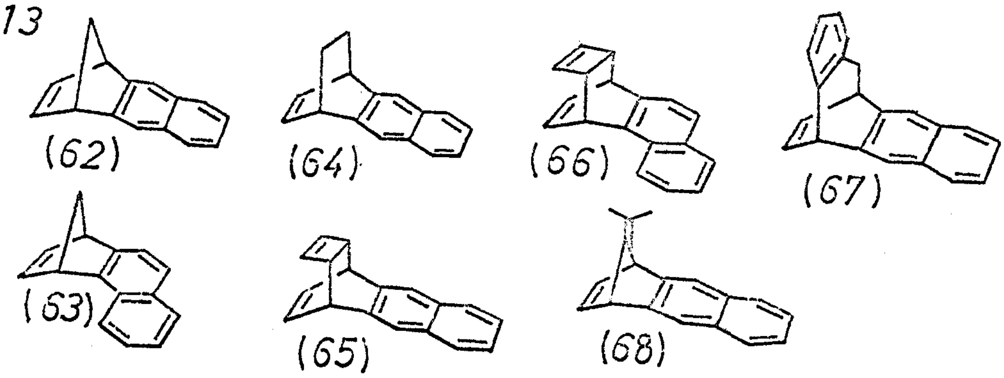
Photolysis of (59) in acetone, immediately, gave rise to rearrangement to afford (60) in almost quantitative yield; ir (KBr): 709 cm^{-1} ; nmr ($CDCl_3$ δ): 3.87 (dt., J=8.8, 3.0 and 3.0 Hz), 4.65 (d, J=8.8 Hz), 5.96 (dd., J=10.0 and 3.4 Hz), 7.3 (dd., J=10.0 and 3.0 Hz) and 7.26-8.06 (m. 10H).

Dehydrogenation of dichlorodicyano-p-benzoquinone afforded crystals (mp 186-188°) in 89% yield. Furthermore, upon photolysis in acetone, followed by subsequent treatment with dichlorodicyano-p-benzoquinone, (57) and (58) converted to (61) in fairly satisfactory yield (72 and 75% respectively).

As these examples indicate the Diels-Alder reaction of 2,3-benzotropone and subsequent (1,3)shift of phenylketone group by photolysis are useful procedures for the synthesis of fluorenone derivatives.

From the point of view mentioned in the previous section, some naphthobicyclics were examined. Compounds studied are as following:

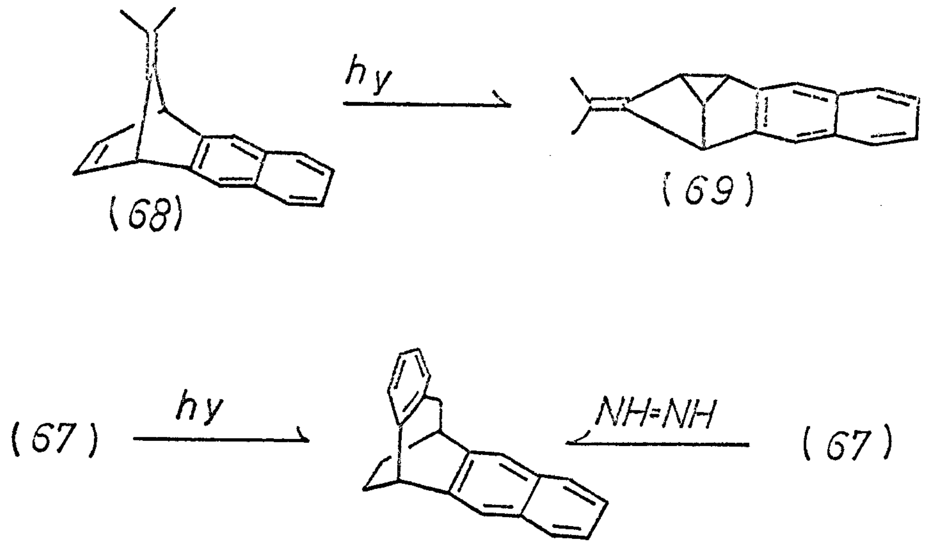
FIG 13



The synthesis of these hydrocarbons, except for (65), (66) and (67), were achieved by the additions 1,2-naphthyne and 2,3-naphthyne, respectively, to the corresponding dienes. Cyclo-octatetraene dibromide was used as a substrate in the case of (65) and (66). The hydrocarbon (67) was obtained by treatment of 2,3-benzotropone with 2,3-naphthyne, followed by Huang-Minlon reduction of the resulting ketonic adduct. 1,2-naphthyne and 2,3-naphthyne were generated from isoamyl-nitrite and the corresponding aminonaphthoic acid.

The structure assigned to these hydrocarbons rest on the mode of preparation and the spectroscopic data. Among these compounds, only (68) undergone photorearrangement under the sensitized condition.

FIG 14



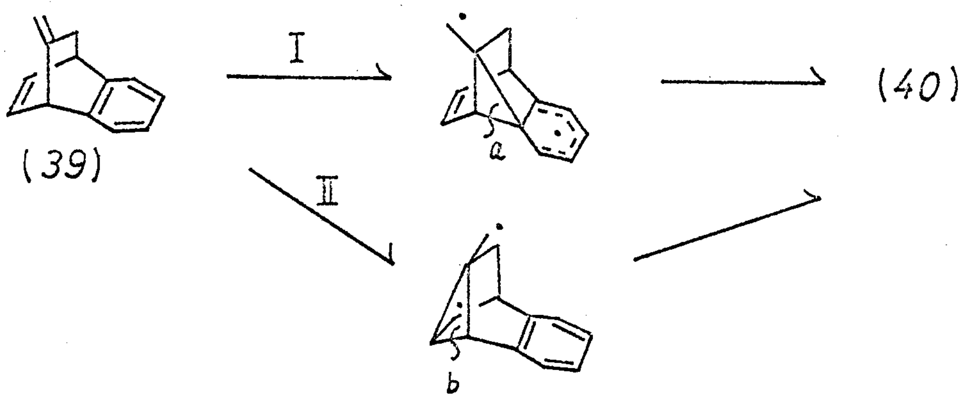
Nmr spectrum of the product (69) (mp. 148-149.5) reveals signals at 2.55 (ddd., J=6.0, 5.4 and 2.6 Hz, H_7), 2.78 (dd., J=6.0 and 5.4 Hz, H_2), 3.52 (ddd., J=5.4, 5.4 and 2.6 Hz, H_1), 3.83 (m, H_5) and 7.2-7.8 (m, 6H), wherein the coupling pattern shows a marked resembalance to that of the benzo-analog (36).16)

Hydrocarbon (67), upon photolysis in acetone for 12 hr, was hydrogenated to give (71) in low yield (10%), the great part of the starting material being unchanged. Similarly photolysis of (62)-(66) under the sensitized condition (acetone , benzophenone, acetophenone) for 12-18 hr resulted in the recovery of starting materials in 70-75% yield.

SECTION 3 Discussion

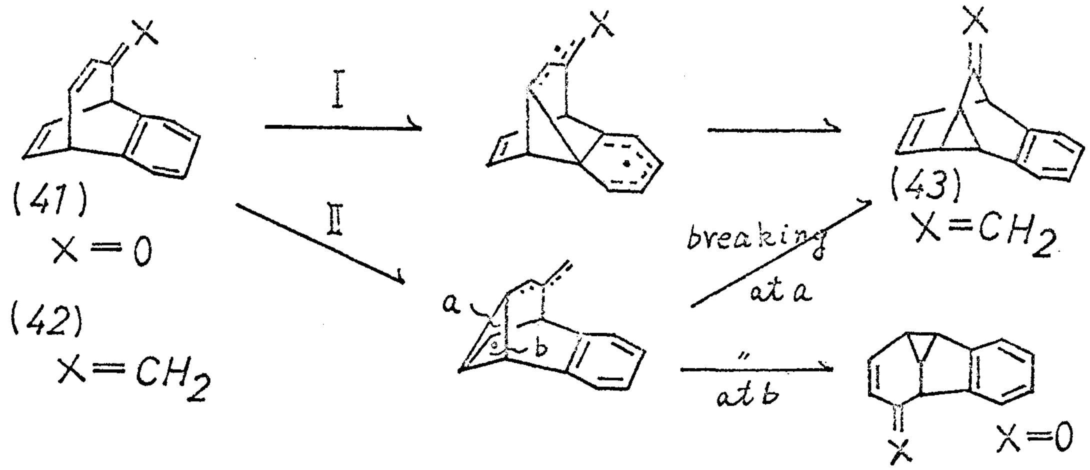
As shown in the previous section, photolysis condition indicates that hydrocarbon (40) arises from the triplet state of (39). With respect to the reaction pathway along which (40) is formed, there is the a priori possibility of vinyl-vinyl bridging or vinyl-benzobridging. According to the energetic argument used by H. E. Zimmerman,17) trans-butadiene (E_T=60 kcal) for vinyl-vinyl bridging and styrene (E_T=61.8 kcal) for vinyl-benzo bridging serve as approximate models.
In contrast with benzobarrelene the difference of values is so small that we can exercise little choise between them. On the other hand as to the bond breaking step, although a preference for bond breaking at (a) in path I in FIG 16 can be recognizable, that at (b) in path II is not entirely reasonable.

FIG 16



Due to the extremely low yield of (40) in this photolysis we have no sufficient evidences for detailed discussion.

FIG 17

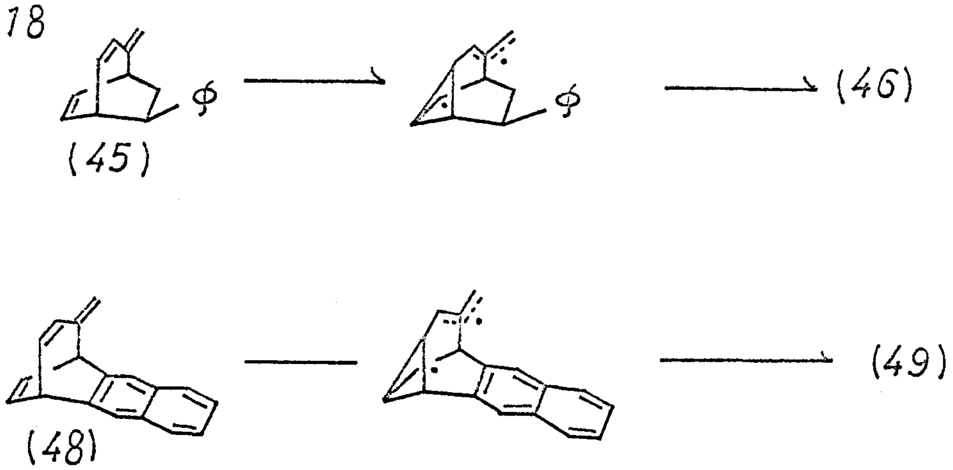


Similar energetic consideration lead to a choise of path II in Fig17. The exceptional high regiospecificity observed in the rearrangement of (42) demands a strong preference for a bond breaking sequence at (a) rather than at (b). The preference is consistent with retention of maximum electron delocalization during the rearrangement. This fact, however, differs markedly from the di-π-methane rearrangement of the related ketone (41) where the alternative bond breaking sequence is favored in triplet state. This aspect is very useful for synthesis of the compounds containing an exo-cyclic methylene group.

The reluctance of the photoconversion of (45) to (46) under direct irradiation, as compared with the sensitized one, is partially ascribed to substitution of phenyl group, from which singlet excitation energy is dissipated.

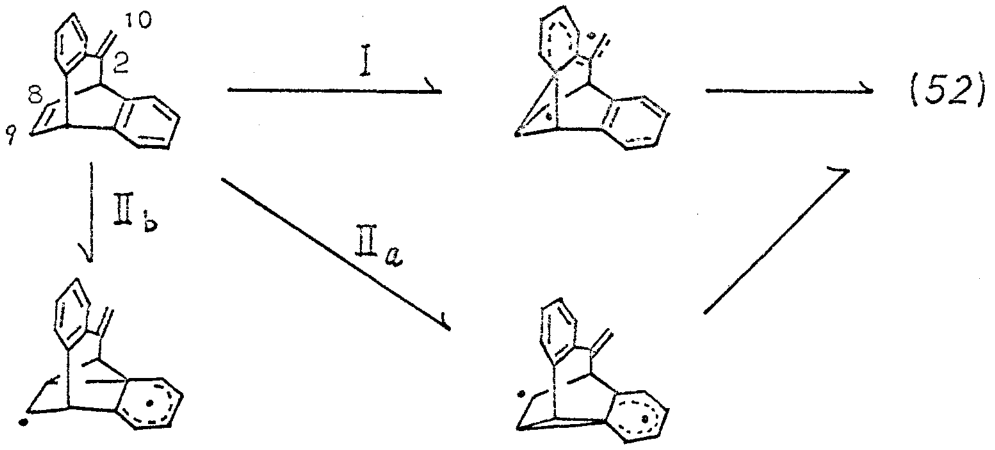
The hydrocarbon (49) can be considered to produce via vinyl-vinyl bridging in the excited state of (48). The preference for the bridging can be predicted from the findings obtained in the study on naphthobarrelenes in which, reluctance of bridging at β-position of naphthalene ring is definitely demonstrated.18)

FIG 18



Two alternative bonding processes, vinyl-styryl and vinyl-benzo bridging (path I and IIa,b in Fig 18),respectively, are possible for the formation of (52) as initial excited state reaction. Energetic consideration and retention of maximum electron delocalization also indicate the preference for path I, and regiospecificity of the reaction gives further support to the exclusion of a possibility of vinyl-benzo bridging path II; any factors which cause such a preference for the bridging IIa as to afford an only single product can't be inferred.

FIG 19

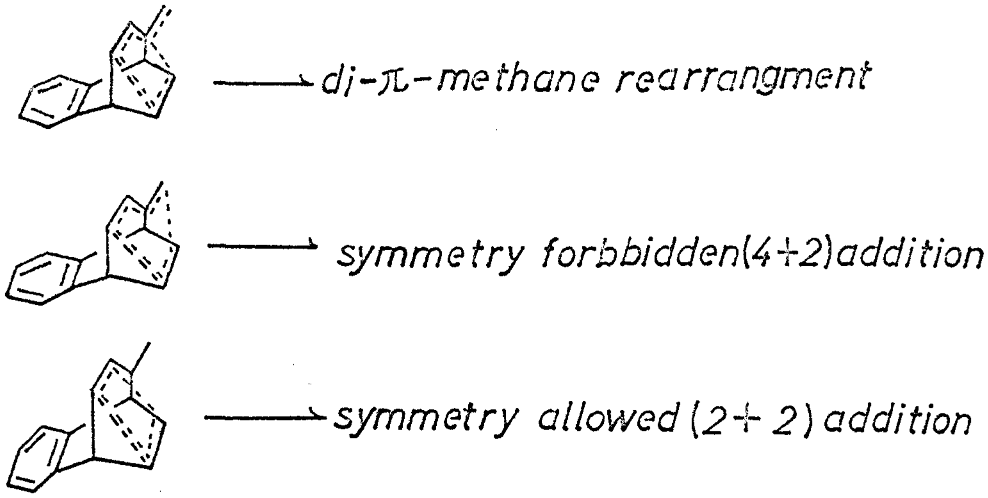


This conclusion leads to the question whether the formation of C_2C_8 bond does occur or not in triplet state. The idea of retention of maximum electron delocalization prefers to C_4C_9 bridging, in which, however, benzenoid character of styrene chromophor has an inclination to disappear. Although benzenoid conjugation still survives during C_2-C_8 bridging process the localization of developing radical on C_{10} takes place. This situation is not entirely improbable since the related bridging has been suggested in the photolysis of (39) [vide supra]. Accordingly, it remains unexplored that whether facility of singlet state is partially attributable to a light wasting reversion of C_2C_8 bridging.

The facility of unsensitized photochemical transformation of (51) to (52) demonstrates that singlet state is, at least partially, responsible for the rearrangement.

The facile photorearrangement of (42), (45) and (48) by direct irradiation does not immediately imply the singlet state reaction. If these photoreactions were due to singlet excited state, one might regard as a violation of the tentative generalization proposed by H.E.Zimmerman. In all cases, however, the electron delocalization including the butadienoid of styrenoid part is apparently favored, wherein one bridging is obviously stronger than the others, and by which any cycloaddition products can't be easily prepared by the steric factors (Fig 20)

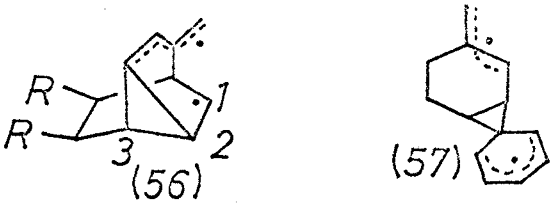
FIG 20



In other words, the geometry is not appropriate to a concerted cycloaddition process, since only one end of butadienoid or styrenoid moiety can approach the isolated double bond. However that end is at least as close as comparable orbitals in other molecules which rearrange readily, and so the excited singlet state of (42), (45), (48) and (51) may directly initiate a di-π-methane rearrangement.[13] Thus, for the constrained di-π-methane excited state, it appears that the preference for the triplet route arises from other type reactions (e.g. cycloaddition) commonly but not invariably being faster for the singlet state.

The most significant finding obtained is that, with these bicyclics (39) (42) (45) (48) and (51), di-π-methane rearrangement proceeds by way of a triplet excited state in apparent violation of the free rotar hypothesis. The experimental data and other qualitative observations described in the recent literatures[8)][16)] show that significant structural limitation may exist on this hypothesis. The reasons for this are not clear but include that; a)the initial bridging is preferred for a geometrical factor; b)the bond breaking step is more favorable for (56) than for (57) since the higher strain energy is expected in (56) than in (57) and the developing radical at C_3 may effectively stabilized by p orbital of the neighboring unsaturated center (Fig 21) except for (45);

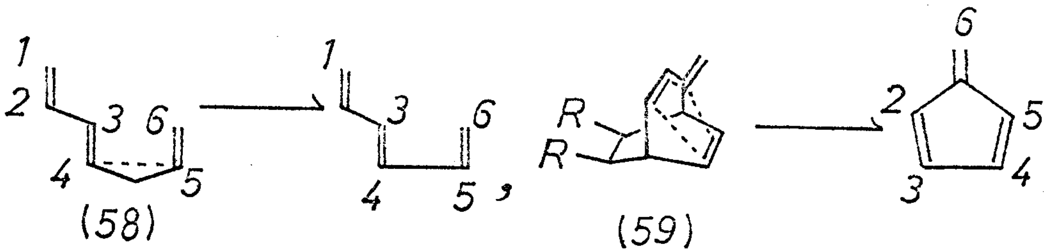
FIG 21



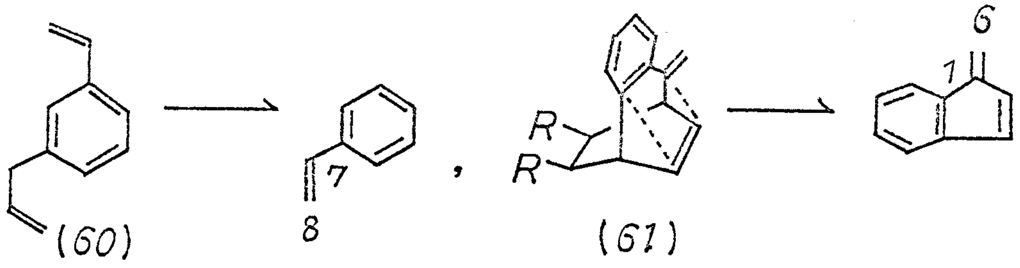
(56) (57)

and lastly c) if hexatriene and pentafulvene are taken as an approximate model for p orbital interaction of (58) and (59) respectively, the variation in bond orders[20] between ground and first excited states of pentafulvene, $\Delta P_{1,6}$ (-0.142), is smaller than that of hexatriene, $\Delta P_{1,2}$ (-0.242), according to the simple molecular orbital calculations. On the contrary, there is no substantial difference between $\Delta P_{3,4}$ for hexatriene and $\Delta P_{2,3}$ for pentafulvene (-0.348, -0.322, respectively). Similar tendency also appears in case of styrene and 2,3-benzopentafulvene. Thus $\Delta P_{7,8}$ for styrene is -0.465 and that for 1,6 bond of 2,3-benzopentafulvene is -0.241. The difference is large as compared with that of nonbenzoanalogs.

FIG 22



(58) (59)



(60) (61)

Although we must await more sophisticated calculations for the precise conclusion, the tendency would be regarded as one of the factors which cause the facile rearrangement by way of a triplet state.

At the present stage, none of the arguement can be given with regard to the photochemical behaviour of the naphthobicyclic system. However qualitative studies seemingly classify naphotobicyclics into two groups. One includes those which rearrange readily upon sensitized photolysis and the other consists of those which are considerably stable under the sensitized condition.

Since the photochemical studies on naphthobicyclic systems appear extremely rare, detailed examinations on photorearrangement of many hydrocarbons are desirable.

7-methylene-5,6-benzobicyclo[2.2.2]octa-2,5-diene (39)

The enone (38) was converted to the hydrocarbon (39) by treatment with methylenetriphenylphosphorane in 38.7% yield, ν_{max}^{NaCl} 3050, 2950, 2900, 1646, 1465, 1455, 1340, 875, 830, 760, 740 and 685 cm^{-1}; Anal. Calcd. for $C_{13}H_{12}$:C, 92.81; H, 7.19. Found: C, 92.59; H, 7.10.

2-methylene-6,7-benzobicyclo[3.2.2]nona-3,6,8-triene (42)

The enone (41) was treated with methylenetriphenylphosphorane in tetrahydrofuran to give the hydrocarbon (42) in 32.8% yield; mp. 43°; ν_{max}^{KBr} 3030, 2925, 1620, 1580, 1475, 1445, 1360, 1340, 880, 814, 745, 680 and 634 cm^{-1}; Anal. Calcd. for $C_{14}H_{12}$: C, 93.29; H, 6.71. Found: C, 93.41; H, 6.75.

The hydrocarbon (45)

The compound was prepared by Wittig reaction of the corresponding ketone (44) in 62% yield, mp. 65.5-67°; ν_{max}^{KBr} 3025, 2925, 1586, 1485, 1450, 1440, 880, 788, 772, 748 and 700 cm^{-1}; δ^{CDCl_3} 1.8-2.2 (m, 1H), 2.2-2.6 (m, 1H), 2.7-3.05 (m, 1H), 3.05-3.4 (m, 1H), 3.6 (m, 1H), 4.73 (d, J=2 Hz, 1H), 4.92 (m, 1H), 5.9-6.4 (m, 4H) and 7.23 (s, 5H).

The hydrocarbon (48)

The enone (47) was converted to the hydrocarbon (48) by treatment with methylenetriphenylphosphorane in 68% yield, mp. 102-103°; ν_{max}^{KBr} 3050, 2950, 1620, 1580, 1500, 1452, 878, 860, 745 and 693 cm^{-1}; δ^{CDCl_3} 4.0 (dt., J=7.0, 7.0 and 1.5 Hz, 1H), 4.3 (d, J=6.2 Hz, 1H), 4.7 (s, 1H), 5.2 (t, J=15 Hz, 1H), 5.62 (d, J=11.0 Hz, 1H), 6.23 (m, 1H), 6.46 (m, 1H), 6.73 (m, 1H) and 7.2-7.9 (m, 6H).

Photolysis of the hydrocarbon (39)

A solution of the hydrocarbon (39) (2.24 g) in 100 ml of olefin-free n-hexane containing 30 ml of acetone was bubbled with nitrogen for 30 minutes. The mixture was irradiated for 6 hours through Pyrex filter with 450-w high-pressure Hg lamp. Removal of the solvent, followed by chromatography over silica gel, gave the product (40) as a colorless oil in 2.3% yield; ν^{NaCl} 3050, 2930, 1465, 1445, 1220, 960, 824, 760, 744, 710 and 684 cm^{-1}; Anal. Calcd. for $C_{13}H_{12}$: C, 92.81; H, 7.19. Found: C, 91.89; H, 7.66.

Photolysis of the hydrocarbon (42)

A solution of the compound (42) (400 mg) in 30 ml of tetrahydrofuran containing 10 ml of acetone was bubbled with nitrogen for 30 minutes. The mixture was irradiated for 6 hours through Pyrex filter with 450-w high-pressure mercury lamp. Evaporation of the solvent, followed by chromatography over silica gel afforded the product (43) as a colorless oil in 65% yield; ν^{NaCl} 3050, 2930, 2850, 1450, 1483, 1456, 870, 780, 750 and 740 cm^{-1}; Anal. Calcd. for $C_{14}H_{12}$: C, 93.18; H, 6.63. Found: C, 93.29; H, 6.71.

Photolysis of the hydrocarbon (45)

The compound (45) (800 mg) in 30 ml of acetone was photolyzed through Pyrex filter with 450-w high-pressure mercury lamp to give the product (46) as a colorless oil in 78% yield; δ^{CDCl_3} 1.6-1.9 (m, 2H), 2.0-2.5 (m, 3H), 2.76 (m, 1H), 3.66 (m, 1H), 4.93 (s, 2H), 5.86 (m, 2H) and 7.30 (m, 5H); Anal. Calcd. for $C_{16}H_{16}$: C, 92.26; H, 7.74. Found: C, 91.99; H, 7.86.

Photolysis of the hydrocarbon (48)

The compound (48) (300 mg) in 60 ml of acetone was photolyzed through Pyrex filter with 450-w high-pressure mercury lamp to afford the product (49) in 81% yield, mp. 92-94; δ^{CDCl_3} 2.23 (ddt., J=7.6, 7.6, 6.0 and 1.8 Hz, 1H), 2.70 (dt., J=7.6, 7.6 and 2.0 Hz, 1H), 2.93 (t, J=7.6 Hz, 1H), 3.85 (dd., J=6.8 and 2.0 Hz, 1H), 4.87 (d, J=2.0 Hz, 1H), 5.03 (d, J=2.0 Hz, 1H), 5.63 (dd., J=9.0 and 6.0 Hz, 1H), 5.87 (ddd., J=9.0, 6.8 and 2.0 Hz, 1H) and 7.2-7.8 (m, 6H); Anal. Calcd. for $C_{18}H_{14}$; C, 93.87; H, 6.13. Found: C, 93.46; H, 6.15. Benzophenone-sensitized or direct photolysis also gave the product (49) in 80 or 75% yield, respectively.

The ketone (50)

2,3-benzotropone (5.2 g) and isoamyl nitrite (4.68 g) in 350 ml of the mixture of dichloromethane and tetrahydrofuran (7:1 v/v) were treated with anthranilic acid (5.48 g) in 200 ml of tetrahydrofuran at 40°C for 6 hours and the product was purified by chromatography over silica gel, mp. 104-105°, 62%; ν_{max}^{KBr} 1670 cm^{-1}; δ^{CDCl_3} 4.55 (dd., J=7.0 and 2.0 Hz, 1H), 4.70 (dd., J=7.0 and 2.0 Hz, 1H), 6.50 (dt., J=7.0, 7.0 and 2.0 Hz, 1H), 6.95 (dt., J=7.0, 7.0 and 2.0 Hz, 1H), 7.19 (m, 7H) and 7.95 (m, 1H, aromatic proton ortho to carbonyl group); Anal. Calcd. for $C_{17}H_{12}O$: C, 87.90; H, 5.21. Found: C, 88.32; H, 5.24.

The hydrocarbon (51)

The compound (51) was obtained as a colorless oil by treatment of the enone (50) with methylenetriphenylphosphorane in 85% yield; ν_{max}^{NaCl} 882 cm^{-1}; Anal. Calcd. for $C_{18}H_{14}$: C, 93.87; H, 6.13. Found: C, 93.52; H, 6.36.

Photolysis of the ketone (50)

Irradiation of 0.0002-0.02 M solution of the ketone (50) in acetone under nitrogen atmosphere with 450-w high-pressure mercury lamp through Pyrex filter for 45 minutes gave a single product (55) in 95% yield, mp. 104-105.5; ν_{max}^{KBr} 1710 cm^{-1}; Anal. Calcd. for $C_{17}H_{12}O$: C, 87.90; H, 5.21. Found: C, 87.89; H, 5.20. Photolysis in tetrahydrofuran also gave the same product (55) in quantitative yield.

Photolysis of the hydrocarbon (51)

The hydrocarbon (51) in tetrahydrofuran was irradiated through Pyrex filter with 450-w Hg lamp. After 4 hours, the solvent was evaporated, and the residue was chromatographed over silica gel and eluted with pet. ether to afford the product (52) as colorless plates in 90% yield, mp. 124° ν_{max}^{KBr} 885 cm^{-1}; Anal. Calcd. for $C_{18}H_{14}$: C, 93.87; H, 6.13. Found: C, 93.44; H, 6.21. Although the sensitized photolysis of (51)

in acetone (0.2 g in 100 ml of acetone) also afforded photoisomer (52) in 50% yield, sensitized photoisomerization took place much slower [18 hr] than the direct one.
The remaining 50% was the starting material contaminated with resinous products.

The ketone (53)

A solution of 100 mg of the hydrocarbon (52), 258 mg of sodium chlorate and 24 mg of osmium tetroxide in 10 ml of water and 40 ml of dioxane was stirred at room temperature for 18 hr. The solution was then diluted with 200ml of ether, washed five times with water, and dried, and the solvent was removed in vacuo to yield an oil, which was then treated with 233 mg of potassium periodate in 60.0 ml of the mixture of ethanol, water and acetone (38:12:10 v/v) for 20 hr with stirring at room temperature. The solution was diluted with ether, washed with water and dried. After evaporation of the solvent, the residue was chromatographed over silica gel to give the ketone (53) in 60% yield, mp. 181-182°; ν_{max}^{KBr} 1680 cm^{-1}.

The ketone (59)

mp. 129-130°; Anal. Calcd. for $C_{21}H_{14}O$: C, 89.33; H, 5.00.

Found: C, 89.01; H, 5.03.

The ketone (60)

mp. 169-170°; Anal. Calcd. for $C_{21}H_{14}O$: C, 89.33; H, 5.00. Found: C, 89.12; H, 5.00.

The ketone (61)

mp. 188°; Anal. Calcd. for $C_{21}H_{12}O$: C, 89.98; H, 4.32. Found: C, 89.77; H, 4.33.

Photolysis of naphthobicyclics (62)-(68)

A solution of naphthobicyclics (100 mg) and benzophenone (2 g) in tetrahydrofuran (60 ml) was bubbled for 2 hours and photolyzed through Pyrex filter with 450-w high-pressure mercury lamp. The solvent was evaporated in vacuo, and the residue was chromatographed over silica gel. The compounds eluted with pet. ether were analyzed by means of nmr measurement. The results and the physical constants of starting are summerized below.

starting material and reaction time	physical constants	product		recovery (%)
			physical constants	
(62)	mp. 85-86°	none		
12 hr	δ 2.4 (broad s, 2H)			74
16	4.02(broad s, 4H)			70
	6.93(broad s, 2H)			
	7.2-7.9(m, 6H)			
(63)	oil	none		
13 hr	δ 2.4 (broad s, 2H)			72
15	4.0 (broad s, 1H)			71
	4.46(broad s, 1H)			
	6.90(broad s, 2H)			
	7.2-7.8(m, 6H)			
(64)	mp. 105-106°	none		
13 hr	δ 1.50(s, 4H)			70
15	3.93(broad s, 2H)			72
	7.2-7.8(m, 6H)			
(65)	mp. 153-154°	none		
18 hr	δ 2.76(m, 2H)			65
12	3.90(m, 2H)			70
	6.08(s, 2H)			
	6.30(m, 2H)			
	7.2-7.8(m, 6H)			
(66)	mp. 70-71°	none		
17 hr	δ 2.60(m, 2H)			71
15	3.86(m, 1H)			71
	4.56(m, 1H)			
	6.13(s, 2H)			
	6.30(m, 2H)			
	7.2-8.1(m, 6H)			
(67)	mp. 147-148°	(71)	mp. 162.5-165.5°,10%,	

20 hr	δ 3.13(m, 2H)	δ 2.16(m,4H)	70
20	3.86(m, 1H)	3.30(m,3H)	70
	4.43(d, 6.0Hz 1H)	4.00(m,1H)	
	6.43(dt,6 and 0.8Hz 1H)	7.0-7.9(m,10Hz)	
	6.77(dt,6 and 0.8Hz 1H)		
	6.9-7.9(m, 10Hz)		
(68)	mp. 155.5-156°	(69) mp. 148-149.5°,62%,	
	1.60(s, 6H)		
	4.46(m, 2H)		
	6.86(m, 2H)		
	7.1-7.8(m, 6H)		

* Acetophenone-sensitized photolysis gave the similar results.

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