OUKA
The University of Osaka
Institutional Knowledge Archive

Title	STUDIES ON THE REACTIONS OF HETEROCUMULENES IN THE PRESENCE OF METAL CARBONYLS
Author(s)	馬場, 章夫
Citation	大阪大学, 1976, 博士論文
Version Type	VoR
URL	https://hdl.handle.net/11094/889
rights	
Note	

The University of Osaka Institutional Knowledge Archive : OUKA

https://ir.library.osaka-u.ac.jp/

The University of Osaka

STUDIES ON THE REACTIONS OF HETEROCUMULENES IN THE PRESENCE OF METAL CARBONYLS

1975

AKIO BABA

Department of Petroleum Chemistry

Osaka University

CONTENTS

Introduction ---------- 1

List of Papers ---------- 3

Chapter I. Reactions of Phenylbromoacetylene with Heterocumulenes in the Presence of Iron Pentacarbonyl

1. Introduction ---------- 4

2. Results and Discussion

2-1. Reactions with Carbodiimides ---------- 5

2-2. Reaction with Phenyl Isocyanate ---------- 8

2-3. Reaction with Diphenylketene ---------- 10

3. Summary ---------- 11

4. Experimental Section ---------- 12

References ---------- 16

Chapter II. Reactions of Diphenylcyclopropenone with Ketenes in the Presence of Nickel Tetracarbonyl

1. Introduction ---------- 17

2. Results and Discussion ---------- 18

3. Summary ---------- 24

4. Experimental Section ---------- 25

References ---------- 29

Chapter III. Reactions of N-Sulfinylamines with Diphenylcyclopropenone, Diphenylacetylene in the Presence of Metal Carbonyls

1. Introduction ---------- 30

2. Results and Discussion

2-A. Reactions of Diphenylcyclopropenone ------ 31
2-B. Reaction of Diphenylacetylene ---------- 38
3. Summary ---------- 40
4. Experimental Section ---------- 41
References ---------- 48

Chapter IV. Reactions of α,α'-Dibromoxylenes with Diphenyl-Ketene in the Presence of Nickel Tetracarbonyl, and the Simple Method of Diphenylketene Dimer and Tetraphenylallene.
IV-I. Reactions of α,α'-Dibromoxylenes with Diphenylketene
1. Introduction ---------- 49
2. Results and Discussion ---------- 50
IV-II. The Simple Method of Diphenylketene Dimer and Tetraphenylallene
1. Introduction ---------- 58
2. Results and Discussion ---------- 58
Summary ---------- 61
Experimental Section ---------- 62
References ---------- 67

Conclusion ---------- 68

INTRODUCTION

Heterocyclic compounds have been studied in many fields. There are so many well known applications not only in manufactural products, but also in medical and agricultural reagents. Especially, their physiologycal activities attract significant attentions of organo chemsts. Now, the chemistry of heterocyclic compounds is developing rapidly and widely.

In the synthetic chemistry of heterocyclic compounds, heterocumulenes (ketene, isocyanate, N-sulfinylamine etc.) are very valuable reagents because of thier dipolar characters. They react readily with high-polar compounds to produce by ordinary methods. But same time, heterocumulenes have not enough reactivities toward low-polar compounds. Consequently, it is considered to be very important that the reactivities of heterocumulenes are enhanced with the aid of other reagents.

Recently, reactions of heterocumulenes with organometallic compounds have been investigated closely and a many of metal complexes have been isolated. Heterocumulenes have high affinities for organometallic compounds, therefore, it is expected that reactions of heterocumulenes with low-polar reagents proceed smoothly by using of appropriate organometallic compounds. On the basis of this standpoint, in this thesis, iron pentacarbonyl and nickel tetracarbonyl which have already been used commercially have been adopted in the reactions of low-polar reagents with heterocumulenes and thier activation effects have been closely investigated

In Chapter 1, reactions of phenylbromoacetylene with carbodiimides, phenyl isocyanate and diphenylketene in the presence of

iron pentacarbonyl are studied noticed to the high affinity of halogen to iron pentacarbonyl.

Chapter 2 deals with reactions of diphenylcyclopropenone with ketenes in the presence of nickel tetracarbonyl. The cycloaddition reactions proceed by a catalytic amount of nickel tetracarbonyl, and thus the reaction mechanisms are proposed.

In Chapter 3, cycloaddition reactions of N-sulfinylamines with diphenylcyclopropenone in the presence of metal carbonyls (nickel tetracarbonyl and iron pentacarbonyl) are investigated. Particularly, the exchange reactions of C=O of nickel tetracarbonyl for S=O of N-sulfinylamines are studied closely.

In Chapter 4, reactions of α,α'-dibromoxylenes in the presence od nickel tetracarbonyl are carried out and the formation of an interesting spiro compound is reported. In addition , a simple method for the preparation of tetraphenylallene and diphenylketene dimer from diphenylketene is described. This method give the products without the formation of polymer of diphenylketene.

LIST OF PAPERS

The papers concerning this thesis are as follows.

1. Reactions of Phenylbromoacetylene with Heterocumulenes in the Presence of Iron Pentacarbonyl

   Akio Baba, Yoshiki Ohshiro, and Toshio Agawa

   J. Organometal. Chem., 87 247 (1975).

2. A Simple Method for the Preparation of Tetraphenylallene and Diphenylketene Dimer

   Akio Baba, Saburo Kitano, Yoshiki Ohshiro, and Toshio Agawa

   Synthesis 537 (1975).

3. Reactions of Diphenylcyclopropenone with N-Sulfinylamines in the Presence of Nickel Tetracarbonyl

   Akio Baba, Yoshiki Ohshiro, and Toshio Agawa

   Chem. Lett., in press.

4. Reactions of Diphenylcyclopropenone with Ketenes in the Presence of Nickel Tetracarbonyl

   Akio Baba, Yoshiki Ohshiro, and Toshio Agawa

   J. Organometal. Chem., in press.

5. Reactions of α,α'-Dibromoxylenes with Diphenylketene in the Presence of Nickel Tetracarbonyl

   Akio Baba, Yoshiki Ohshiro, and Toshio Agawa

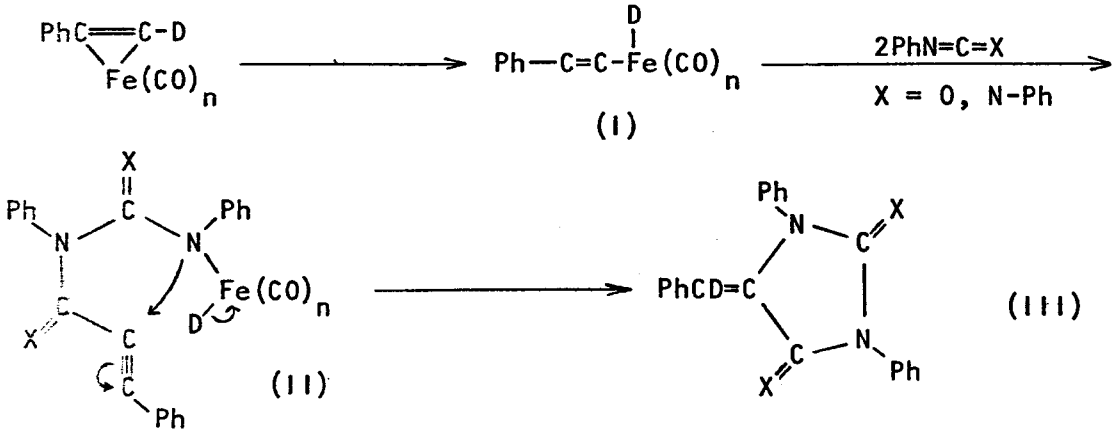
   J. Organometal. Chem., in contribution.

Chapter 1. REACTIONS OF PHENYLBROMOACETYLENE WITH HETEROCUMULENES IN THE PRESENCE OF IRON PENTACARBONYL

1) Introduction

It has been reported previously[1] that phenylacetylene reacts with isocyanates or carbodiimides in the presence of iron pentacarbonyl to give imidazolidine derivatives III. In this reaction, it was suggested that isocyanates or carbodiimides were inserted into the C-Fe bond of the σ-complex I, and that the hydrogen atom attached to the iron of the intermediate II returned to the acetylenic carbon in the ring closure step to III.

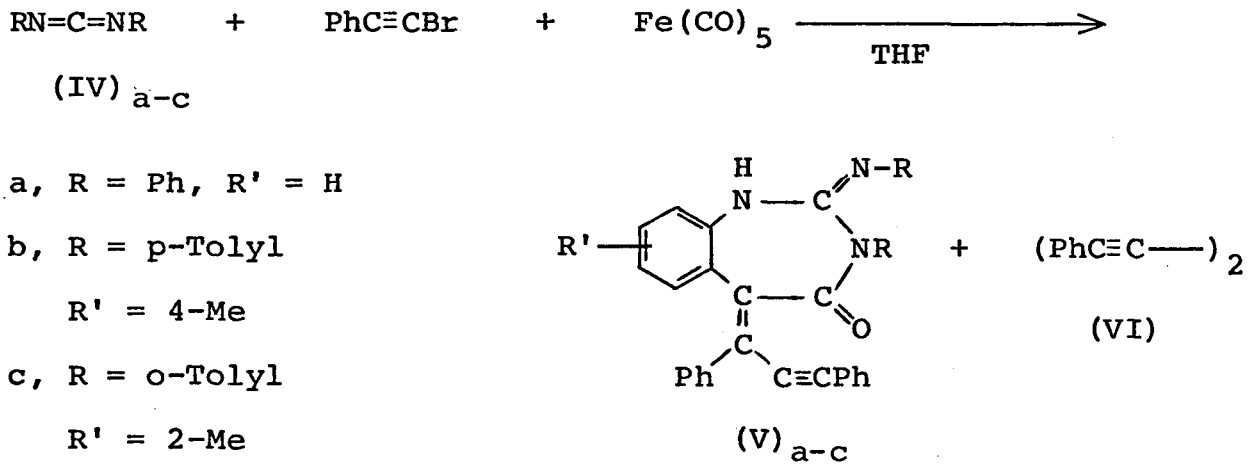
When phenylbromoacetylene is employed instead of phenylacetylene, some significant differences in the observed reaction is expected due to the affinity of bromine for iron. When the authors investigated reactions of phenylbromoacetylene with heterocumulenes in the presence of iron pentacarbonyl, this was indeed found to be the case. In the cyclization step of these reactions, coupling reactions of phenylbromoacetylene should have occurred. We had noticed such a coupling reaction of phenylbromoacetylene to give diphenylbutadiyne in the presence of iron pentacarbonyl in my preliminary experiments and it has been reported to be effected by cuprous salts[2] as well.



2) Results and discussion

2-1) Reactions with carbodiimides

Reactions of phenylbromoacetylene with arylcarbodiimides IVa-IVc in the presence of iron pentacarbonyl at 90-100° gave the benzodiazepinone derivatives Va-Vc and the diacetylene VI. It seemed that the benzodiazepinones Va-Vc were formed from an aryl-carbodiimide, an arylisocyanate and two moles of phenylethynyl groups, and that the diacetylene VI was formed by the coupling reaction of phenylbromoacetylene. The reactions proceeded with violence unless they were controlled by adding a solvent such as tetrahydrofuran.



The results of the reactions are shown in Table 1.

The structure of the benzodiazepinone Va was determined by spectral data. In the IR spectrum, the absence of the absorption due to the triple bond implied its strong conjugation with the double bond. The NMR spectrum showed the signal of amine proton at δ 7.7 in DMSO-d_6. In the product Va, the cofiguration of the phenyl group attached to the olefinic carbon was not determined.

A decrease in the mole ratio of $Fe(CO)_5$ to the acetylene to unity led to a decrease in the yield of the product Va, but an increase in the mole ratio caused no remarkable effect. These

TABLE 1

THE REACTIONS OF PhC≡CBr WITH RN=C=NR

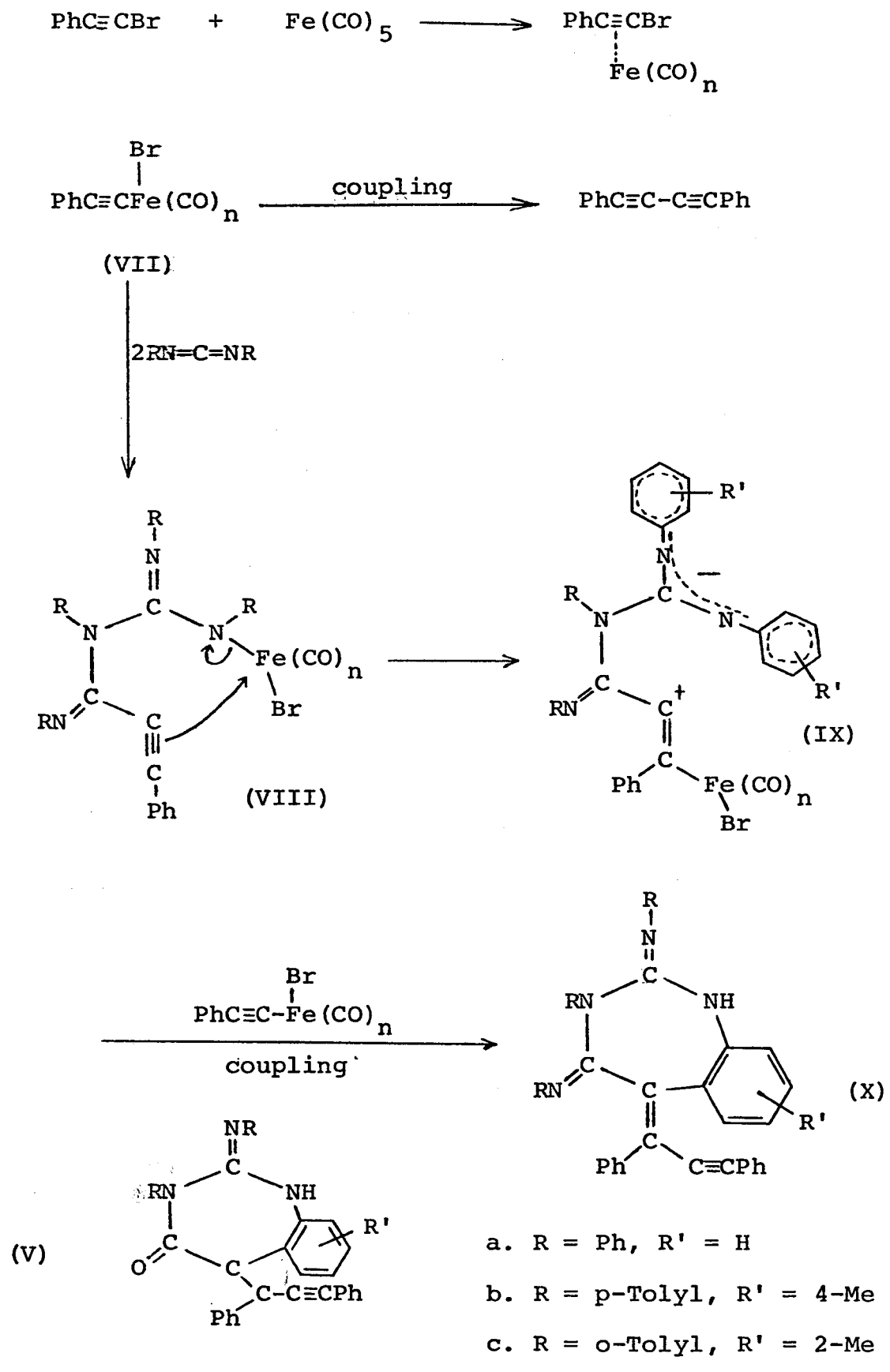
RN=C=NR	Molar ratio					Yield[b] (%)	
R	PhC≡CBr	RN=C=NR	$Fe(CO)_5$	Temp. (°C)	Time(hr)	V	VI
Phenyl	1	1	2	90-100	2	41	23
Phenyl	1	1	1	90-100	2	40	19
Phenyl	1	1	0.8	90-100	2	29	25
Phenyl	1	1	0.5	90-100	2	14	30
p-Tolyl	1	1	1	90-100	2.5	33	17
O-Tolyl	1	1	1	90-100	4	17	36
c-Hexyl[a]	1	1	1	90-100	4.5	0	88

[a] This reaction was carried out without solvent, and all other reactions were carried out in THF. [b]Based on phenylbromoacetylene.

results indicate that an equimolar amount of iron pentacarbonyl is necessary for the reaction. A substituent on the ortho position of the arylcarbodiimide depressed the formation of the benzodiazepinone Vc by its steric hindrance. In the case of cyclohexylcarbodiimide, no benzodiazepinoe was obtained because of poor reactivity of the carbodiimide, and the diacetylene VI was formed quantitatively.

We assumed the reaction mechanism as shown in the Scheme 1 in analogy with the proposed mechanism for the reaction between phenylacetylene and a carbodiimide[1]. The smooth formation of the acetylide complex VII would be followed by succesive insertion of two moles of the carbodiimide giving the intermediate VIII. Both the fission of the iron-nitrogen bond and the attack of the π-electrons of the C≡C bond at the iron atom will lead to the

SCHEME 1



a. R = Ph, R' = H

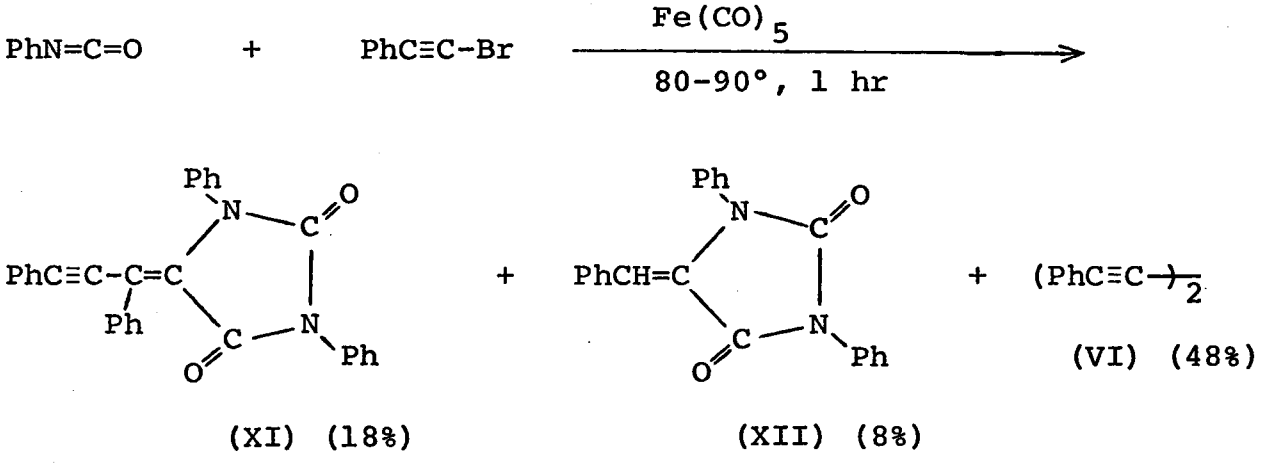
b. R = p-Tolyl, R' = 4-Me

c. R = o-Tolyl, R' = 2-Me

intermediate IX without a shift of bromine to the acetylenic carbon although the ring closure of II which corresponds to VIII was accompanied by a prototropic shift in the reaction of phenylacetylene. This is because of the higher affinity of bromine for iron as compared with that of hydrogen. The subsequent coupling reaction between the intermediate IX and the acetylide complex VII which gives the benzodiazepine derivative X could be deduced from the results of coupling of organohalo compounds by iron carbonyls[3]. The benzodiazepine X was not isolated but was obtained as the hydrolyzed product, the diazepinone V, after chromatographic treatment on alumina.

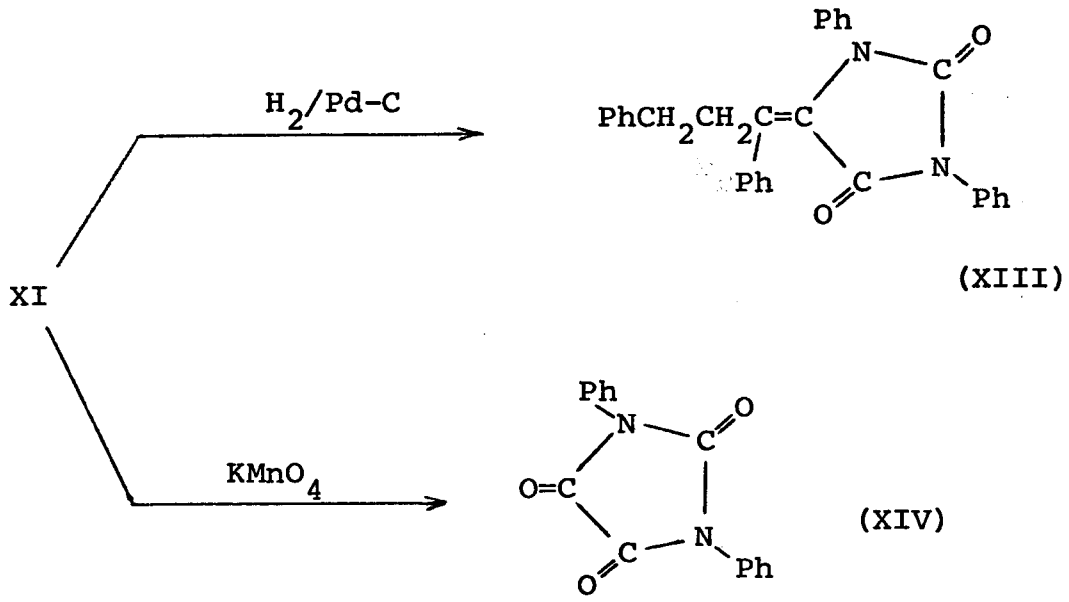
2-2) Reaction with phenyl isocyanate

The reaction of phenylbromoacetylene with phenyl isocyanate in the presence of an equimolar amount of iron pentacarbonyl gave the hydantoin derivatives XI and XII instead of a diazepinone. The structure of XI was determined by means of spectral and analytical data (see Experimental).



In the hydrogenation of the hydantoin XI with Pd/C catalyst, only the acetylenic group was reduced to give the hydantoin XIII, and the carbon-carbon double bond remained unchanged under such

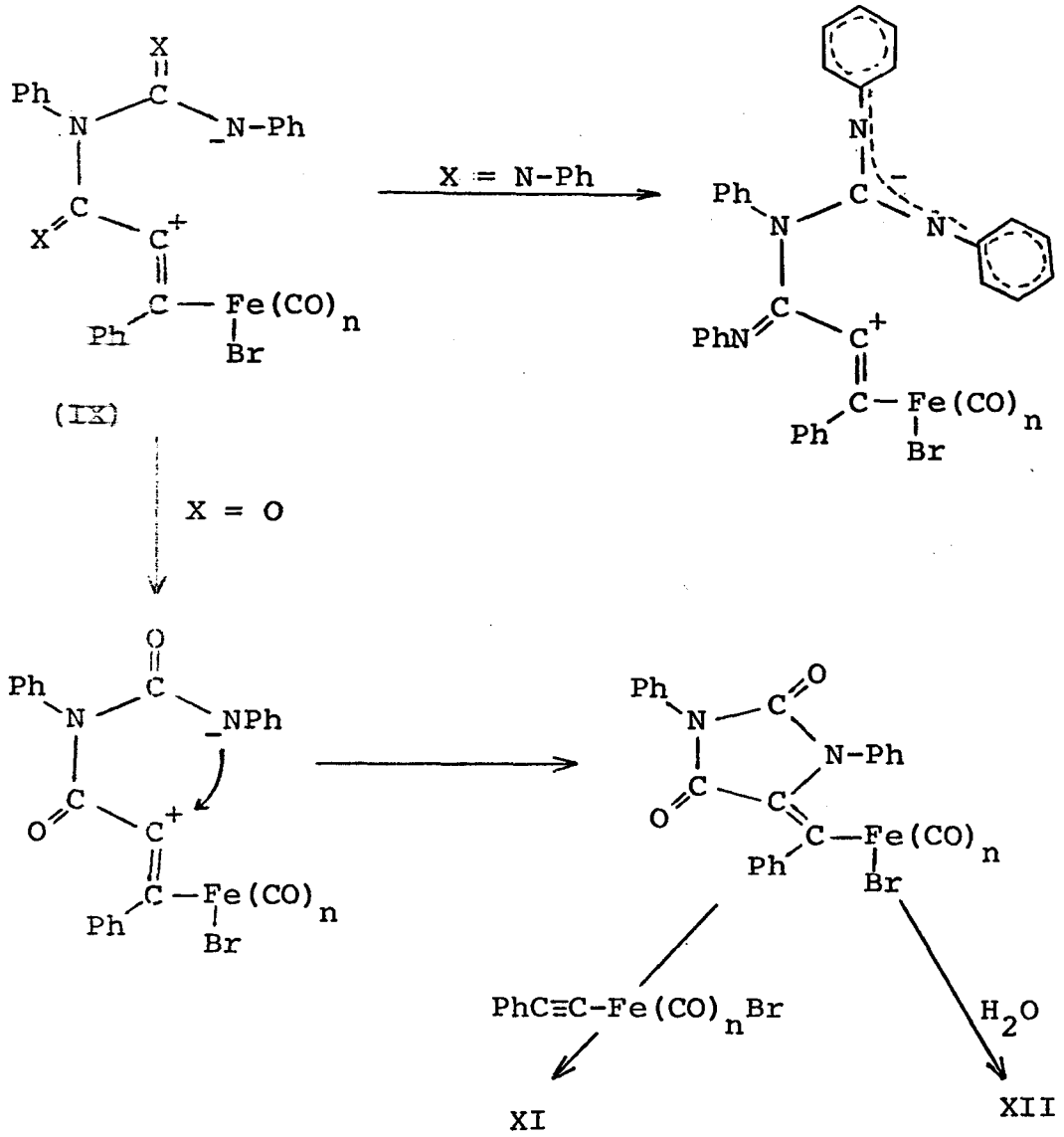
conditions. In the IR spectrum, the hydantoin XIII showed an absorption band which was assigned to the C=C group at 1630 cm^{-1}. The hydantoin XI was oxidized with $KMnO_4$ to diphenylparabanic acid (XIV) in 67% yield.



The structure of the hydantoin XII was confirmed by comparison with previously reported spectral data[1].

The author considered the mechanistic distinction between the reactions of a carbodiimide and an isocyanate as follows. The primary difference surely would be in the stability of the negative charge developed on the nitrogen atom by the fission of the N-Fe bond of the intermediate VIII. The charge would be distributed into phenyl rings by the strong resonance effect in the case of the carbodiimide. On the other hand, the charge on the nitrogen would be stabilized by the electron-withdrawing carbonyl group in the reaction of the isocyanate, and therefore the attack of the nitrogen at the acetylenic carbon would become predominant (Scheme 2).

SCHEME 2

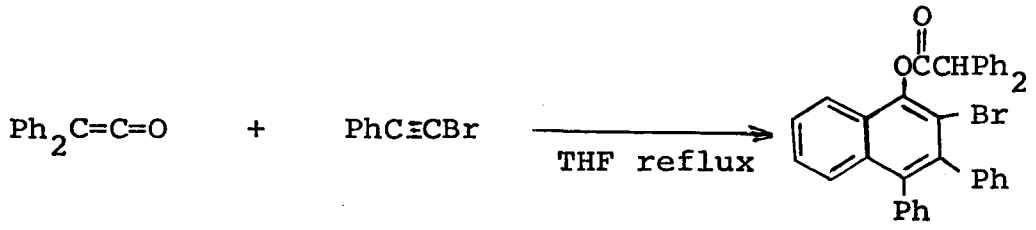


In the reaction with the isocyanate, the slow rate of the insertion of the isocyanate into the C-Fe bond of the intermediate VII led to the major coupling reaction of itself, and the diacetylene VI was produced in a high yield.

2-3) Reaction with diphenylketene

In the presence of iron pentacarbonyl, the reaction of phenylbromoacetylene with diphenylketene gave 2-bromo-3,4-diphenyl-1-diphenylacetoxynaphthalene (XV) in 22% yield together with the

diacetylene VI. In this reaction, no adduct formed by insertion of diphenylketene into the acetylide complex VII was obtained.



A similar naphthalene derivative is obtained from the reaction of phenylacetylene with diphenylketene without catalyst[4]. This non-catalytic reaction is carried out under mild conditions and the naphthalene is produced in high yield.

From these results, the reaction of the ketene with the acetylene would be predominant over the formation of the acetylide complex VII.

3) Summary

Reactions of phenylbromoacetylene with heterocumulenes in the presence of iron pentacarbonyl have been studied. The reactions with arylcarbodiimides gave diazepinone derivatives in 41-17% yields. The reaction with phenyl isocyanate gave two hydantoin derivatives, in 18 and 8% yields. On the other hand, the reaction with diphenylketene was not catalyzed by iron pentacarbonyl and gave 2-bromo-3,4-diphenyl-1-diphenylacetoxynaphthalene. In all cases coupling of phenylbromoacetylene to give diphenylbutadiyne was also observed. Reaction mechanisms were discussed.

4) Experimental section

All melting points were determined on a Yanagimoto micro melting point apparatus and are uncorrected.

IR spectra were recorded on Nujol mulls of solids with a Jasco IR-E spectrophotometer. NMR spectra were taken with a JEOL LNM-3H-60 spectrometer with TMS. Mass spectra were taken with a Hitachi RMU-6E spectrometer.

All reactions were carried out under nitrogen atmosphere. Chromatographic separations were carried out on activated alumina.

Materials

Commercial iron pentacarbonyl was used without further purification. Commercial phenyl isocyanate was used after distillation. Diphenylcarbodiimide, di-p-tolylcarbodiimide and di-o-tolylcarbodiimide were prepared by the reported method[5]. Phenylbromoacetylene was prepared from phenylacetylene and sodium hypobromide in the usual way[6].

Reactions of phenylbromoacetylene with carbodiimides

(a). Reaction with diphenylcarbodiimide. A mixture of phenylbromoacetylene (0.025 mol) and iron pentacarbonyl (0.025 mol) in 5 ml of THF was stirred for 30 min at room temperature. Diphenylcarbodiimide (0.025 mol) was added dropwise to the mixture at room temperature and then this mixture was heated at 90-100° for 2 hr until evolution of carbon monoxide ceased. The reaction mixture was extracted with 200 ml of benzene, and the benzene layer was washed twice with 300 ml of water. The benzene solution was dried over Na_2SO_4 concentrated in vacuo, chromatographed and eluted with hexane (fraction 1) and ethyl acetate (fraction 2).

From the first fraction, 0.48 g (19%) of diphenylbutadiyne (VI) was obtained and recrystallized (hexane-benzene): m.p. 88-89°; no depression of melting point was observed for the mixture with an authentic sample[7]. From the second fraction, 2.57 g (40%) of 6,7-benzo-3-phenyl-2-phenylimino-5-(α-phenylethynyl)benzylidene-1,2,-4,5-tetrahydro-1,3-diazepin-4-one (Va) was obtained and recrystallized (benzene-hexane): pale yellow needles; m.p. 150-151°; IR: 3290 (NH), 1640 (C=O) and 1615 cm^{-1} (C=N); mass spectrum: m/e 515 $[M]^+$, 395 $[M - PhN=CNHPh]^+$, 202 $[PhC{\equiv}CPhC=C]^+$ and 194 $[PhNCNPh]^+$; NMR (DMSO-d_6): δ 7.2 (broad, 1H, NH), 7.6-6.8 (22H, aromatic protons).

Analysis found: C, 83.81; H, 5.15; N, 8.37. $C_{36}H_{25}N_3O$ calcd: C, 83.86; H, 4.89; N, 8.15%.

(b) Reactions with other carbodiimides. Reactions between carbodiimides (0.025 mol), phenylbromoacetylene (0.025 mol) and iron pentacarbonyl (0.025 mol) were carried out in a similar manner (see Table 1 for reaction times, temperatures and yields). The reaction with di-p-tolylcarbodiimide gave 4'-methyl-6,7-benzo-3-p-tolyl-2-phenylimino-5-(α-phenylethynyl)benzylidene-1,2,4,5-tetrahydro-1,3-diazepin-4-one (Vb) (1.2 g): yellow needles (from benzene hexane); m.p. 188-190°; IR: 3290 (NH), 1640 (C=O) and 1615 cm^{-1} (C=N); mass spectrum: m/e 558 $[M]^+$, 543 $[M - CH_3]^+$, 467 $[M - CH_3-C_6H_4]^+$, 292 $[CH_3C_6H_4C=CPhC{\equiv}CPh]^+$ and 222 $[CH_3C_6H_4N=C=NC_6H_4CH_3]^+$; NMR($CDCl_3$): δ 2.2 (s, 3H, CH_3), 2.15 (s, 6H, $2CH_3$) and 6.6-7.4 (m, 20H, NH and aromatic protons).

Analysis found: C, 83.68; H, 5.91; N, 7.25. $C_{39}H_{31}N_3O$ calcd: C, 83.99; H, 5.60; N, 7.54%.

The reaction with di-o-tolylcarbodiimide gave 1'-methyl-6,7-benzo-3-o-tolylimino-5-(α-phenylethynyl)benzylidene-1,2,4,5-tetrahydro-1,3-diazepin-4-one (Vc) (2.3 g): white needles (from benzene-hexane); m.p. 181-182°; IR: 3290 (NH), 1640 (C=O) and 1615 cm^{-1} (C=N); mass spectrum: m/e 543 $[M - CH_3]^+$, 467, 292 and 222; NMR ($CDCl_3$): δ 2.6-3.6 (m, 9H, $3CH_3$), 6.2-7.4 (m, 19H, aromatic protons) and 8.0 (broad, 1H, NH).

Analysis found: C, 84.14; H, 5.68; N, 7.52. $C_{39}H_{31}N_3O$ calcd: C, 83.99; H, 5.60; N, 7.54%.

The reaction with dicyclohexylcarbodiimide gave no diazepinone derivative, but diphenylbutadiyne (VI) (88%) was isolated.

Reaction of phenylbromoacetylene with phenyl isocyanate

A mixture of phenylbromoacetylene (0.025 mol) and iron pentacarbonyl (0.025 mol) was stirred at 80° for 10 min. Phenyl isocyanate (0.025 mol) was added dropwise to the mixture, and stirring was continued for 4 hr at 80-90° until evolution of carbon monoxide ceased. The reaction mixture was extracted with benzene, concentrated in vacuo, and chromatographed and eluted with hexane (fraction 1) and benzene (fraction 2 and 3). From the first fraction 1.2 g (48%) of diphenylbutadiyne (VI) was obtained and recrystallized (hexane). From the second fraction, 0.9 g (18%) of 4-(α-phenylethynyl)benzylidene-1,3-diphenylhydantoin (XI) was obtained and recrystallized (benzene-hexane): pale yellow needles; m.p. 228-230°; IR: 1765 and 1720 cm^{-1} (C=O); mass spectrum: m/e 440 $[M]^+$, 293 $[PhC{\equiv}CPhC{=}C{=}NPh]^+$ and 190 $[PhC{\equiv}CCPh]^+$; NMR($CDCl_3$) δ 6.8-7.7 (all aromatic protons).

Analysis found: C, 81.90; H, 4.58; N, 6.36. $C_{30}H_{20}N_2O_2$ calcd: C, 82.28; H, 4.53; N, 6.33%.

From the third fraction, 0.7 g (8.3%) of 4-benzylidene-1,3-diphenylhydantoin (XII) was obtained and recrystallized (benzene-hexane): white needles; m.p. 198° (lit.[8] 193-194°), the melting point of a mixture of compound XII and an authentic sample was not depressed.

Oxidation of XI. Potassium permanganate (0.17 g) was added at room temperature over 30 min to the hydantoin XI (0.2 g) dissolved in pyridine (10 ml)/water (1 ml). Water (5 ml) was added to the reaction mixture, and stirring was continued for 1 hr. The solution was made acid to congo red with dilute sulfuric acid decolorized by sodium bisulfite. The resultant precipitate was recrystallized (benzene-hexane) to give 0.08 g (67%) of diphenylparabanic acid (XIV): white needles; m.p. 210°, no depression of the melting point was observed for a mixture with an authentic sample[1]. IR 1770 and 1735 cm^{-1} (C=O); mass spectrum m/e 266 $[M]^+$ and 119 $[PhNCO]^+$.

Catalytic reduction of XI. The hydrogenation of the hydantoin XI (150 mg) in 150 ml of absolute EtOH over 10% of palladium on carbon (90 mg) with hydrogen (4 atom.) was undertaken at room temperature over a period of 30 hr. After filtering off the catalyst the solution was evapolated and the residue was recrystallized from ethanol-benzene to afford 72 mg (49%) of 4-(α-pheylethynyl)benzylidene-1,3-diphenylhydantoin (XIII): pale yellow needles; m.p. 176-178°; IR: 1765 and 1720 (C=O), and 1630 cm^{-1} (C=C); mass spectrum: m/e 444 $[M]^+$ and 353 $[M - PhCH_2]^+$; NMR($CDCl_3$): δ 3.4-3.7 (m, 2H, CH_2), 2.6-2.9 (m, 2H, CH_2).

Analysis found: C, 81.06; H, 5.57; N, 6.43. $C_{30}H_{24}N_2O_2$ calcd: C, 81.06; H, 5.44, N, 6.30%.

Reaction of phenylbromoacetylene with diphenylketene

A mixture of phenylbromoacetylene (0.01 mol) and iron pentacarbonyl (0.01 mol) in 25 ml THF was stirred at 66° for 30 min. Diphenylketene (0.02 mol) was added dropwise to the solution, and the mixture was heated at 66° for 15 hr with stirring. After the evapolation of the solvent, the residue was chromatogrphed and eluted with hexane (fraction 1) and benzene (fraction 2). From the first fraction, 0.4 g (39%) of diphenylbutadiyne (VI) was obtained. From the second fraction, 1.2 g (22%) of 2-bromo-3,4-diphenyl-1-diphenylacetoxynaphthalene (XV) was obtained, and recrystallized (benzene-hexane): white needles; m.p. 210-212°; IR: 1750 cm^{-1} (C=O); mass spectrum: m/e 569 $[M]^+$, 489 $[M - Br]^+$ and 375 $[M - Ph_2C=C=O]^+$; NMR($CDCl_3$): δ 6.6 (s, 1H).

Analysis found: C, 76.25; H, 4.49. $C_{36}H_{25}BrO_2$ calcd: C, 75.92; H, 4.43%.

References

1. Y. Ohshiro, K. Kinugasa, T. Minami and T. Agawa, J. Org. Chem.,35 2136 (1970).
2. G. Eglinton and W. McRae, Advan. Org. Chem., 4 225 (1963).
3. C.E. Coffey, J. Amer. Chem. Soc., 83 225 (1961).
4. L.I. Smith and H.H. Hoehn, J. Amer. Chem. Soc., 61 2619 (1936).
5. H. Ulrich, B. Tucker and A.A.R. Sayigh, Tetrahedron Lett., 1731 (1967).
6. F. Straus and L. Kolleck, Ber., 63 1878 (1930).
7. I.D. Campbell and F.G.A. Stone, Org. Syn., 45 39 (1965).
8. A.G. Davies and R.J. Puddephatt, J. Chem. Soc. C, 317 (1968).

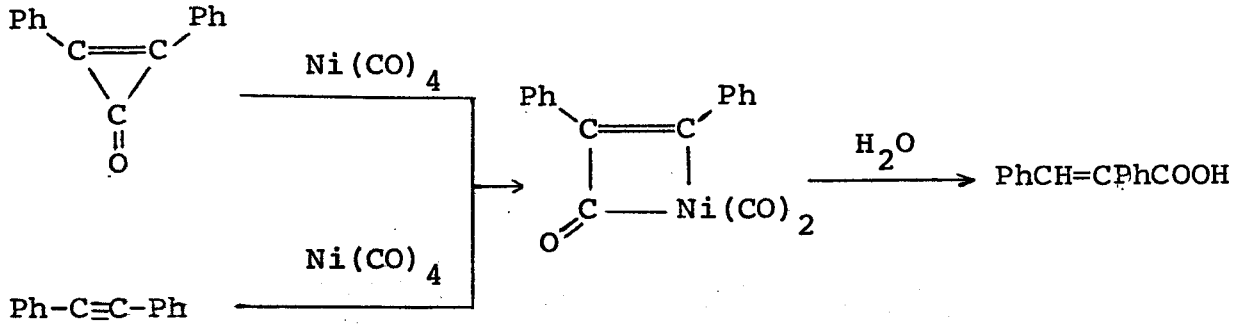
Chapter II. REACTIONS OF DIPHENYLCYCLOPROPENONE WITH KETENES IN THE PRESENCE OF NICKEL TETRACARBONYL

1) Introduction

Because of its aromaticity, the stability and the reactivity of cyclopropenones are different from those of other three membered rings. Although diphenylcyclopropenone has high reactivity toward nucleophile reagents, it has not reacted with heterocumulenes except activated isocyanates (e.g. chrolosulfonyl isocyanate)[1]. Particularly, cycloaddition reactions with heterocumulenes have not been reported. In general, for cycloaddition reactions with diphenylcyclopropenone, many reactions across the carbon-carbon double bond have reported,[2,3,4] but the reports of reactions at carbon-carbon single bond are rare[5]. The results of studies of cycloaddition reactions of diphenylcyclopropenone with ketenes in the presence of catalytic amounts of nickel tetracarbonyl have been reported in this chapter. The authors found that diphenylcyclopropenone underwent cycloadditions via cleavage of carbon-carbon single bond with ketenes to give the cyclopentene-1,2-diones and the cyclopentene-1,3-dione.

Diphenylcyclopropenone reacts with diphenylketene at 160° without catalyst to produce 2,3,4-triphenyl-1-naphthyldiphenylacetate,[6] but this product arises from the reaction with diphenylacetylene which is formed by decarbonylation of diphenylcyclopropenone.

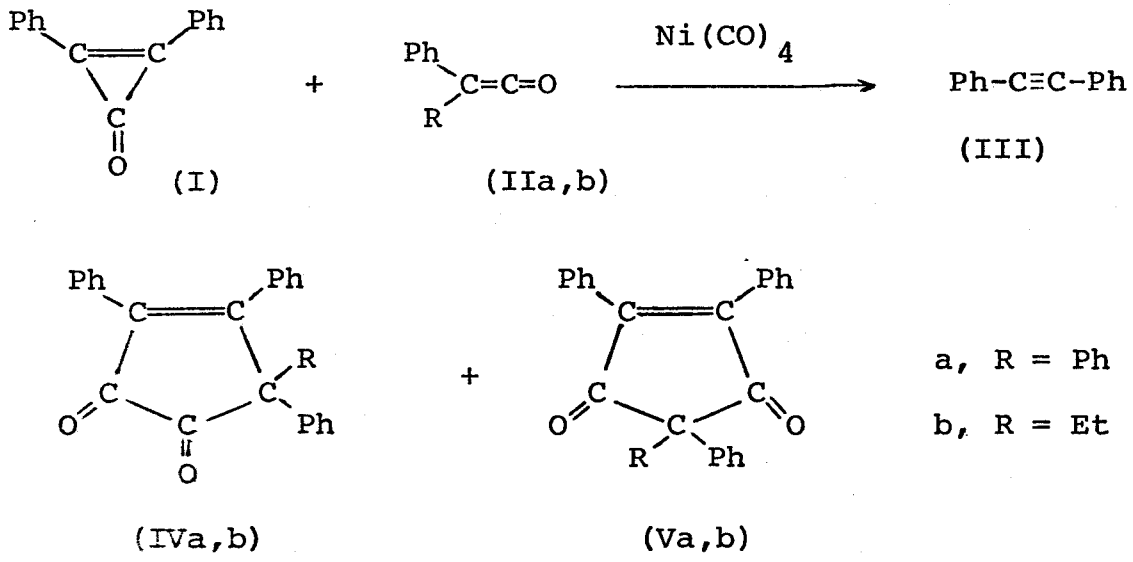
The reaction with nickel tetracarbonyl is thought to give the nickelacyclobutenone complex[7], the same complex is assumed in the reaction of diphenylacetylene[8].



On the other hand, it is reported that diphenylcyclopropenone reacts with iron carbonyls [$Fe_2(CO)_9$ or $Fe_3(CO)_{12}$] to form stable metal complexes and diphenylacetylene[9].

2) Results and discussion

In the presence of nickel tetracarbonyl, the reactions of diphenylcyclopropenone with ketenes IIa,b at 55-60° in DMF (N,N-dimethylformamide) gave diphenylacetylene (III), the cyclopentene-1,2-diones IVa,b and the cyclopentene-1,3-dione Va.



The identification of the 1,2-dione IVa and the 1,3-dione Va was carried out by ^{13}C-NMR. The spectra of these products are

shown in Fig. 1. The structure of 2,2,4,5-tetraphenyl-4-cyclopentene-1,3-dione (Va) is symmetric and the spectrum showes its one carbonyl carbon signal and one olefinic carbon signal at 201 and 152 ppm, respectively. The spectrum of 3,4,5,5-tetraphenyl-3-cyclopentene-1,2-dione (IVa) showes two carbonyl carbon signals and two olefinic carbon signals at 239, 169, 150 and 145 ppm, respectively. The 1,2-dione IVa was identified by a comparison with an authentic sample[10]. Other data of the products are shown in the experimental section.

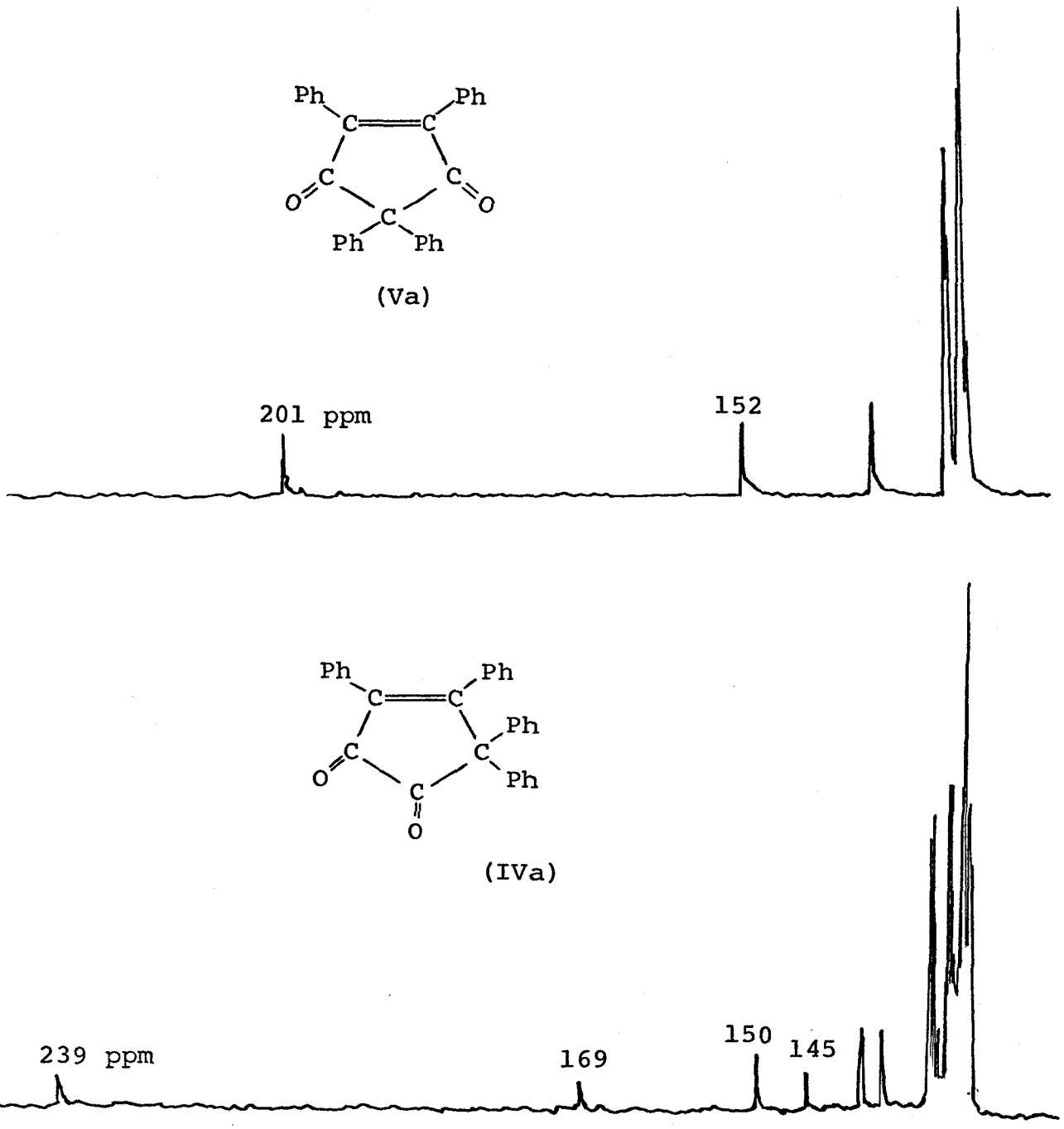
Diphenylacetylene was produced by the decarbonylation of diphenylcyclopropenone with nickel tetracarbonyl. This was confirmed in the reaction of diphenylcyclopropenone with nickel tetracarbonyl in anhydrous DMF; diphenylacetylene was isolated in 28% yield.

The results of the reactions are summarized in Table 1.

It is clear that this reaction proceeded smoothly with a catalytic amount of nickel tetracarbonyl. Previously, the authors reported that the same products were obtained in the reaction of diphenylketene with diphenylacetylene in the presence of iron pentacarbonyl, but in this case an equimolar amount of iron pentacarbonyl was necessary and the yield and the selectivity were lower[10].

The effect of solvents was significant. DMF was the most appropriate solvent and the 1,2-dione was produced selectively in the yield above 80%. The yield and the selectivity of the products were lower in THF (tetrahydrofuran), and the 1,2-dione IVa and the 1,3-dione Va were scarcely produced in benzene. The yield of the 1,2-dione IVa was lower in HMPA (hexamethylphospholic triamide) which is strong donor solvent.

Fig 1.



^{13}C-NMR spectra of the cyclopentene-1,2-dione (IVa) and the cyclopentene-1,3-dione (Va).

TABLE 1

REACTIONS OF DIPHENYLCYCLOPROPENONE WITH KETENES

PhRC=C=O					Yield (%)		
R	Cat. (molar ratio)	Solv.	Temp. (°C)	Time (hr)	III	IV	V
Ph	$Ni(CO)_4$ (1.0)	DMF	55-60	3	4.8	85.9	t**
Ph	$Ni(CO)_4$ (0.5)	DMF	55-60	3	4.8	84.5	t**
Ph	$Ni(CO)_4$ (0.3)	DMF	55-60	3.5	9.2	83.4	-*
Ph	$Ni(CO)_4$ (0.1)	DMF	55-60	4	9.1	78.8	-*
Ph	$Ni(CO)_4$ (1.0)	C_6H_6	65-70	5	14.7	7.8	3.1
Ph	$Ni(CO)_4$ (0.1)	C_6H_6	65-70	6	56.0	3.7	-*
Ph	$Ni(CO)_4$ (1.0)	THF	55-60	4	24.1	11.0	8.5
Ph	$Ni(CO)_4$ (0.3)	HMPA	55-60	3.5	9.4	29.1	-*
Et	$Ni(CO)_4$ (0.3)	DMF	55-60	3.5	5.8	85.3	-*
Ph***	$Fe(CO)_5$ (0.5)	DMF	80	5	9.4	-*	-*
Ph****	$Ni(CO)_4$ (0.3)	DMF	r.t.	120	t**	17.5	-*

* Not detected. ** Trace amount. *** Cyclopropenone was recovered in 88% yield.

**** This reaction was carried out in a seald tube.

This reaction proceeded even at room temperature, but the rate was slow. Iron pentacarbonyl did not act as a catalyst, and thus diphenylcyclopropenone was recovered quantitatively.

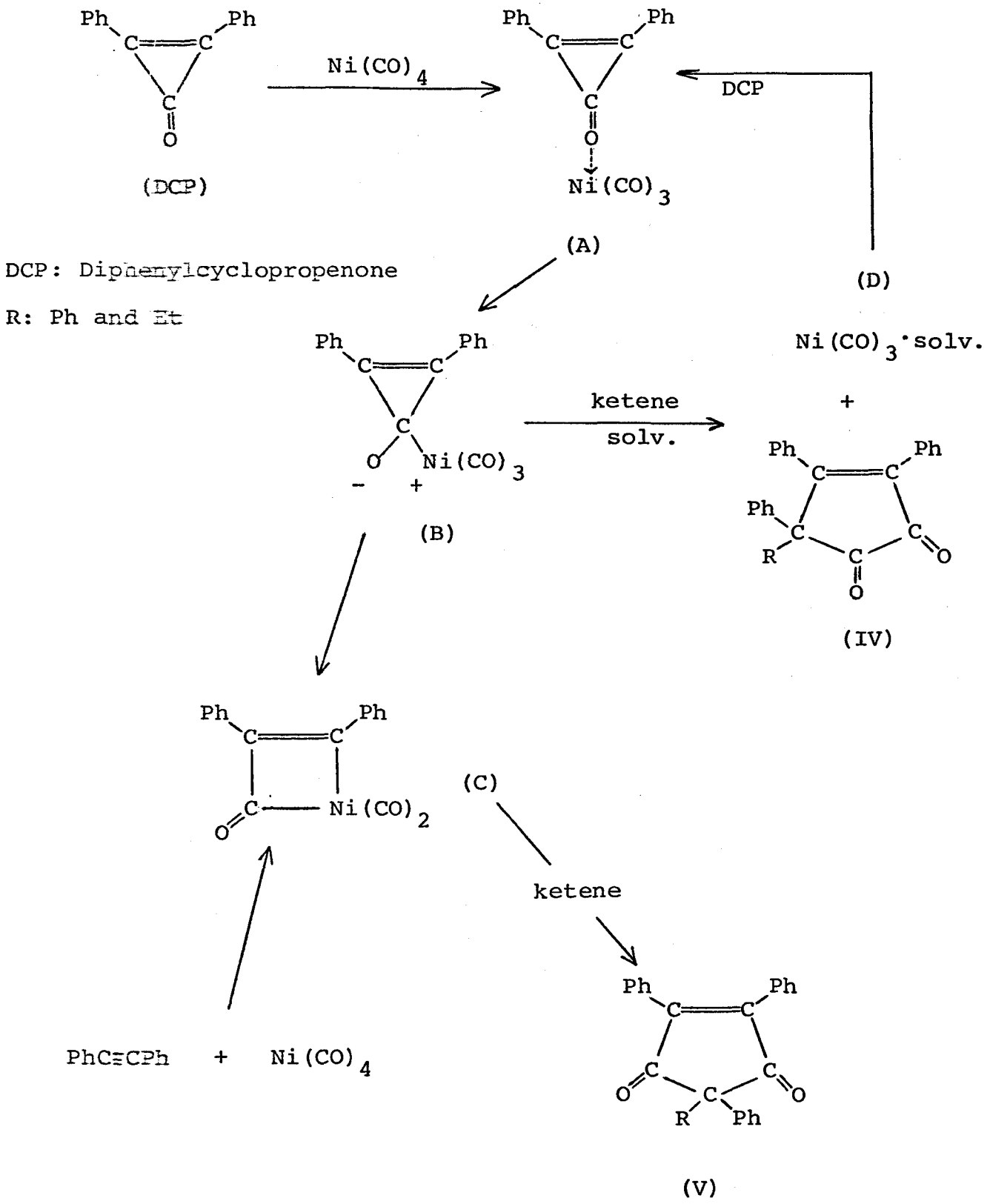
A possible mechanism is shown in Fig 2.

Previously, the reaction of diphenylacetylene with diphenylketene in the presence of an equimolar amount of nickel tetracarbonyl was reported[10], and only the 1,3-dione was produced in 12 % yield without the formation of the 1,2-dione. In it, the 1,3-dione Va was believed to be produced *via* the nickelacyclobutenone complex C. If the reactions of diphenylcyclopropenone proceeded *via* the nickelacyclobutenone complex, an equimolar amount of nickel tetracarbonyl would be necessary and the cyclopentene-1,3-dione Va,b would be obtained as main products. C.W. Bird and coworkers reported that a cyclopropenone was liable to coordinate to metal from oxigen[11].

From these facts, the reaction path was assumed as follows. The oxigen coordinated complex A was formed first, and then it changed to the intermediate B. One molar equivalent of the ketene reacted with the intermediate B to produce the cyclopentene-1,2-dione IVa,b. On the other hand, the complex B changed to the nickelacyclobutenone complex C and the ketene reacted to produce the cyclopentene-1,3-dione Va,b.

The complex B was considered to be stabilized by polar solvent. DMF was the most effective solvent in this reaction and the formation of the 1,2-dione was predominant by the smooth reaction of the ketene. The formation of IV was not selective in THF. In HMPA, however, the yield of the 1,2-dione was low although HMPA was thought to stabilize the complex B. To explain the solvent effect, the complex D, $Ni(CO)_3 \cdot solv.$, would be considered

Fig 2.


Ph
Ph
Ni(CO)4
DCP
(DCP)
Ni(CO)3
(A)
(D)
DCP: Diphenylcyclopropenone
R: Ph and Et
Ni(CO)3·solv.
+
ketene
solv.
Ni(CO)3
(B)
(IV)
Ni(CO)2
(C)
ketene
PhC≡CPh + Ni(CO)4
(V)

as an actve species from the fact that the reaction of using DMF proceeded smoothly with catalytic amounts of nickel tetracarbonyl. A similar species was assumed by P. Koch and coworkers.[12] In HMPA its coordinating ability was too strong to reform the complex B from the active species D with diphenylcyclopropenone. The solvent must have a suitable coordinating property to become effective. DMF was the most suitable solvent and the reaction did not proceed in a non-coordinating solvent (benzene).

3) Summary

Reactions of diphenylcyclopropenone with ketenes in the presence of catalytic amounts of nickel tetracarbonyl have been studied. The 1:1 cycloadducts, cyclopentene-1,2-dione derivatives, were obtained in the yields above 80% from the reactions in DMF. In these reactions, solvent effects were significant, and DMF was the most excellent solvent. Iron pentacarbonyl did not act as a catalyst. Reaction mechanisms and solvent effcts were discussed. An active species of this reaction was proposed [$Ni(CO)_3 \cdot solv.$].

4) Experimental Section

All melting points were determined on Yanagimoto micro melting point apparatus and are uncorrected.

Infrared spectra were recorded on Nujol mulls of solids with a JASCO IR-E spectrometer. Proton magnetic resonance spectra were taken with a JEOL LNM-3H-60 specrometer with TMS as the internal standard. Mass spectra were taken with a HITACHI RMU-6E. ^{13}C-NMR spectra were taken on a JEOL FX-100 spectrometer with TMS as the internal standard.

All reactions were carried out under a nitrogen atmosphere in a four necked flask equipped with a magnetic stirrer and a reflux condenser.

Reactions and post-treatments were carried out in a closed system, and residual nickel carbonyl was decomposed by addition of iodine, and all glasswares were washed with iodine-acetone solution.

Chromatographic separations were carried out using silica gel columns.

Materials

Nickel tetracarbonyl[13], diphenylketene, ethylphenylketene,[14] and diphenylacetylene[15] were prepared by reported methods. Commercial iron pentacarbonyl was used without further purification. Diphenylcyclopropenone was prepared from dibenzylketone in the usual way.[16]

DMF and HMPA were dried over calcium hydride. THF and benzene were dried by refluxing over sodium wire.

Reactions of diphenylcyclopropenone with ketenes.

(a). Reaction with diphenylketene in the presence of nickel tetracarbonyl. A mixture of diphenylcyclopropenone (8 mmol) and nickel tetracarbonyl (2.4 mmol) in 30 ml of DMF was stirred for 30 min at room temperature. Diphenylketene (8 mmol) was added to the mixture, and then this mixture was heated at 55-60° for 3.5 hr with stirring. Subsequently, 100 ml of 15% of HCl was added and the mixture was extracted with 150 ml of ether. The organic layer was dried over Mg_2SO_4, concentrated in vacuo, and the residue was recrystallized from benzene-hexane to give 2.0 g of 3,4,5,5-tetraphenyl-3-cyclopentene-1,2-dione (IVa): green-yellow needles; m.p. 230-232° (lit[10]. 231-232°); IR: 1755 cm^{-1} (C=O); mass spectrum: m/e 400 $[M]^+$, 372 $[M - CO]^+$, 344 $[M - 2CO]^+$, 194 $[Ph_2C=C=O]^+$ and 178 $[PhC=CPh]^+$; NMR($CDCl_3$): δ 6.8-7.3 (all aromatic protons).

Analysis found: C, 87.19; H, 4.79. $C_{29}H_{20}O_2$ calcd: C, 86.97; H, 5.03%.

The filtrate was chromatographed and eluted with hexane (fraction 1) and hexane-benzene (fraction 2 and 3). From the first fraction 0.13 g of diphenylacetylene (III) was obtained and recrystallized (hexane-benzene); white needles; m.p. 60-61° (lit.[15] 60-61°). No depression of the melting point was observed for the mixture with an authentic sample. From the second fraction, a trace amount of 2,2,4,5-tetraphenyl-4-cyclopentene-1,3-dione (Va): yellow needles ; m.p. 198-200° (lit.[10] 196.5-197.5); IR: 1730 and 1700 cm^{-1} (C=O); mass spectrum: m/e 400$[M]^+$, 372, 344, 194 and 178.

Analysis found: C, 86.81; H, 4.90. $C_{29}H_{20}O_2$ calcd: C, 86.97; H, 5.03%.

From the third fraction, 0.7 g of the 1,2-dione IVa was obtained (total yield 83.4%).

Other reactions of diphenylcyclopropenone with diphenyketene in the presence of nickel tetracarbonyl were carried out in the same manner as above. The results of the reactions are summarized in Table 1.

(b) The reaction with ethylphenylketene in the presence of nickel tetracarbonyl. Ethylphenylketene (9.7 mmol), diphenylcyclopropenone (9.7 mmol) and nickel tetracarbonyl (2.9 mmol) were heated in 35 ml of DMF at 55-60° for 3.5 hr with work-up carried out in a manner similar to that described above. Diphenylacetylene (0.1 g) (III) was obtained (5.8% yield). 5-Ethyl-3,4,5-triphenyl-3-cyclopentene-1,2-dione (IVb) was obtained (2.9 g, 85.3% yield) and recrystallized (benzene-hexane): green-yellow needles; m.p. 196-198°; IR: 1750 cm^{-1} (C=O); mass spectrum: m/e 352 $[M]^+$, 347 $[M - CH_3]^+$, 324 $[M - CO]^+$, 323 $[M - Et]^+$, 234 $[PhC-CPhCOCO]^+$, 206 and 178 $[PhC=CPh]^+$; NMR($CDCl_3$) δ 0.68 (t, 3H, $-CH_3$), 2.15 (q, 2H, $-CH_2-$), 7.1-7.48 (m, 15H, aromatic protons).

Analysis found: C, 85.12; H, 5.95. $C_{25}H_{20}O_2$ calcd: C, 85.20; H, 5.72%.

Pure 2-ethyl-2,4,5-triphenyl-4-cyclopentene-1,3-dione (Vb) was not isolated because of its very low yield, but it was identified by means of its IR spectrum (1730 and 1700 cm^{-1} as C=O).

(c) The reaction with diphenylketene in the presence of iron pentacarbonyl Diphenylcyclopropenone (6 mmol), diphenylketene (6 mmol) and iron pentacarbonyl (3 mmol)were allowed to react in 25 ml of DMF at 80° for 5 hr. Thirty ml of 15% of HCl was added and the mixture was extracted with 200 ml of ether, concentrated and chromatographed. Diphenylacetylene was obtained (0.1 g, 9.4%

yield). Diphenylketene was converted to diphenylacetic acid by adding water (1.1 g, 86% yield). Diphenylcyclopropenone was recovered (eluted with ethanol, 1.1 g, 88% yield).

Reaction of diphenylcyclopropenone with nickel tetracarbonyl.

Diphenylcyclopropenone (4 mmol) was heated with 2 mmol of nickel tetracarbonyl in 15 ml of anhydrous DMF for 5 hr. The reaction mixture was extracted with 100 ml of ether and washed with 100 ml of water. The organic layer was concentrated and chromatographed. Diphenylacetylene was obtained (eluted with hexane, 0.2 g, 25.8% yield).

^{13}C Nuclear magnetic resonance spectral data of the 1,2-dione IVa and the 1,3-dione Va.

(a) Va ($CDCl_3$); ppm (TMS; internal standard) 200.762, 151.677, 138.026, 130.018, 128.562, 127.712, and 63.887.

(b) IVa ($CDCl_3$); ppm (TMS; internal standard) 239.597, 168.898, 149.858, 144.703, 138.757, 136.510, 131.477, 131.112, 130.384, 129.593, 128.807, 128.501, 127.895, and 127.229.

References

1. L. A. Paquette, T. J. Barton and N. Harton, Tetrahedron Lett., 5039 (1967); 2289 (1968).
2. M. Franc-Neuman, Tetrahedron Lett., 341 (1966).
3. J. W. Lown, T. W. Malloney and G. Dallas, Can. J. Chem., 48 89 (1970).
4. J. Ciabattoni and G. A. Berchtold, J. Amer. Chem. Soc., 87 1404 (1965).
5. N. Obata and T. Takizawa, Tetrahedron Lett., 3403 (1969).
6. R. Gompper, A. Staudeneer and W. Elser, Tetrahedron Lett., 1019 (1968).
7. G. Ayrey, C. W. Bird and E. M. Briggs, Organometal. Chem. Syn., 1 (1970/71) 187.
8. C. W. Bird and E. M. Briggs, J. Chem. Soc. C, 1265 (1967).
9 C. W. Bird and E. M. Briggs, ibid., 1862 (1967).
10. K. Kinugasa and T. Agawa, Organometal. Chem. Syn., 1 (1972) 427.
11. C. W. Bird and E. M. Briggs, J. Chem. Soc. C, 1004 (1967).
12. P. Koch and E. Perrotti, J. Organometal. Chem., 81 111 (1974).
13. G. P. Chiusoli and G. Mondelli, Chem. Ind.(Milan), 43 259 (1961).
14. L. I. Smith and H. H. Hoehn, Org. Syn. Collective Vol. 3 356 (1955).
15. A. C. Cope, D. S. Smith and R. J. Cotter, ibid., Vol. 4 377 (1955).
16. R. Breslow and J. Posner, ibid., Vol. 5 514 (1973).

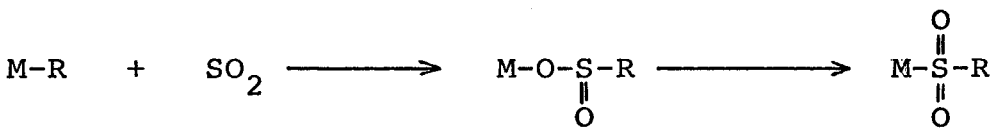
Chapter III. REACTIONS OF N-SULFINYLAMINES WITH DIPHENYLCYCLOPROPENONE, DIPHENYLACETYLENE IN THE PRESENCE OF METAL CARBONYLS.

1) Introduction

In the chapter II, it was defined that reactions of diphenylcyclopropenone with ketenes have proceeded smoothly in the presence of a catalytic amount of nickel tetracarbonyl.

In this chapter, N-sulfinylamines have been taken up as heterocumulenes. Generally, sulfur compounds have high affinity for transition metals, and a many of organometal complexes have been isolated.[1,2]

In the studies of the interactions of metal carbonyls with heterocumulenes, the interaction with sulfur dioxide has been studied most closely. Sulfur dioxide inserts smoothly between the carbon-metal bonds of metal complexes in the way to be shown in the following scheme[3].



Moreover, reactions of organometal complexes with sulfur dioxide in other mode have been reported.[4,5]

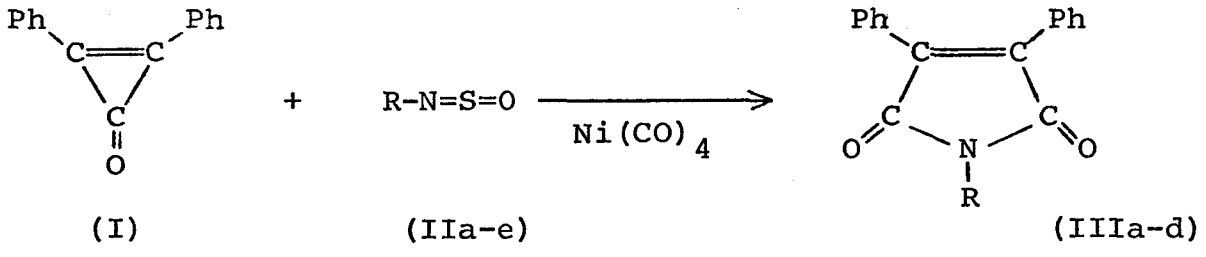
From these facts, it is expected that N-sulfinylamines would also react with a metal complex, indeed, metal complexes of N-sulfinylamines have been isolated.[6]

In this chapter, N-sulfinylamines have been used, and the reactions of them with diphenylcyclopropenone or with diphenylacetylene in the presence of metal carbonyls have been investigated in comparison with the reactions of ketenes in Chapter II.

2) Results and discussion

2-A. Reactions of diphenylcyclopropenone with N-sulfinynylamines in the presence of metal carbonyls.

Reactions of diphenylcyclopropenone with N-sulfinylamines were carried out in the presence of an equimolar amount of nickel tetracarbonyl. In these reactions, pyrroline-2,5-dione derivatives (IIIa-d) and/or isothiazolone-1-oxide derivatives (IVd,e) were produced. The results of these reactions are shown in Table 1.



(I) (IIa-e) (IIIa-d)

and/or

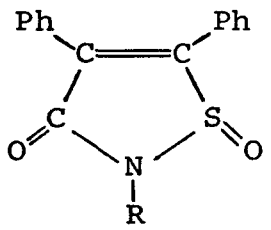
a, R = Ph

b, R = p-Cl-C_6H_4

c, R = p-CH_3-C_6H_4

d, R = p- CH_3O-C_6H_4

e, R = Cyclohexyl



(IVd,e)

The structure of the products were determined by the spectral and analytical data. The ir spectrum of the 1:1 cycloadduct, 2-p-methoxyphenyl-4,5-diphenyl-3-isothiazolone-1-oxide (IVd), showed one absorption band at 1700 cm^{-1} (C=O), and 1-p-methoxyphenyl-3,4-diphenylpyrroline-2,5-dione (IIId) was charactarized by two absorption bands of carbonyl groups at 1730 and 1700 cm^{-1} (C=O).

As shown in TABLE 1, the reactivity was affected significantly

TABLE 1. REACTIONS OF N-SULFINYLAMINES WITH DIPHENYLCYCLOPROPENONE.

R-N=S=O R	cat.	solv.	temp.(°C)	time(hr)	yields (%) (III)	 (IV)
Phenyl	$Ni(CO)_4$	DMF	65-70	3	78	t*
p-Cl-C_6H_4	"	"	"	3	95	-**
p-CH_3-C_6H_4	"	"	"	3	42	-*
p-CH_3O-C_6H_4	"	"	"	3	33(mix.)***	
Cyclohexyl	"	"	"	4	-*	36
Phenyl	" (1/3)	"	"	5	24	-*
Phenyl****	"	benzene	75-80	4	42	-*
Phenyl	$Fe(CO)_5$	DMF	80-85	5.5	-*	22

*Not detected.

** Trace amount.

*** The each yields of IIId and IVd were not determined.

**** In this reaction, extraction was not carried out.

by the substituent group of a N-sulfinylamine. A N-sulfinylarylamine had higher reactivity than a N-sulfinylalkylamine, moreover, an electron-withdrawing substituent promoted the cycloaddition reactions.

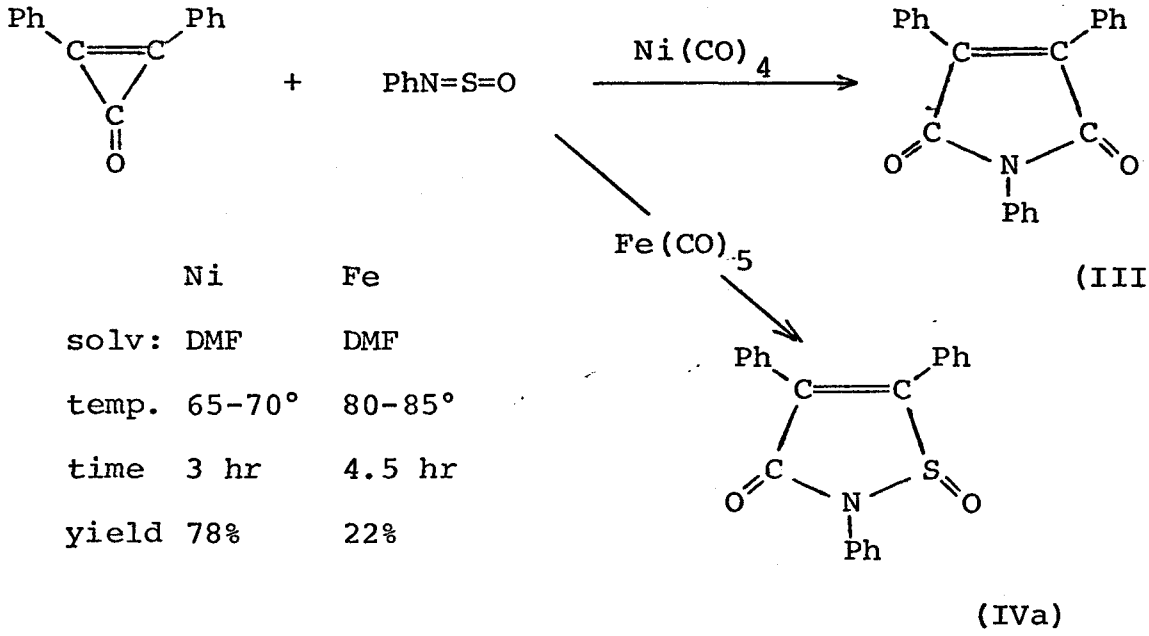
In these reactions, solvent effect was not so significant in comparison with it in the reactions of ketenes with diphenylcyclopropenone, that is, even in benzene an adduct was produced in 42% yield (See TABLE 1). The reaction of diphenylketene scarcely produced the cycloadduct in benzene (See Chapter II).

Unlike the reaction of a ketene in the presence of catalytic amounts of nickel tetracarbonyl, an equimolar amount of a metal carbonyl was necessary in the reaction of a N-sulfinylamine.

While the products IV were ordinary 1:1 adducts of a N-sulfinylamine and diphenylcyclopropenone, the products III were regarded as 1:1 adducts of an isocyanate and diphenylcyclopropenone. So, the reaction of pheny isocyanate and diphenylcyclopropenone was carried out, but the product IIIa (1,3,4-triphenylpyrroline-2,5-dione) was not obtained at all, this reaction gave the trimer of the isocyanate quantitatively. From this result, the pyrroline-2,5-dione derivatives III were thought to be produced by the exchange of C=O of nickel tetracrbonyl for S=O of a N-sulfinylamine in the course of the cycloaddition reaction.

Substituent effects were observed not only in the reactivity, but in the interesting exchange reactions, namely an electron-withdrawing substituent stimulated the exchange of C=O for S=O. The reaction of N-sulfinyl-p-chloroaniline produced the exchanged product, quantitatively. On the other hand, N-sulfinyl-p-anisidine yielded both the exchanged and unexchanged products. A N-sulfinylalkylamine produced only the unexchanged 1:1 cycloadduct.

Iron pentacarbonyl was also active in this reaction. Although the yield of the product was lower, but only the unexchanged product was obtained by iron pentacarbonyl even in the case of the reaction to give the exchanged product in the presence of nickel tetracarbonyl. For example, the reaction of N-sulfinylaniline with diphenylcyclopropenone gave 1,3,4-triphenylpyrroline-2,5-dione (IIIa) in the presence of nickel tetracarbonyl, on the other hand, in the reaction of using iron pentacarbonyl 2,4,5-triphenyl-3-isothiazolone-1-oxide (IVa) was obtained.



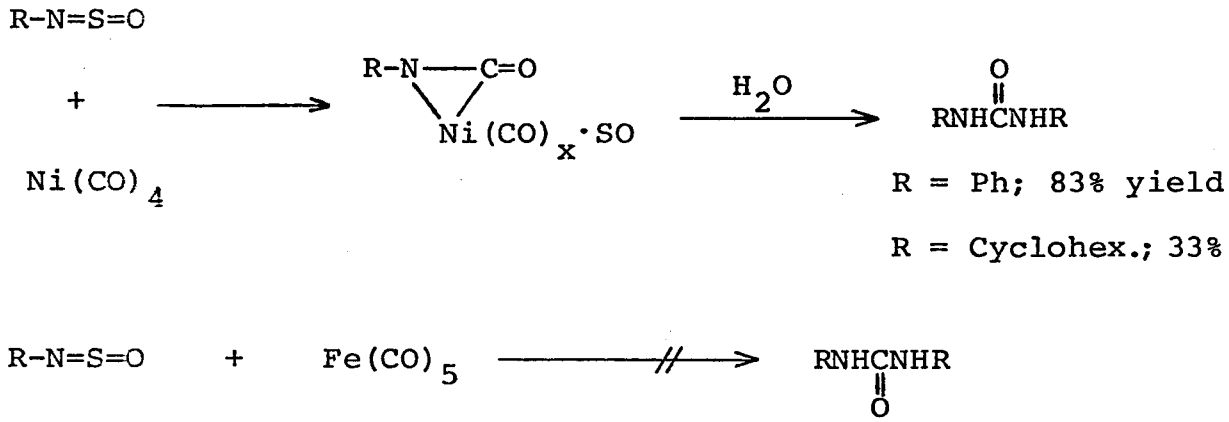
(IIIa)

(IVa)

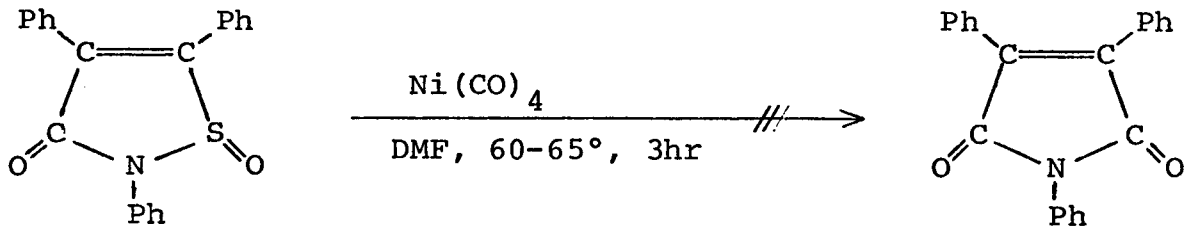
Now, the author carried out the reactions of N-sulfinylamines with nickel tetracarbonyl, and with iron pentacarbonyl, to investigate those interactions, and it was defined that an exchange reaction was caused by nickel tetracarbonyl, but iron pentacarbonyl did not act in the exchange reaction. Substituent effects of N-sulfinylamines were also observed in these investigations.

From this investigation, it was quite possible that the distinction between the reaction of using iron pentacarbonyl and

the reaction in the presence of nickel tetracarbonyl was because of the difference in the interaction of a metal carbonyl with a N-sulfinylamine.



Although it was already defined that the exchanged products were not formed by an isocyanate with diphenylcyclopropenone, it was thought considerably that unexchanged product was produced once, and then it was converted to an exchanged product by nickel tetracarbonyl. Consequently, the reaction of isothiazolone-1-oxide IVa with nickel tetracarbonyl was tried out, but no exchange reaction was occurred.



(IVa)

From these results, the exchange reaction of C=O for S=O would be occurred in the intermediary complex, and a free isocyanate would not be formed in this reaction.

On the basis of these investigations, the reaction mechanisms

were assumed as shown in Scheme 1. Two reaction paths (A and B) could be assumed.

Path A: In the similar manner as the reactions with ketenes, the complex A was formed first. From the fact that there was no adduct to be produced from this complex A with N-sulfinylamine like as the reaction with a ketene (products a and b), the complex A was transformed smoothly into the nickelacyclobutenone complex B. A N-sulfinylamine reacted with this complex to form the intermediary complex C, and then a pyrroline derivative and an isothiazolone derivative were produced by exchange and unexchange of C=O for S=O, respectively.

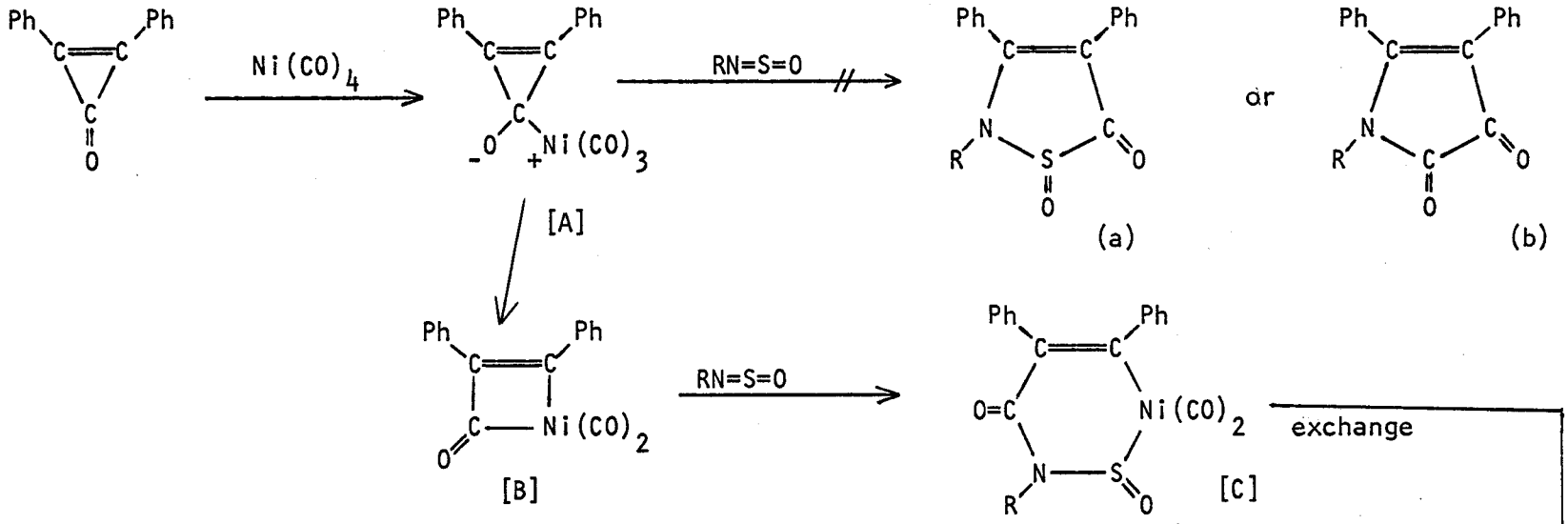
Path B: In this reaction path, the formation of the complex D by a N-sulfinylamine with nickel tetracarbonyl was the first step, and then diphenylcyclopropenone reacted with the D to form the intermediate C or E. Subsequently, the complex C and E were converted into the isothiazolone and the pyrroline, respectively. It could not be determined how and when the exchange reaction of C=O for S=O was occurred.

The author could not defined which path was correct, but the path B would be more possible because of the results that the products a and b were not produced, and that N-sulfinylamines interacted with nickel tetracarbonyl more strongly than diphenylcyclopropenone.

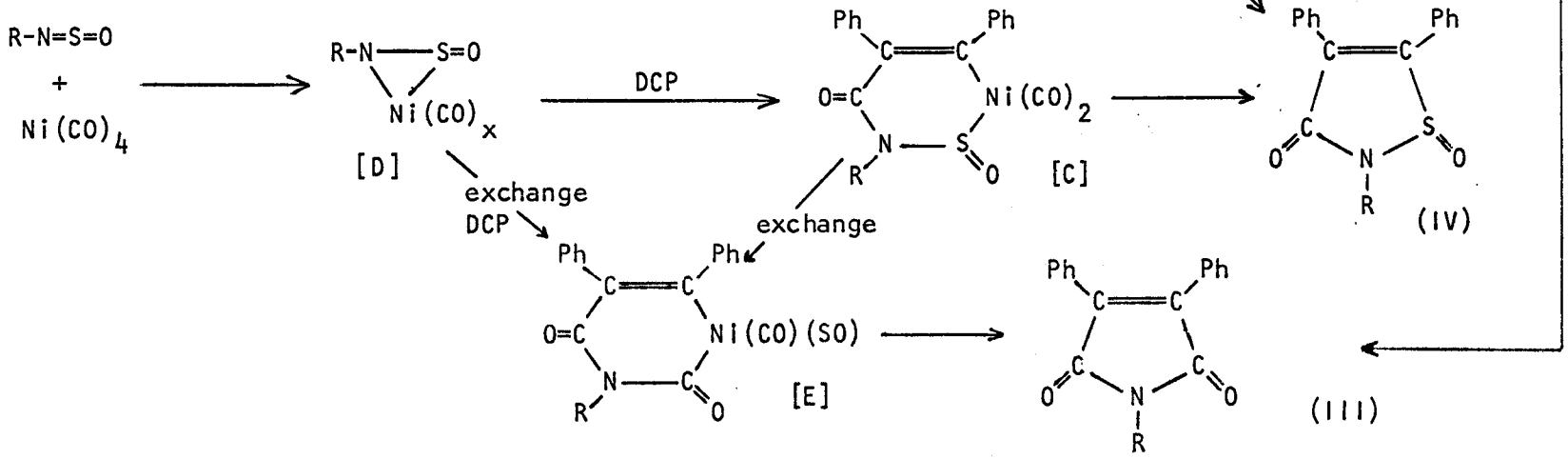
In this section, the procedure of the syntheses of heterocyclic compounds by the reactions of diphenylcyclopropenone with N-sulfinylamines was presented. These cycloaddition reactions did not proceed without metal carbonyls, moreover the interesting exchange reactions of C=O for S=O were occurred readily by nickel tetracarbonyl, and the exchange reaction could be prevented by

Scheme 1

Path A:



Path B:

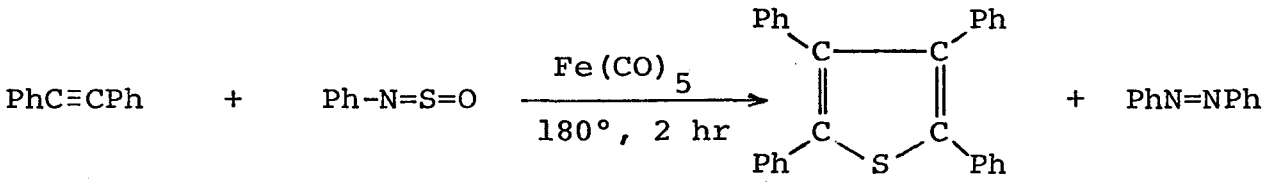


using of iron pentacarbonyl instead of nickel tetracarbonyl and ordinary 1:1 cycloadducts could be obtained.

2-B. Reaction of diphenylacetylene with N-sulfinylaniline in the presence of metal carbonyls.

As already described, nickelacyclobutenone complex was thouhgt to be formed not only from a cyclopropenone, but from an acetylene. At first, the reaction of diphenylacetylene with N-sulfinylaniline was carried out in the presence of nickel tetracarbonyl, but the interaction of the aniline with nickel tetracarbonyl was too strong to react with diphenylacetylene, and diphenylurea was obtained quantitatively without adducts with the acetylene.

Instead of nickel tetracarbonyl, iron pentacarbonyl was used in this investigation. The reaction was carried out at 180° for 2 hr without solvent, and gave tetraphenylthiophene in 74% yield together with azobenzene.

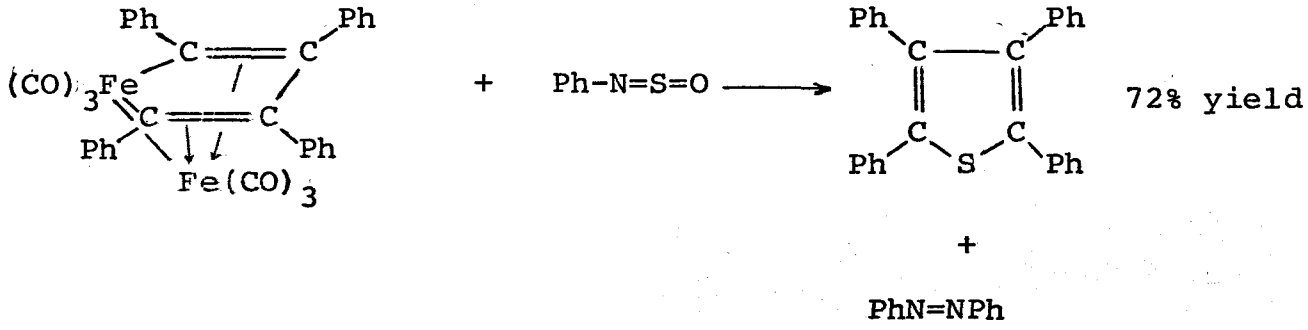


74% yield

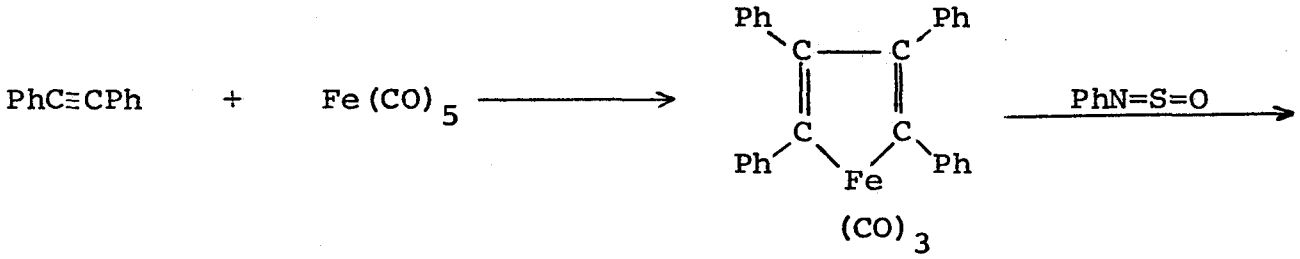
From the results, this reaction was seemed to be essentially different from the reaction with diphenylcyclopropenone.

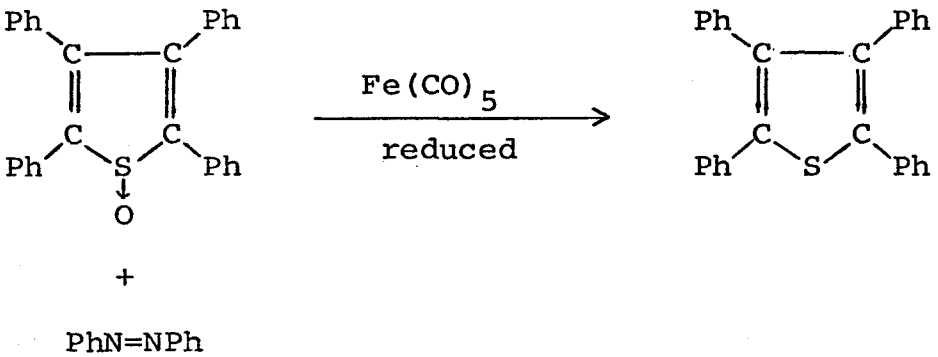
E. Bray and coworkers[7] reported on the formation of tetraphenylthiophene by the reaction of ferracyclopentadiene with sulfur. On the basis of this report, the reaction of the ferracyclopentadiene complex with N-sulfinylaniline was tried out and gave

tetraphenylthiophene in 72% yield.



From this investigation, in this reaction, N-sulfinylaniline did act a similar part as sulfur in the Bray's study. Reaction scheme was assumed as shown in following scheme.





At first, a ferracyclopentadiene complex was formed, and then a sulfoxide was produced. This sulfoxide was reduced to tetraphenylthiophene by iron pentacarbonyl.

It was clear that the difference of the reactions with diphenylcyclopropenone between the reaction with diphenylacetylene was based on the distinction of the ability of the formation of

the complex with a metal carbonyl.

3. Summary

Under the presence of a metal carbonyl, the reaction of diphenylcyclopropenone with N-sulfinylamines were investigated in the section A. In these studies, it was defined that the cycloaddition reaction proceeded smoothly by using metal carbonyls to gave pyrroline-2,5-dione derivatives and isothiazolone-1-oxide derivatives. A substituent of a N-sulfinylamine affected excellently this reaction, and an electron-withdrawing substituent promoted the cycloaddition reaction. The pyrroline derivative was produced by the exchange of C=O of nickel tetracarbonyl for S=O of a N-sulfinylamine, a substituent of a N-sulfinylamine also affected this exchange reaction. Iron pentacarbonyl prevented the exchange, and gave the ordinary 1:1 adduct, the isothiazolone derivative. In comparison with the reaction with a ketene, solvent effect was not so significant, and an equimolar amount of a metal carbonyl was necessary. In this reaction, the formation of the complex of a N-sulfinylamine with a metal carbonyl would be the first step, and a possible reaction path was proposed.

In the section B, the reaction of N-sulfinylaniline with diphenylacetylene was not occurred by nickel tetracrbonyl, but occurred by iron pentacarbonyl. This reaction proceeded via a ferracyclopentadiene complex and essentially different from the reaction of diphenylcyclopropenone.

4) Experimental section

The melting points, IR, mass, and nmr spectra were taken with the same instruments in Chapter II.

All reactions were carried out in a draft, and the residual metal carbonyls were decomposed by iodine-acetone solution.

Materials.

N-Sulfinylamines[8], diphenylcyclopropenone[9], diphenylacetylene[10], nickel tetracarbonyl[11] and ferracyclopentadiene complex[12] were prepared in reported procedures.

Commercial iron pentacarbonyl and phenyl isocyanate were used without further purification.

A. Reactions with diphenylcyclopropenone.

A-1. Reactions in the presence of nickel tetracarbonyl.

Reaction of the N-sulfinylamine IIa.

A solution of diphenylcyclopropenone (9.7 mmol) with nickel tetracarbonyl (9.7 mmol) in 30 ml of DMF was stirred at room temperature for 0.5 hr. N-Sulfinylaniline (IIa) (9.7 mmol) was added to the mixture, and then the reaction mixture was heated at 65-70°C for 3 hr. Subsequently, the mixture was extracted with 150 ml of ether and washed with 200 ml of water. After drying over Mg_2SO_4, the solution was concentrated and then the residual needles were recrystallized from benzene-hexane, the filtrate was concentrated and was chromatographed on silica gel [eluted with hexane (fraction 1) and benzene-hexane (fraction 2)].

From the first fraction, 0.1 g of diphenylacetylene was obtained (5.8% yield): white needles; m.p. 60-61°(lit.[10] 60-61°).
From the recrystallization and the fraction 2, 2.45 g of 1,3,4-triphenylpyrroline-2,5-dione (IIIa) was obtained (78% yield); yellow needles; m.p. 184-185°; IR(Nujol): 1760 and 1700 cm^{-1} (C=O); mass: m/e 325 $[M]^+$, 297 $[M - CO]^+$, 206 [cyclopropenone]$^+$, and 178 $[PhC{=}CPh]^+$; nmr($CDCl_3$): δ 7.1-7.65 (H_{arom}).

Analysis found: C, 81.31; H, 4.58; N, 4.32. $C_{22}H_{15}O_2N$ calcd: C, 81.21; H, 4.65; N, 4.31%.

Reaction of N-sulfinylamine IIb.

N-Sulfinyl-p-chroloaniline (IIb) (6 mmol), diphenylcyclopropenone (6 mmol) and nickel tetracarbonyl (6 mmol) were reacted in the similar manner as above, but in this reaction a column treatment was not necessary.

1-p-Chrolophenyl-3,4-diphenylpyrroline-2,5-dione (IIIb) was obtained from benzene-hexane (2.2 g; 95% yield): yellow needles; m.p. 195-197°; IR(Nujol): 1755 and 1700 cm^{-1} (C=O); mass: m/e 359 $[M]^+$, 331 $[M - CO]^+$, 206 and 178; nmr($CDCl_3$): δ 7.15-7.60 (H_{arom}).

Analysis found: C, 73.41; H, 3.76; N, 4.02. $C_{22}H_{14}O_2NCl$ calcd: C, 73.43; H, 3.92; N, 3.91%.

Reaction of N-sulfinylamine IIc.

N-Sulfinyl-p-toluidine (IIc) (6 mmol), diphenylcyclopropenone (6 mmol) and nickel tetracarbonyl (6 mmol) were reacted in a similar manner as described in the reaction of IIa.

1-p-Tolyl-3,4-diphenylpyrroline-2,5-dione (IIIc) was obtained (0.85 g; 42% yield): yellow needles; m.p. 193-194°; IR(Nujol): 1755 and 1700 cm^{-1} (C=O); mass: m/e 339 $[M]^+$, 311 $[M - CO]^+$, 247 [M -

$CH_3C_6H_4]^+$, 206 and 178; nmr($CDCl_3$): δ 2.38 (s, 3H, CH_3) and 7.15-7.65 (m, 14H, aromatic).

Analysis found: C, 81.20; H, 5.14; N, 4.23. $C_{23}H_{17}O_2N$ calcd: C, 81.39; H, 5.05; N, 4.13%.

Reaction of N-sulfinylamine IId.

N-Sulfinyl-p-anisidine (IId) (6 mmol), diphenylcyclopropenone (6 mmol) and nickel tetracarbonyl (6 mmol) were reacted in a similar manner as above. Although both the pyrroline derivative and isothiazolone derivative were produced, the complete separation was very difficult and so the each yields were not determined. The total yield of the products was 33% (0.7 g).

1-p-Methoxyphenyl-3,4-diphenylpyrroline-2,5-dione(IIId): yellow needles; m.p. 196-197°; IR(Nujol): 1752 and 1700 cm^{-1} (C=O); mass: m/e 355$[M]^+$, 340 [M - CH_3], 327 $[M - CO]^+$, 206 , 178 and 149 [$CH_3OC_6H_4$-N=C=O]; nmr($CDCl_3$): δ 3.58 (s, 3H, $-OCH_3$) and 6.9-7.65 (m, 14H, aromatic).

Analysis found: C, 77.79; H, 4.62; N, 3.93. $C_{23}H_{17}O_3N$ calcd: C, 77.73; H, 4.82; N, 3.94%.

2-p-Methoxyphenyl-4,5-diphenyl-3-isothiazolone-1-oxide (IVd): pale yellow needles; m.p. 153-155°; IR(Nujol): 1705 (C=O) and 1100 cm^{-1} (S=O); mass: m/e 375 $[M]^+$, 360 $[M - CH_3]^+$, 210 $[PhC{=}CPhS]^+$, 206 and 178: nmr($CDCl_3$): δ 3.85 (s, 3H, $-OCH_3$) and 6.95-7.6 (m, 14H, aromatic).

Analysis found: C, 70.65; H, 4.59; N, 3.80. $C_{22}H_{17}O_3NS$ calcd: C, 70.39; H, 4.57; N, 3.73%.

In this reaction, trace amount of diphenylacetylene was obtained.

Reaction of N-sulfinylaniline IIe.

N-sulfinylcyclohexylamine (6 mmol), diphenylcyclopropenone (6 mmol) and nickel tetracarbonyl (6 mmol) were reacted in a similar manner as described in the reaction of IIa.

2-Cyclohexyl-4.5-diphenyl-3-isothiazolone-1-oxide (IVe) was obtained by recrystallization from benzene-hexane (0.75 g, 36% yield): pale yellow needles; m.p. 183-184°; IR(Nujol): 1685 (C=O) and 1085 cm^{-1} (S=O); mass: m/e 351 $[M]^+$, 335 $[M - O]^+$, 254 [M - $C_6H_{11}N$], 226 [M - $C_6H_{11}NCO$] and 178; nmr($CDCl_3$): δ 1.00-2.36 (m, 10H, $-(CH_2)_5-$), 4.00-4.44 (m, 1H, N-CH) and 7.12-7.48 (m, 10H, aromatic).

Analysis found: C, 71.57; H, 6.02; N, 4.05; S, 9.06. $C_{21}H_{21}NO_2S$ calcd: C, 71.78; H, 6.01; N, 3.99; S, 9.10%.

A-2. Reaction of N-sulfinylaniline with dipnenylcyclopropenone in the presence of iron pentacarbonyl.

The mixture of N-sulfinylaniline (6 mmol),diphenylcyclopropenone (6 mmol) and iron pentacarbonyl (6 mmol) was heated at 80-85° for 4.5 hr in 30 ml of DMF. Subsequent treatments were similar as described in the reaction of IIa.

In this reaction, 2,4,5-triphenyl -3- isothiazolone -1-oxide (IVa) was obtained by recrystallized from benzene-hexane (0.45 g; 22% yield): pale yellow needles; m.p. 159-160°; IR(Nujol): 1700 (C=O) and 1100 cm^{-1} (S=O); mass: m/e 345 $[M]^+$, 329 $[M -O]^+$, 297 $[M -SO]^+$, 206 and 178; nmr($CDCl_3$): δ 7.15-7.65 (m, aromatic).

Analysis found: C, 73.26; H, 4.26; N, 3.99. $C_{21}H_{15}O_2NS$ calcd: C, 73.03; H, 4.38; N, 4.06%.

A-3. Reaction of N-sulfinylaniline with diphenylacetylene in the presence of nickel tetracarbonyl.

The mixture of N-sulfinylaniline (6 mmol), diphenylacetylene (6 mmol) and nickel tetracarbonyl (6 mmol) was heated at 60-70° for 4 hr. The mixture was extracted with 150 ml of ether, then the solution was concentrated after drying over Mg_2SO_4. The residual needles were washed with benzene, and 0.5 g of diphenylurea (white needles, 78% yield) was obtained: m.p. 250-251°; IR (Nujol): 3300 (NH) and 1640 cm^{-1} (C=O).

The benzene solution was concentrated and 0.9 g of diphenylacetylene was obtained (white needles; 84% yield): m.p. 60-61°.

In this reaction, the formation of any adducts of diphenylacetylene with N-sulfinylaniline was not observed.

A-4. Reactions of N-sulfinylamines with metal carbonyls.

Reaction of N-sulfinylaniline with nickel tetracarbonyl.

N-Sulfinylaniline (8 mmol), nickel tetracarbonyl (8 mmol) were reacted in 20 ml of DMF at 65-70° for 5 hr. Diphenylurea was isolated by the extraction with 200 ml of ether, and recrystallized from ethanol (0.75 g; 82% yield).

Reaction of N-sulfinylcyclohexylamine with nickel tetracarbonyl.

N-Sulfinylcyclohexylamine (8 mmol), nickel tetracarbonyl (8 mmol) were reacted as above.

Dicyclohexylurea was isolated by recrystallization from ethanol (0.3 g; 33% yield): white needles; m.p. 132-133°; IR(Nujol): 3290 (NH) and 1620 cm^{-1} (C=O); mass: m/e 224 $[M]^+$.

Reaction of N-sulfinylaniline with iron pentacarbonyl.

The reaction was carried out as described above, but only aniline was recognized but diphenylurea was not isolated at all.

A-5. Reaction of 2,4,5-triphenyl-3-isothiazolone-1-oxide (IVa) with nickel tetracarbonyl.

The IVa (320 mg) to be isolated by the reaction of using iron pentacarbonyl was heated with 0.3 ml of nickel tetracarbonyl in 15 ml of DMF, at 60-65° for 3 hr. Subsequently, the reaction mixture was extracted with 150 ml of ether-benzene (1:1), and the solution was concentrated.

The IVa was recovered (300 mg; 94% yield), but the exchanged product IIIa was not obtained at all.

B. Reaction with diphenylacetylene.

B-1. Reaction of N-sulfinylaniline in the presence of iron pentacarbonyl.

The mixture of diphenylacetylene (0.025 mol) with iron pentacarbonyl (0.025 mol) was heat at 100° for 0.2 hr, then N-sulfinylaniline (0.05 mol) was added to the mixture and the reaction mixture was heated at 180° for 2 hr. Subsequently, the mixture was extracted with 200 ml of benzene and the benzene solution was concentrated, and the residue was chromatographed on alumina. [eluted with hexane (fraction 1), benzene (fraction 2)]

From the first fraction, the mixture of diphenylacetylene with azobenzene (4.2 g) was obtained. The separation of the both was very difficult and so the the yield of azobenzene was not determined.

From the second frction, 3.6 g of tetraphenylthiophene was yielded (74% yield): white needles; m.p. 192-193° (lit.[12] 184°); mass: m/e 388 $[M]^+$.

Analysis found: C, 86.34; H, 5.17. $C_{28}H_{20}S$ calcd: C, 86.57; H, 5.19%.

B-2. Reaction of the ferracyclopentadiene complex with N-sulfinylaniline.

The mixture of N-sulfinylaniline (6 mmol) and ferracyclopentadiene complex(3 mmol) was heated at 215° for 3 hr without solvent. The reaction mixture was extracted with benzene, and after concentration the residue was recrystallized from benzene-ethanol to yield tetraphenylthiophene (0.9 g; 72% yield). The filtrate was concentrated and the residue was chromatographed on alumina. [Eluted with hexane]. Azobenzene was obtained (0.5 g; 96% yield): red needles; m.p. 65-66° : The mixture of it with the commercial authentic sample did not depress the melting point.

References

1. C. J. Cooksey, D. Dodd, C. Gatford, M. D. Johnson, G. J. Lewis and D. M. Titchmarsh, J. Chem. Soc. Perkin Trans. II 655 (1972).
2. D. A. Ross, Ph. D. Thesis, The Ohio State University (1970).
3. S. E. Jacobson and P. Reich-Rohrwig and A. Wojcicki, Inorg. Chem. 12 717 (1973).
4. J. E. Thomasson, P. W. Robinson, D. A. Ross, and A. Wojicicki, Inorg. Chem., 10 2130 (1971).
5. A. Cutler, R. W. Fish, W. P. Giering and M. Rosenblum, J. Amer. Chem. Soc., 94 4354 (1974).
6. S. Otsuka, Anual meeting of the Chem. Soc. of Japan 1968 April.
7. E. H. Braye and W. H. Hubel, Chem. Ind., 1250 (1959).
8. A. Michaelis and K. Petou., Chem. Ber., 31 (1898).
9. R. Breslow and J. Posner, Org. Syntheses Coll. Vol. 5 514 (1973).
10. A. C. Cope, D. S. Smith and R. J. Cotter, Org. Syntheses Coll. Vol. 4 377 (1955).
11. G. P. Chuisoli and G. Mondelli, Chem. Ind. (Milan), 43 259 (1961).
12. G. N. Schrauzer, J. Amer. Chem. Soc., 81 5307 (1959).

Chapter IV. REACTIONS OF α,α'-DIBROMOXYLENES WITH DIPHENYLKETENE IN THE PRESENCE OF NICKEL TETRACARBONYL, AND THE SIMPLE METHOD OF DIPHENYLKETENE DIMER AND TETRAPHENYL-ALLENE.

In this chapter, the reaction of α,α'-dibromo-o-xylene with diphenylketene in the presence of nickel tetracarbonyl is investigated. In this reaction, an interesting spiro compound has been obtained without an expected 1:1 adduct. In the study of the solvent effect of this reaction, the author found a simple method for the preparation of diphenylketene dimer and tetraphenylallene. The method is described in the second section of this chapter.

IV - I. Reactions of α,α'-dibromoxylenes with diphenylketene in the presence of nickel tetracarbonyl.

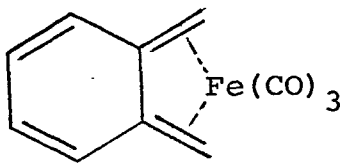
1) Introduction

In the chapter 1, the reaction of phenylbromoacetylene with heterocumulenes in the presence of iron pentacarbonyl are investigated, and the combinated reactions of an insertion of heterocumulenes with a coupling reaction of the bromoacetylene have been studied in it.

In general, organohalocompounds easily react with metal carbonyls such as iron pentacarbonyl and nickel tetracarbonyl[1].

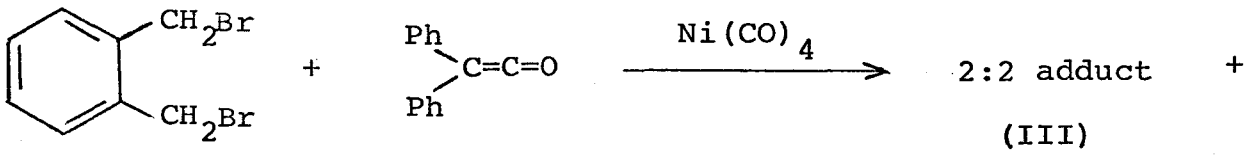
In this chapter, the reaction of α,α'-dibromo-o-xylene with diphenylketene in the presence of nickel tetracarbonyl are investigated. In particular, α,α'-dibromo-o-xylene forms a stable

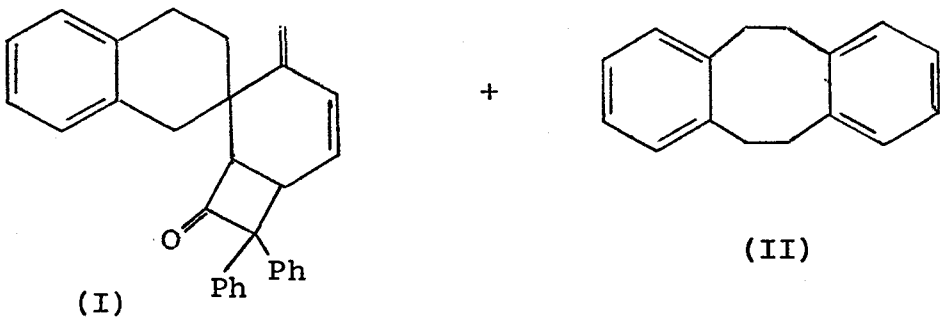
π-complex with $Fe_2(CO)_9$. Though this complex is too stable to be used for a further reaction, this complex would be available for organic syntheses by use of other metal carbonyls such as nickel tetracarbonyl.



2) Results and discussion

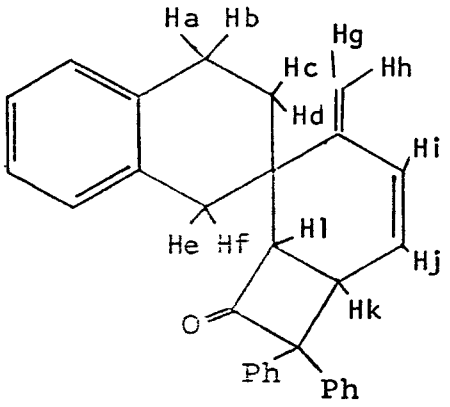
A reaction of diphenylketene with α,α'-dibromo-o-xylene in the presence of an equimolar amount of nickel tetracarbonyl gave an interesting product, spiro[3-methylene-7,7-diphenyl-8-oxo-bicyclo-[4,2,0]oct-4-ene-2,2'-1',2',3',4'-tetrahydronaphthalene] (I), in 60% yield without any expected 1:1 adduct of o-xylyl group and diphenylketene.





The ir spectrum of the spiro compound I indicated the absorption bands at 1768 and 890 cm^{-1} which were assigned to cyclobutenone group and vinyl group, respectively. In the ^1H-NMR

spectrum of the spiro compound I, the signals were successfully assigned with the aid of spin decoupling by double resonance. The spin decoupling spectrum is shown in Fig. 1.



The signals according to the diene group appeared at 6.05 (d, J_{ij}= 10Hz, 1H), 5.34 (dd, J_{ij}= 10Hz, J_{jk}= 4Hz, 1H), 4.76 (s, 1H) and 4.88 (s, 1H) which were assigned to H_i, H_j, H_g and H_h, respectively. The peaks assigned to H_e and H_f appeared at 2.98 (d, J_{ef}= 16Hz, 1H) and 3.50 (d, J_{ef}= 16Hz, 1H), AB pattern spectrum, and the peaks assigned to H_k and H_l were indicated at 3.96 (dd, J_{jk}= 4Hz, J_{kl}= 10Hz, 1H) and 3.47 (d, J_{kl}= 10Hz, 1H).

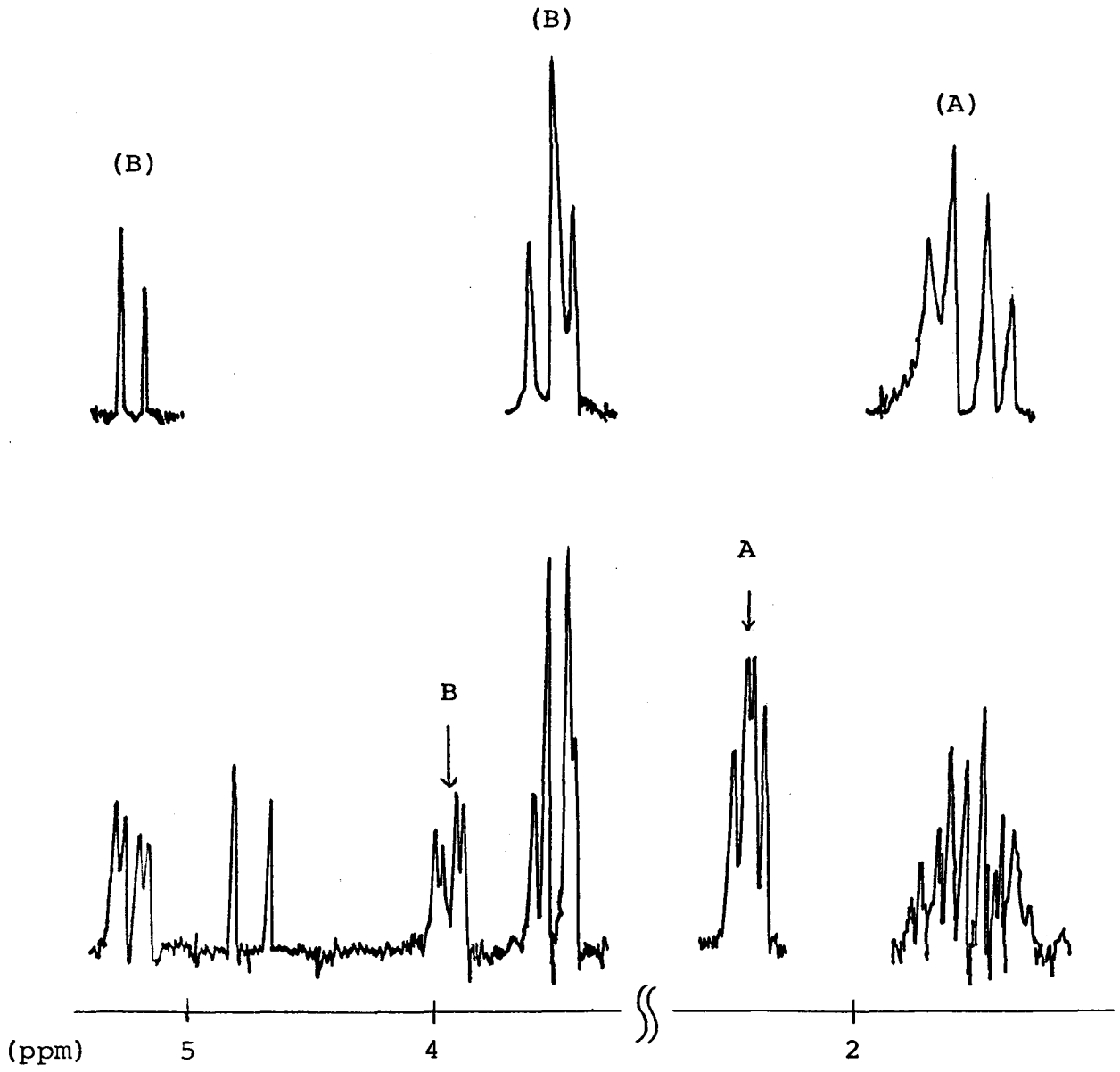
As shown in Fig. 1, an irradiation at 3.96 resulted in the sharpening of the peaks (3.47 and 5.34), and an irradiation at 2.66 (H_a and H_b) resulted in the sharpening of the peaks (m, 1.4-2.0, 2H, H_c and H_d).

In the ^{13}C-NMR spectrum, the signals according to the carbonyl carbon, the terminal olefin carbon and the spiro carbon indicated at 207.6, 111.5 and 37.5 ppm, respectively. The ^{13}C-NMR spectrum and its off-resonance spectrum are shown in Fig. 2. These spectral data are well compatible with the structure of the spiro compound I.

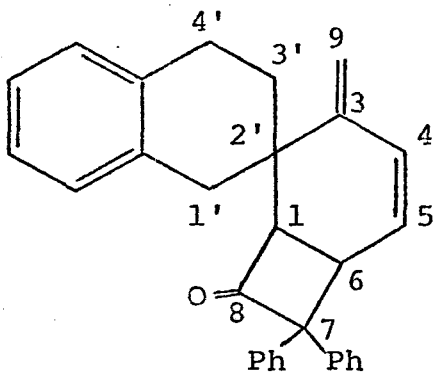
The carbonyl group of the spiro compound I was reduced to the hydroxy group by $LiAlH_4$. The hydrogenation of the olefinic group of the compound I could be carried out by only Rh-PPh_3 complex, and gave the hydrogenated product V in 67% yield.

Fig 1.

The nmr spectrum of the spiro compound I, and their spin decoupled patterns upon irradiations at frequencies of the signals [A (H_a and H_b) and B (H_j)] by double resonance.



^{13}C-NMR data of the spiro compound I (ppm)



1', 38.0	1, 64.1
2', 37.5	6, 35.4
3', 25.6	7, 76.8
4', 32.3	8, 207.6
	9, 111.5

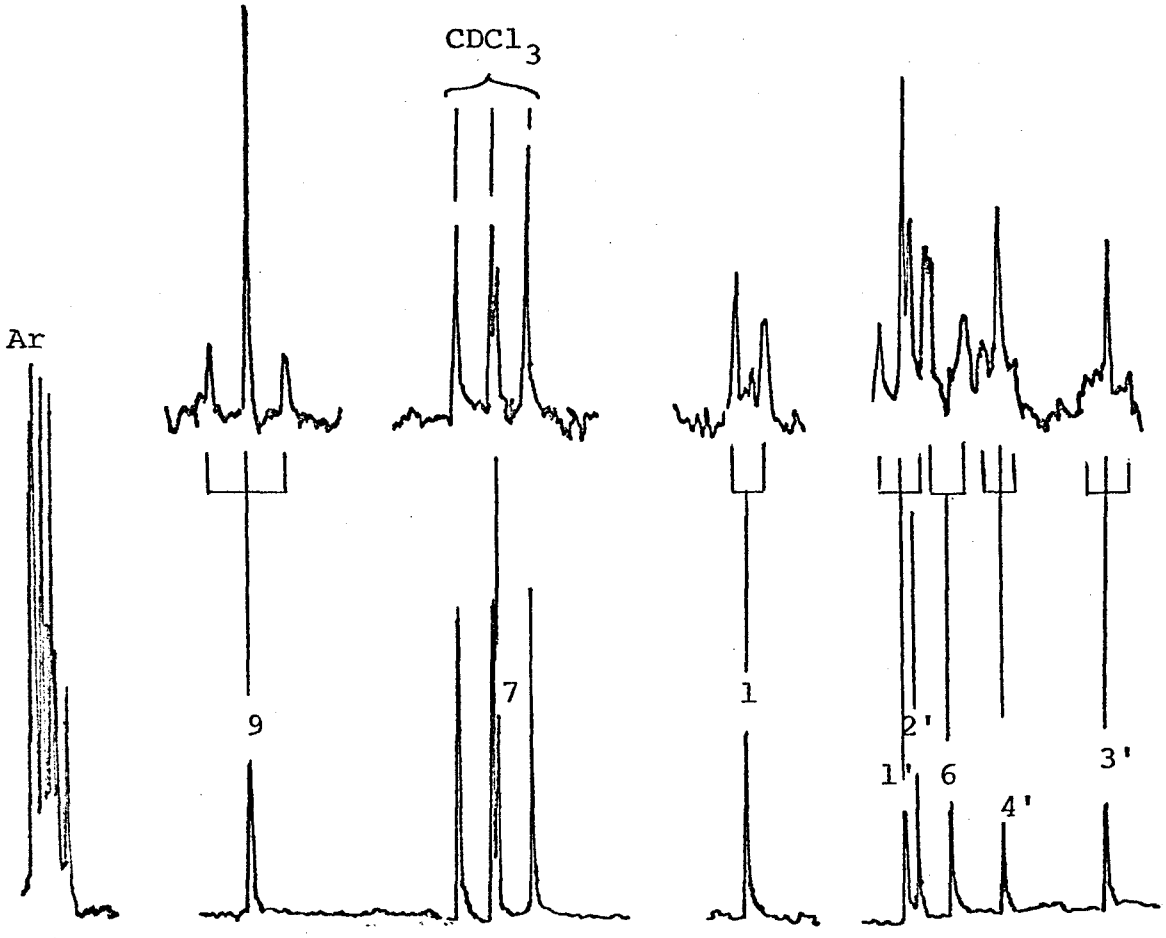
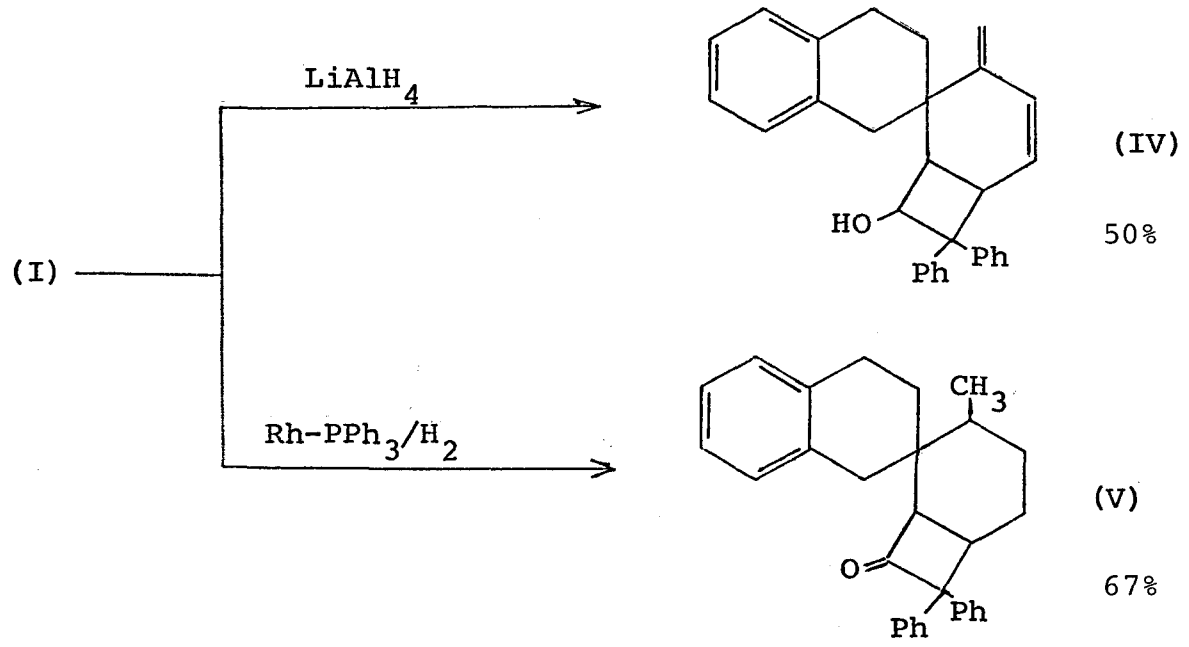


Fig. 2

^{13}C-NMR spectrum and its off-resonance spectrum ($CDCl_3$, conc. 15%, TMS; internal standard)



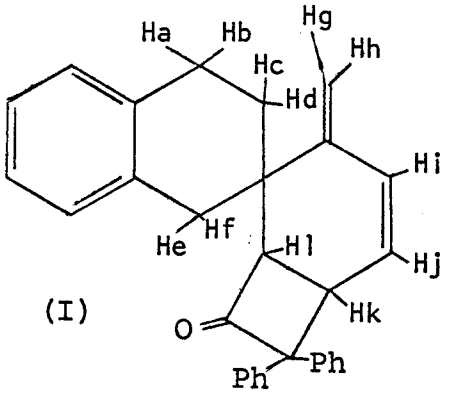
The proton magnetic resonance spectral data of I, IV and V are shown in Table 1. The hydrogenated product V showed the doublet signal according to the methyl group at 0.85 ppm. The reduced product IV indicated the triplet according to the C_1 methine proton at 2.20 ppm.

From these chemical and spectral data, the structure of the spiro compound I was decided.

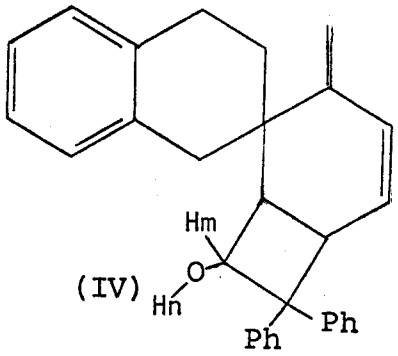
o-Cyclophane and 2:2 adduct of o-xylyl group and diphenylketene were produced as by-products in 8% and 4% yields, respectively. The structure of the 2:2 adduct was very complicated and could not be determined. o-Cyclophane was produced by the coupling reaction of α,α'-dibromo-o-xylene by nickel tetracarbonyl. The reaction of α,α'-dibromo-o-xylene with nickel tetracarbonyl was carried out and gave the cyclophane in 12% yield, and no spiro compound was obtained.

From these results, it was thought that the formation of a spiro compound might be caused by the reaction of diphenylketene to an intermediate. We assumed the reaction mechanism as follows.

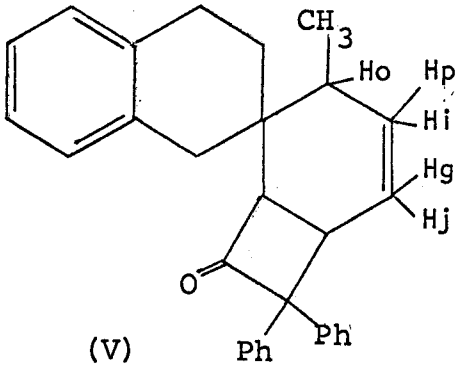
TABLE 1. The ^{1}H-NMR spetral data of I, IV and V.



(I)



(IV)

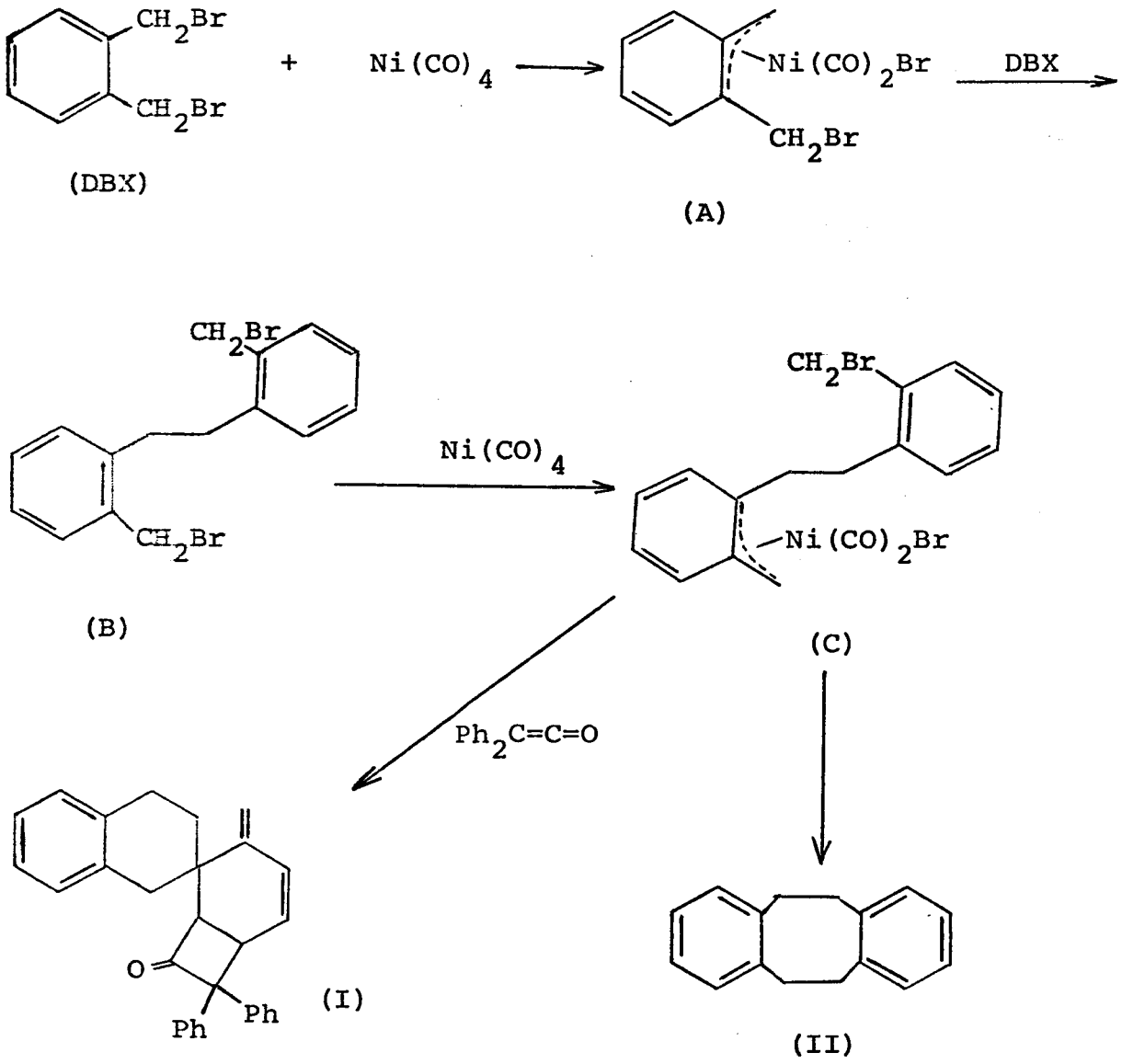


(V)

proton	chem. shift(ppm)	J(Hz)	chem. shift(ppm)	J(Hz)
a and b	2.66(dd)	6, 8	2.65(dd)	6, 8
c and d	1.4-2.0(m)	-	1.1-1.9(m)	-
e and f	2.98(d), 3.50(d)	16	2.74(d), 3.16(d)	16
g and h	4.76(s), 4.88(s)	-	4.78(s), 4.95(s)	-
i	6.05(d)	10	5.95(d)	10
j	5.34(dd)	4, 10	5.33(dd)	4, 10
k	3.96(dd)	4, 10	3.72(dd)	4, 10
l	3.47(d)	10	2.20(t)	8
aromatic	6.90-7.52(m)	-	6.98-7.54	-
m	-	-	4.59(t)	8
n	-	-	1.37(d)	8

0.85(d, J = 7 Hz, $-CH_3$)
0.92-1.75(m, 7H, c, d, i, j, o,p,q)
2.36-3.40(m, 6H, a,b, e,f,k,l)
6.70-3.40(m, 14H, aromatic)

Fig. 3.



α,α'-Dibromo-o-xylene reacts with nickel tetracarbonyl to form the complex A, and then the compound B is formed by A with dibromoxylene. Nickel tetracarbonyl reacts with B to form the intermediate C. With this complex C, diphenylketene reacts, and the ring closure to form the spiro compound I follows, namely the attack of diphenylketene would be a driving force of the formation of the spiro compound, but the detailed mechanism is not clear. o-Cyclophane was produced from the intermediate C

by a simple coupling reaction without the attack of diphenylketene.

The reaction mechanisms are shown in Fig. 3.

Solvent effect was significant in this reaction, the results are shown in Table 2. DMF was the most excellent solvent, and the spiro compound was produced in 60% yield. On the other hand, in HMPA the yield of the compound I was lower, but the yield of the cyclophane was higher. This reaction did not proceeded in non polar solvent (benzene).

Iron pentacarbonyl did not act in this reaction.

TABLE 2.

THE REACTIONS OF α,α'-DIBROMO-o-XYLENE WITH DIPHENYLKETENE

			yields (%)		
solvent	temp.(°C)	time(hr)	(I),	(II)	(III)*
DMF	50-55	3	60	8	4
HMPA	50-55	3	17	38	0
THF	55-60	5	trace	trace	0
benzene	60	7	0	0	0
DMF**	80	4	0	0	0

* The 2:2 adduct of o-xylyl group and diphenylketene.

** $Fe(CO)_5$ was used instead of $Ni(CO)_4$.

In the reaction of α,α'-dibromo-p and m-xylenes with diphenylketene in the presence of nickel tetracarbonyl, no corresponding spiro compound was obtained, and so the formation of the spiro compound seemed to be characteristic in α,α'-dibromo-o-xylene.

IV - II. A Simple method for the preparation of tetraphenylallene and diphenylketene dimer.

1) Introduction

The dimer of diphenylketene (VI), a β-lactone, has been obtained (yield not reported) by treatment of the ketene with a catalytic amount of sodium ethoxide in benzene[3].

Tetraphenylallene (VIII) has been prepared from diphenylketene by the Wittig reaction[4], by treatment with potassium ethoxide in benzene[5], and by pyrolysis of the ketene dimer[6]. However, these procedures afford only low yield and are accompanied by polymerization of the ketene.

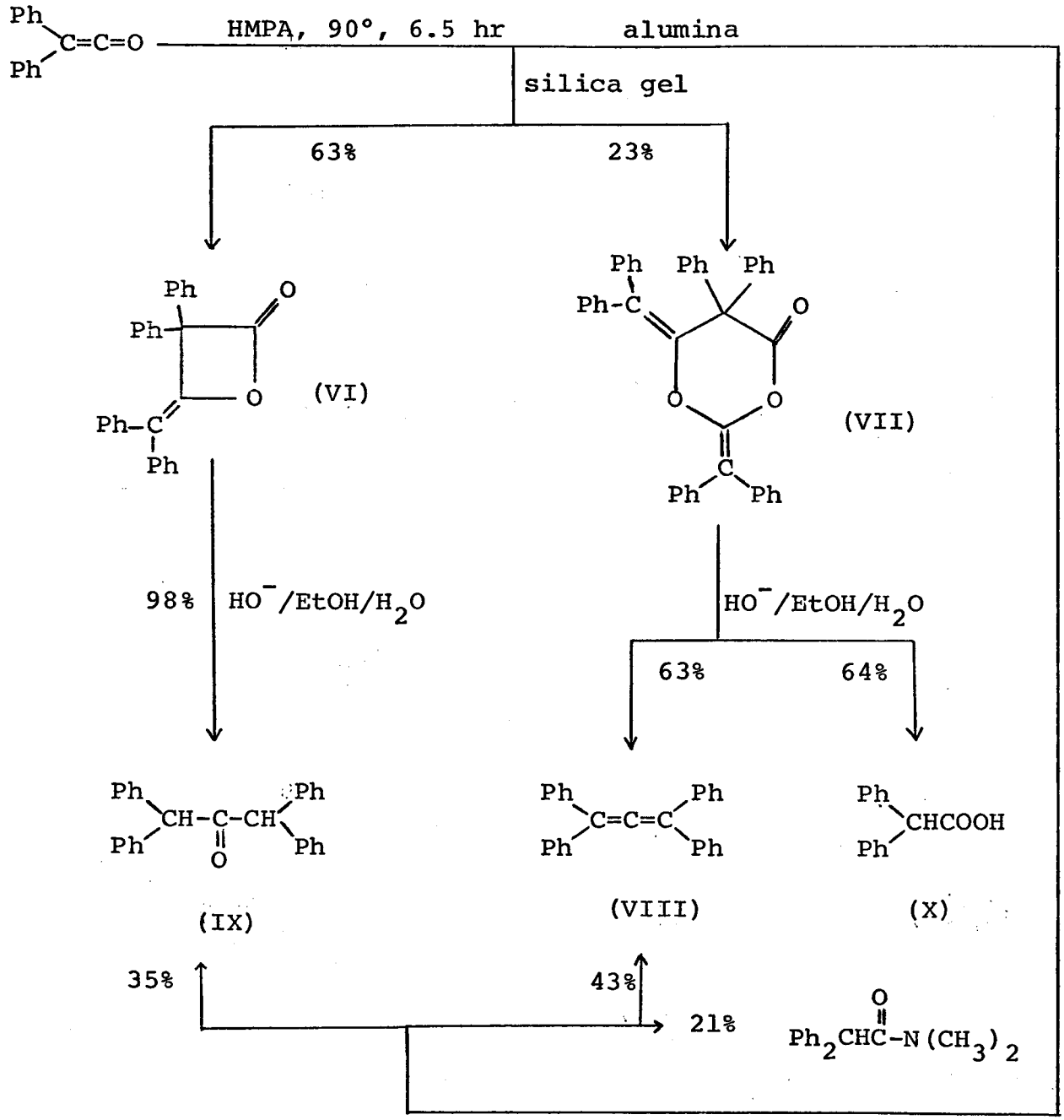
In this chapter, the synthesis of diphenylketene dimer (tetraphenyl-3-buten-3-olide, VI) and tetraphenylallene (VIII) from diphenylketene in hexamethylphosphoric triamide (HMPA) is described. The method is simple and gives good yields without formation of polymers. Moreover, it is investigated that the formation of tetraphenylallene is not due to the decomposition of the dimer VI, but is due to the hydrolysis of the trimer of diphenylketene (VII).

2) Results and discussion

On heating a solution of diphenylketene in HMPA at 90° for 6.5 hr and chromatography of the reaction product on silica gel, diphenylketene dimer (VI) and trimer (VII) were obtained in 63 and 23% yields, respectively. The trimer was readily hydrolyzed to tetraphenylallene (VIII) and diphenylacetic acid (X).

Tetraphenylallene (VIII) was directly obtained in better yield when a large excess of HMPA was used and the crude reaction mixture

was chromatographed on alumina. In this case, 1,1,3,3-tetraphenylacetone (IX) was obtained as a side product. (TABLE 3)



Tetraphenylallene was not obtained from the dimer VI by treatment with Lewis acids such as AlCl and BF_3, and by pyrolysis at 200°. The dimer VI was hydrolyzed to the ketone IX quantitatively and no decarboxylation to an allene was observed. From these

TABLE 3. Reaction Conditions of Conversion of Diphenylketene into its Dimer(VI), Trimer(VII), Tetraphenylallene(VIII), and 1,1,3,3-Tetraphenyacetone(IX).

Solvent	Weight ratio solvent/ diphenylketene	Reaction temperature	Reaction time (hr)	Yields of products VI	VII	VIII	IX
HMPA[a]	5	90°	6.5	63	23	-	-
HMPA[b]	5	80-90°	6.5	-	-	43	35
HMPA[b]	1	80-90°	8.0	-	-	9.4	26
HMPA[b]	0.3	80-90°	8.0	-	-	4.0	6.0
HMPA[a,c]	5	80-90°	6.5	70	0	9.6	0
$(C_6H_5)_3PO$[d]	1	90-100°	10	0	0	0	0

a Chromatography on silica gel.

b Chromatography on alumina.

c A catalytic amount of sodium ethoxide was added.

d No solvent or toluene was used.

results, it is concluded that the allene is produced from the trimer VII. The reaction is probably favoured by the moderate basicity of hexamethylphosphoric triamide; dimethylformamide or benzene are not suitable as solvents.

The reaction of isocyanates with triphenylphosphine oxide leads to the formation of carbodiimides via a Wittg-type reaction involving decarbonylation[7]. The author found that tetraphenylallene (VIII) cannot be obtained by analogous reaction of diphenylketene with triphenylphosphine oxide.

The addition of a catalytic amount of sodium ethoxide to the HMPA solution of diphenylketene increases the yield of the dimer VI whereas the trimer VII cannot be isolated. Under these conditions, the trimer VII is readily cleaved to tetraphenylallene.

Summary

In the first section, reactions of α,α'-dibromoxylenes with diphenylketene in the presence of nickel tetracarbonyl have been described. Especially, the reaction of the o-xylene with diphenylketene gave an interesting spiro compound, and the structure was determined by the reduction with $LiAlH_4$, and by the hydrogenation with $Rh\text{-}PPh_3$. Additional, ^{13}C-NMR of these products were taken to determine the structure finally. The formation of a spiro compound was characteristic in the reaction of the o-xylene.

Reaction mechanisms have been proposed and the attack of diphenylketene would be a driving force of the formation of the spiro compound.

In the second section, a simple method for the preparation of tetraphenylallene and diphenylketene dimer were described.

These products were easily obtained by heating of diphenylketene in HMPA. Moreover, it was defined that tetraphenylallene was produced from the trimer of diphenylketene.

Experimental section

All melting points were recorded on a Yanaco micro melting point apparatus and are uncorrected.

IR spectra were taken with a Jasco IR-E spectrometer and were corrected with a polystylene film. ^{1}H-NMR spectra were taken with a JEOL JNM-3H-60 spectrometer with TMS as an internal standard. ^{13}C-NMR spectra were taken with a JEOL-FX-60 spectrometer. Mass spectra were taken with a Hitachi RMU-6E spectrometer.

Nickel tetracarbonyl is very poisonous, and so all reactions were carried out in a draft and residual nickel carbonyl was decomposed by an iodine-benzene solution.

Materials

Diphenylketene[8], nickel tetracarbonyl[9] and α,α'-dibromoxylenes[10] were prepared according to the established procedures. DMF and HMPA were dried over CaH_2 and were distilled.

Reaction of α,α'-dibromo-o-xylene with diphenylketene in the presence of nickel tetracarbonyl. The mixture of α,α'-dibromo-o-xylene (0.015 mol), diphenylketene (0.01 mol) and nickel tetracarbonyl (0.01 mol) in 50 ml of DMF was heated at 50-55° for 3 hr with stirring. Subsequently, DMF was evapolated, the benzene solution was concentrated. The residue was chromatographed on Al_2O_3 column and eluted with hexane (fraction 1), benzene-hexane

(fraction 2) and benzene (fraction 3).

From the first fraction, 0.12 g of o-cyclophane (II) was obtained (8% yield), recrystallized from hexane-benzene: white needles; m.p. 111-112° (lit.[11] 109-111°); mass: m/e 208 $[M]^+$, 104; nmr: ($CDCl_3$) δ 3.02 (s, 8H), 6.6-7.2 (m, 8H, aromatic protons).

Analysis found: C, 92.18; H, 7.44. $C_{16}H_{16}$ calcd: C, 92.26; H, 7.74%.

From the second fraction, 1.8 g of spiro[3-methylene-7,7-diphenyl-8-oxo-bicyclo[4,2,0]oct-4-ene-2,2'-1',2',3',4'-tetrahydronaphthalene (I) was produced (60% yield), recrystallized from benzene-hexane: white needles; m.p. 212-213°; IR (Nujol) 1768 cm^{-1} (C=O); nmr: ($CDCl_3$) the data are shown in Table 2.

Analysis found: C, 89.39; H, 6.42. $C_{30}H_{26}O$ calcd: C, 89.51; H, 6.51%.

From the third fraction, 0.2 g of the 2:2 adduct was obtained (5% yield), recrystallized from benzene-hexane: white needles; m.p. 232-234°; IR (Nujol) 1765 cm^{-1} (C=O); mass: m/e 596 $[M]^+$, 402, 208, 194, 104; nmr:($CDCl_3$) δ 1.2-1.8 (m, 2H), 2.12-3.04 (m, 4H), 3.54 (d, 1H), 3.6-4.4 (m, 1H), 4.68 (s, 1H), 5.0 (s, 1H), 5.78-6.40 (m, 4H), 6.6-7.6 (m, 22H).

Analysis found: C, 88.61; H, 6.29. $C_{44}H_{36}O_2$ calcd: C, 88.56; H, 6.08%.

$LiAlH_4$ reduction of I. The spiro compound I (220 mg) in 20 ml of THF was added dropwise to the mixture of $LiAlH_4$ (200 mg) in 20 ml of THF on ice-water bath. The reaction mixture was heated at 60° for 5 hr, and then 20 ml of HCl (15%) was added and it was extracted with 200 ml of ether. After drying over Na_2SO_4,

the ether was evapolated and 110 mg of spiro[3-methylene-7,7-diphenyl-8-hydroxy-bicyclo[4,2,0]oct-4-ene-2,2'-1',2',3',4'-tetrahydronaphthalene (IV) was obtained (50% yield): white needles; m.p. 210-211°; mass: m/e 404 $[M]^+$, 388, 299, 208, 194; nmr:($CDCl_3$) the data are shown in Table 1.

Analysis found: C, 88.97; H, 6.99. $C_{30}H_{28}O$ calcd: C, 89.07; H, 6.98%.

Hydrogenation of I. The solution of 300 mg of the spiro compound I in 150 ml of ethanol was shaken in the presence of 100 mg of Rh-PPh_3 complex under a 4 Kg/cm^{-1} pressure of a hydrogen atmosphere. Then 200 mg of spiro[3-methyl-7,7-diphenyl-8-oxo-bicyclo-[4,2,0]octane-2,2'-1',2',3',4'-tetrahydronaphthalene (V) was obtained (67% yield): white needles; m.p. 234-236°; IR(Nujol) 1765 cm^{-1} (C=O); mass: m/e 406 $[M]^+$, 233, 206, 161; nmr:($CDCl_3$) the data are shown in Table 1.

Analysis found: C, 88.41; H, 7.44. $C_{30}H_{30}O$ calcd: C, 88.63; H, 7.44%.

Reaction of α,α'-dibromo-o-xylene with nickel tetracarbonyl. The mixture of α,α'-dibromo-o-xylene (0.01 mol) and nickel tetracarbonyl (0.01 mol) was heated at 50-55° for 3 hr in 50 ml of DMF. Subsequently, DMF was evapolated, the residue was extracted with benzene, and the solution was concentrated and chromatographed on Al_2O_3 column, and eluted with hexane. o-Cyclophane (0.12 g, 12% yield) was obtained.

Reactions of α,α'-dibromo-p and m-xylene with diphenylketene were carried out in a same manner, but no adduct was obtained.

In the reaction of the p-xylene, small amount (8%) of p-cyclophane was obtained: white needles; m.p. ca. 210° (sublimed); mass: m/e 208 $[M]^+$, 104.

Analysis found: C, 92.06; H, 7.47. $C_{16}H_{16}$ calcd: C, 92.26; H, 7.74%.

Tetraphenyl-3-buten-3-olide(Diphenylketene Dimer,VI) and 2,4-Bis[diphenylethylene]-5,5-diphenyl-6-oxo-1,3-dioxane (Diphenylketene Trimer, VII) A solution of diphenylketene (0.97 g, 5 mmol) in HMPA (5 ml) was heated at 90° for 6.5 hr. The solvent was then evaporated and and the residue was chromatographed on silica gel [elution with hexane (fraction 1), hexane/benzene (fraction 2), benzene (fraction 3)].

Fraction 1; tetraphenylallene (trace).

Fraction 2; Dimer VI; yield: 0.63 g (63%); m.p. 154-155° (from benzene/hexane) (lit.[12] m.p. 148° decomp.); mass: m/e 388$[M]^+$, 360, 344, 194, 166; IR(Nujol) 1850 and 1660 cm^{-1} (C=O); ^{1}H-NMR:($CDCl_3$) δ 6.70-7.35 ($H_{arom.}$).

Analysis found: C, 86.67; H, 4.97. $C_{28}H_{20}O_2$ calcd: C, 86.57; H, 5.19%.

Fraction 3; Trimer VII; yield: 0.23 g (23%); m.p. 237-238° (from benzene/hexane); mass: m/e 582 $[M]^+$, 554, 388, 194, 166; IR(Nujol) 1770, 1655 and 1620 cm^{-1}; ^{1}H-NMR:($CDCl_3$) δ 6.25-7.30(H_{arom}).

Analysis found: C, 86.83; H, 4.91. $C_{42}H_{30}O_3$ calcd: C, 86.57; H, 5.19%.

Tetraphenylallene(VIII). A solution of diphenylketene (0.97 g, 5 mmol) in HMPA (5 ml) was heated at 80-90° for 6.5 hr. The solvent was evaporated and the residue was chromatographed on

alumina [elution with hexane (fraction 1), benzene (fraction 2), and benzene/ethanol 1:1 (fraction 3)].

Fraction 1; Tetraphenylallene; yield: 0.38 g (43%); m.p. 172-173° (from ethanol) (lit[4], m.p. 165°);mass: 344[M]$^+$, 267, 166; ^{1}H-NMR: ($CDCl_3$) δ 7.1-7.5 (H_{arom}).

Analysis found: C, 94.00; H, 5.84. $C_{27}H_{20}$ calcd: C, 94.15; H, 5.85%.

Fraction 2; 1,1,3,3,-tetraphenylacetone (IX); yield: 0.33 g(35%); m.p. 140-142° (from benzene/hexane); mass: 362 [M]$^+$, 195, 167.

Analysis found: C, 89.26; H, 6.12. $C_{27}H_{22}O$ calcd: C, 89.47; H, 6.12%.

Fraction 3; N,N-Dimethylphenylacetamide; yield: 0.26 g (21%).

Hydrolysis of diphenylketene trimer VII. The trimer VII (0.15 g, 0.3 mmol) was dissolved in ethanol (50 ml) and water (1 ml) and potassium hydroxide (0.5 g) was added. The mixture was heated on the water bath for 10 hr and then extracted with ether (200 ml) and with water (200 ml). Work-up of the ether layer gave tetraphenylallene (VIII); yield: 0.55 g (63%). The water layer was acidified with conc. hydrochloric acid, extracted with ether (100 ml), and the ether was evaporated to give diphenylacetic acid (X); yield: 0.0035 g (64%).

Hydrolysis of diphenylketene dimer VI. The reaction was carried out as described above. Tetraphenylacetone (IX) was obtained; yield: 0.18 g (98%).

References

1. E. J. Corey, C. V. Kim, R. H. K. Chen and M. Takeda, J. Amer. Chem. Soc., 94 4395 (1972).
G. P. Chiusoli, G. Cmetti and S. Morsoni, Organometal. Chem. Syn., 94 (1972) 439.
2. W. R. Roth and J. D. Meier, Tetrahedron Lett., 2053 (1967).
3. J. Kopecky and J. Smejkal, Chem. Ind. (London), 1529 (1966).
4. P. Meyer, Chem. Ber., 89 842 (1956).
5. H. Staudinger and P. Meyer, Helv. Chim. Acta., 5 656 (1922).
6. J. C. Martin, U. S. Patent 3131234 (1964), Eastman-Kodak; C. A., 61 2969 (1964).
7. J. J. Monagle, J. Org. Chem., 27 3851 (1962).
8. L. I. Smith and H. H. Hoehn, Org. Syn. Collective Vol. 3, 356 (1955).
9. G. P. Chiusoli and G. Mondelli, Chem. Ind.(Milan), 43 259 (1961).
10. E. F. M. Stephenson, Org. Syn. Collective Vol. 4, 984 (1963).
11. L. A. Errede, J. Amer. Chem. Soc., 83 949 (1961).
12. R. Anet, Chem. Ind. (London), 1313 (1961).

CONCLUSION

The studies on the reactions of heterocumulenes in the presence of metal carbonyls have been described in this thesis.

By use of metal carbonyls, it was recognized that the smooth reactions of heterocumulenes with low-active reagents (phenylbromoacetylene, diphenylcyclopropenone, and α,α'-dibromo-o-xylene) proceeded, and gave interesting cyclic compounds. These low-active reagents cannot react with heterocumulenes in ordinary methods.

In Chapter I, the reactions of phenylbromoacetylene with heterocumulenes in the presence of iron pentacarbonyl have been described in comparison with the reaction of phenylacetylene with heterocumulenes. Reactions of phenylbromoacetylene with arylcarbodiimides gave benzodiazepinone derivatives, but the reaction with phenyl isocyanate produced a hydantoin derivative which was a similar product in the reaction of phenylacetylene. The distinction between the reaction of the carbodiimide and the isocyanate was thought to be caused by the distinction of the stability of the intermediate, and a possible mechanism was proposed. On the other hand, iron pentacarbonyl did not play any parts in the reaction with diphenylketene because of the high reactivity of the ketene toward phenylbromoacetylene. The naphthalene derivative was produced independently of iron pentacarbonyl in this case.

In Chapte II, the reactions of diphenylcyclopropenone with ketenes in the presence of nickel tetracarbonyl were investigated. Two kinds of 1:1 cycloadducts were obtained in the reaction. (cyclopentene-1,2-dione and cyclopentene-1,3-dione). The yields

and the selectivities of these products were affected significantly by reaction solvents, and DMF was the most suitable solvent for the prepalation of the 1,2-dione. Moreover, this reaction could proceed by a catalitic amount of nickel tetracarbonyl. In this formation of the 1,2-dione by a catalitic amount of nickel tetracarbonyl, it was considered that the reaction would not proceed *via* a nickelacyclobutenone complex, and so a new active species [$Ni(CO)_3$solv.] was proposed in this reaction. On the basis of this species, a possible reaction scheme was assumed.

Chapter III has dealed the reactions of diphenylcyclopropenone with N-sulfinylamines in the presence of metal carbonyls. In the reactions of using nickel tetracarbonyl, two kinds of heterocyclic compounds, isothiazolone-1-oxide and pyrroline-2,5-dione, were produced. The former was an ordinary 1:1 cycloadduct, but the latter was regarded to be formed by the exchange reaction of C=O of nickel tetracarbonyl for S=O of N-sulfinylamine. This reaction was affected enormously by the substituents of N-sulfinylamines, and electron-withdrawing substituents promoted the exchange reaction. The exchange could be prevented by using of iron pentacarbonyl. These reactions were not so affected by solvents compared to the reaction with ketenes which was described in Chapter II. A reaction mechanism was assumed in comparison with the reaction of diphenylcyclopropenone with ketenes.

On the other hand, in the reaction of diphenylacetylene with N-sulfinylaniline, nickel tetracarbonyl was not appropliate, and iron pentacarbonyl was adopted. This reaction would proceed *via* a ferracyclopentadiene complex.

In Chapter IV, the reaction of α,α'-dibromo-o-xylene with diphenylketene in the presence of nickel tetracarbonyl gave an interesting spiro compound. The structure of the spiro compound was determined finally by ^{13}C-NMR. In addition, a simple method for the preparation of diphenylketene dimer and tetraphenylallene was reported. This method gave the products by only heating of diphenylketene in HMPA and no polymer was produced.

ACKNOWLEDGEMENT

I would like to express my grateful acknowledgement to Professor Toshio Agawa for his continuous support and encourgement throughout the work.

I am also grateful to Dr. Yoshiki Ohshiro for his stimulating discussions and helpful advices.

I wish to thank Dr. Toru Minami and Dr. Mitsuo Komatsu for helpful suggestions.

I wish also to thank Messrs. Masaru Matsumoto, Saburo Kitano, Hitoshi Nanimoto, and all other members of Agawa Laboratory.