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Cyclopropene Derivatives. IV.*[1] The Reactions of Acylcyclopropene

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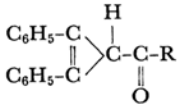
The reactions of acylcyclopropenes, such as 3-benzoyl-1, 2-diphenyl- and 3-acetyl-1, 2-diphenyl-cyclopropene, were investigated. These ketones gave normal hydrazones with 2, 4-dinitrophenylhydrazine. With *p*-toluenesulfonylhydrazine, the acetyl compound gave ordinary hydrazone, but the benzoyl derivative did not give its hydrazone. The reaction with hydrazine hydrate caused the expansion of the cyclopropene ring and produced pyridazine derivatives in both the ketones. The carbenic decomposition of 3-acetyl-1, 2-diphenylcyclopropene *p*-toluenesulfonylhydrazone with sodium methoxide in diglyme gave diphenylacetylene and 3, 4-diphenyl-6-methylpyridazine. On irradiation with ultraviolet light, 3-benzoyl-1, 2-diphenylcyclopropene produced 1, 2, 4, 5-tetraphenylbenzene. In the case of 3-acetyl-1, 2-diphenylcyclopropene, the same benzene derivative and 1, 2, 4, 5-tetraphenyl-3, 6-diacetyltricyclo[3, 1, 0, $0^{2,4}$]hexane were obtained. The latter material was transformed into a benzene derivative upon further irradiation. Tricyclohexane could be an intermediate in the transformation of ketones to a benzene derivative.

A series of investigations of the cyclopropenyl derivatives have been made by Breslow and his co-workers.1) They report the facile ring expansion of the cyclopropene in a number of cases.1) Since it is known that the olefinic group plays an important role in a carbene reaction2) and in the photochemical reaction3), the reaction of cyclopropenylcarbene and the photochemistry of cyclopropenylketone are of great interset. Unusual reaction products other than the ring-expanded one might be formed. In this respect, the thermal decomposition of 1, 2-diphenylcyclopropenyldiazoethane and the photochemical reaction of 3-acyl-1, 2-diphenylcyclopropene will be investigated here.

The Reaction of Methyl-1, 2-diphenylcyclopropene-3-yl Carbene.—It has been shown4) that the reaction of 3-benzoyl-1, 2-diphenylcyclopropene with hydrazine hydrate gives a ring-expanded isomer, dihydropyridazine, whereas the reaction with hydroxylamine gives an unrearranged cyclopropenyl oxime. It seems, therefore, that a ring expansion in the hydrazone formation is not inevitable in the cyclopropenyl ketone. Accordingly, the reactions of 3-benzoyl-1, 2-diphenylcyclopropene (Ia) and 3-acetyl-1, 2-diphenylcyclopropene (Ib) with some hydrazines were investigated.



Ia: $R=C_6H_5$

Ib: $R=CH_3$

The reaction of ketone Ia with hydrazine hydrate gave a mixture of yellow and white materials. The yellow material gradually changed to the white one during recrystallization from ethanol or benzene. The white material was purified and identified as 3, 4, 6-triphenylpyridazine (IIIa), m. p. 171—172°C. The spectral study of a crude yellow material, m. p. 167—178°C, showed that the material contained the N-H group and a less extended conjugating system. Therefore, the yellow material could be the dihydropyridazine (IIa) reported by Breslow.4),*3 It seems that IIa is formed by the reaction of ketone Ia with hydrazine hydrate, but that IIa is oxidized to IIIa, presumably by oxygen in the air, during the recrystallization. Such an easy oxidation of the dihydropyridazine to the pyridazine is observed in many cases.5)

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*1 Part III of this series: N. Obata and I. Moritani, *Tetrahedron Letters*, in press.

*2 All correspondence should be addressed to I. M.

1) a) R. Breslow, J. Lockhart and A. Small, *J. Am. Chem. Soc.*, **84**, 2793 (1960). b) R. Breslow and M. Battiste, ibid., **82**, 3626 (1960). c) R. Breslow in P. de Mayo, ed., "Molecular Rearrangement," Vol. I, John Wiley & Sons, New York (1963), Chapter 4.

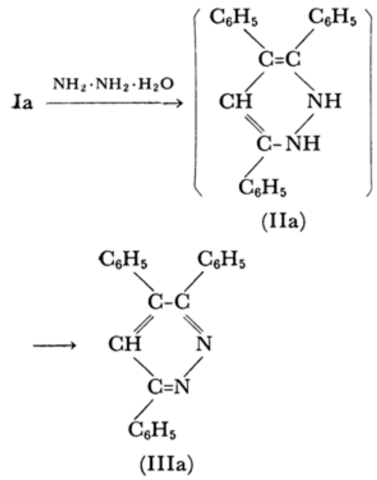
2) For summaries Re: carbene chemistry see: a) J. Hine, "Divalent Carbon," The Ronald Press Co., New York, N. Y. (1964). b) W. Kirmse, "Carbene Chemistry," Academic Press, New York, N. Y. (1964).

3) a) W. A. Noyes, Jr., G. S. Hammond and J. N. Pitts, Jr., ed., "Advances in Photochemistry," Vol. I, Interscience Publishers, New York (1963). b) P. de Mayo in R. A. Raphael, E. C. Taylor and H. Wynberg, ed., "Advances in Organic Chemistry," Vol. II, Interscience Publishers, New York (1960), p. 367.

4) R. Breslow, R. Boikess and M. Battiste, *Tetrahedron Letters*, **26**, 42 (1960).

*3 Breslow did not give the melting point of IIa.

5) See, for example, C. Paal and E. Dencks, *Ber.*, **36**, 495 (1903); K. Alder and H. Niklas, *Ann.*, **585**, 6 (1954).

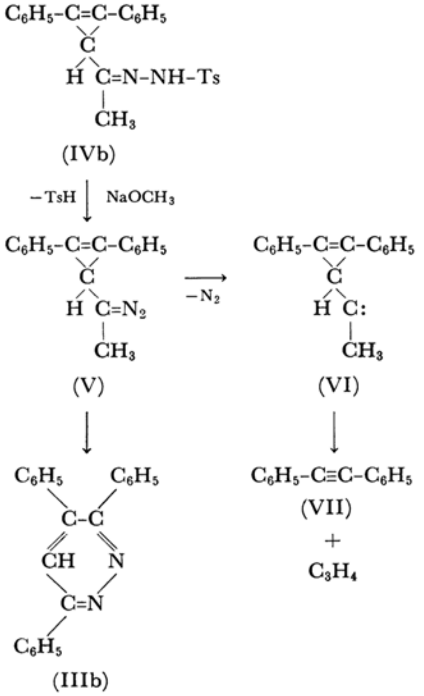


The same result was also obtained in the reaction of ketone Ib with hydrazine hydrate.

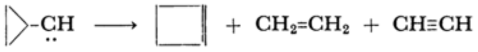
Unlike the reaction with hydrazine, however, ketone Ia and Ib gave 2, 4-dinitrophenylhydrazone with no skeletal rearrangement.[6] The existence of the 1, 2-diphenylcyclopropenyl group in the resulting hydrazones was clearly shown by the characteristic patterns in infrared and ultraviolet spectra.[7] The 2, 4-dinitrophenyl group might diminish the nucleophilic character of β-nitrogen and prevent its further attack on a cyclopropene ring. In a similar way, the reaction of ketone Ib with *p*-toluenesulfonylhydrazine also gave an unrearranged cyclopropenylhydrazone. However, ketone Ia failed to react under the same reaction conditions.

Since the preparation of the hydrazone without any ring expansion was successful, the reaction of cyclopropenylcarbene was also studied. A solution of *p*-toluenesulfonylhydrazone (IVb) of ketone (Ib) in diglyme was added dropwise to a solution of sodium methoxide in diglyme at 140°C. Gas was evolved gently. The collected gas was analyzed by means of a mass spectrometer. A mother peak for C_3H_4, probably methylacetylene and/or allene, was found in addition to a large amount of nitrogen. The reaction products were isolated and separated by alumina-column chromatography. From a hydrocarbon fraction, diphenylacetylene (VII) was obtained in a 28.4% yield. No other hydrocarbon could be detected in the products. From a later fraction of the chromatography, 3, 4-diphenyl-6-methylpyridazine (IIIb) was isolated in a 26.1% yield.

The diazo compound V of the desired structure, formed by the base catalyzed decomposition of *p*-toluenesulfonylhydrazone (IVb), produced methyl-1, 2-diphenylcyclopropene-3-yl carbene (VI), which then splits into two olefinic materials, diphenylacetylene (VII) and C_3H_4. If a ring expansion in carbene VI occurs, the compound derived from cyclobutadiene might be formed. If the intramolecular addition of carbene VI to a double bond occured, the tetrahedrane derivative might be formed. However, such was not the case in the present experiment. A pyridazine, IIIb, was formed by the ring expansion of the diazo compound V.



A similar splitting of the three-membered ring in the carbene reaction has been reported by Friedman and Shechter.[8] Cyclopropylcarbene, prepared similarly from the corresponding *p*-toluenesulfonylhydrazone, gave ethylene, acetylene and cyclobutene.



Recently, Masamune and Kato[9] decomposed 3-formyl-1, 2-diphenylcyclopropene *p*-toluenesulfonylhydrazone with sodium methoxide at −20°C under irradiation with ultraviolet light. The major reaction product was also diphenylacetylene in this case, but a tetrahedrane derivative was also obtained in a 0.05—0.1% yield. In the present experiment, *p*-toluenesulfonylhydrazone (IVb) was investigated under very similar conditions, but

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[6] N. Obata and I. Moritani, This Bulletin, in press.

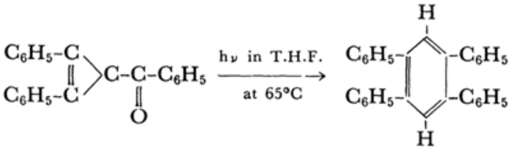
[7] The 1, 2-Diphenylcyclopropene skeleton exhibits very characteristic absorptions in the IR and UV regions; see R. Breslow and Chin Yuan, *J. Am. Chem. Soc.*, **80**, 5991 (1958); R. Breslow, T. Eicher, A. Krebs. R. A. Peterson and J. Posner, ibid., **87**, 1320 (1965),

[8] L. Friedman and H. Shechter, *J. Am. Chem. Soc.*, **82**, 1002 (1960).

[9] S. Masamune and M. Kato, ibid., **87**, 4190 (1965).

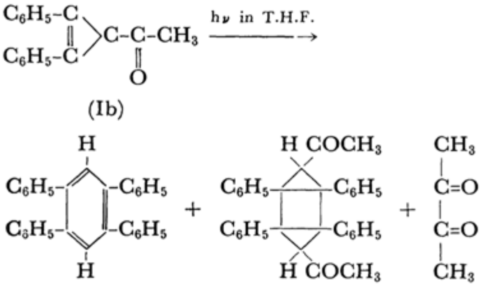
no evolution of nitrogen gas was observed at such a low temperature. Sodium salt of *p*-toluenesulfonylhydrazone was apparently formed, but its decomposition to a diazo compound might require a much higher temperature. In the present study we failed to obtain the tetrahedrane derivative.

The Photochemical Reaction of 3-Acyl-1, 2-diphenylcyclopropene.—A solution of 3-acylcyclopropene in tetrahydrofuran was irradiated by a high-pressure mercury lamp. The products were then separated by means of alumina-column chromatography. 3-Benzoyl-1, 2-diphenylcyclopropene (Ia) gave a hydrocarbon when eluted by petroleum ether and a glassy material when eluted by benzene or ether. The structure of the hydrocarbon was established to be 1, 2, 4, 5-tetraphenylbenzene (VIII) by comparison with an authentic material prepared through a known route.[10] The yield of VIII was 25.3%.



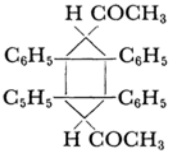
(Ia) (VIII)

Under the same conditions, the 3-acetyl derivative (Ib) gave a new compound IX in addition to tetraphenylbenzene (VIII), biacetyl (X), and a glassy material. When IX was dissolved in tetrahydrofuran and irradiated further under the same conditions, VIII was formed in a 43.4% yield, besides a glassy material. Consequently, it is clear that IX is the intermediate in the transformation of a cyclopropenyl ketone (Ib) to 1, 2, 4, 5-tetraphenylbenzene (VIII).

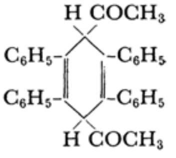


(VIII) (IX) (X)

Compound IX is considered to be 1, 2, 4, 5-tetraphenyl-3, 6-diacetyltricyclo[3, 1, 0, $0^{2,4}$]hexane on the basis of the following observations.[11] The spectral study of IX in the infrared and ultraviolet region shows clearly that the 1, 2-diphenylcyclopropene skeleton is absent in the compound IX. The analytical results and the molecular weight determination indicate that IX must be a dimeric material of the Ib ketone. Since IX has been found to be a precursor of VIII, it should have a structure which gives 1, 2, 4, 5-tetraphenylbenzene. Therefore, the compound IX may be considered to be either 1, 2, 4, 5-tetraphenyl-3, 6-diacetyltricyclo[3, 1, 0, $0^{2,4}$]hexane (IXa) or 1, 2, 4, 5-tetraphenyl-3, 6-diacetylcyclohexa-1, 4-diene (IXb):



(IXa)



(IXb)

In the infrared region, IX exhibited characteristic absorptions at 1700 cm^{-1} and at 1020 cm^{-1}. The carbonyl stretching frequency observed corresponds to that expected for cyclopropylketone.[12] The 1020 cm^{-1} absorption is due to the cyclopropane skeleton. The ultraviolet absorption spectrum of IX showed a broad maximum at 226 mμ (log ε 4.21) and a shoulder at 275 mμ (log ε 3.74). It has been reported that 1, 2-diphenylcyclopropane[13] exhibits maxima at 234 mμ (log ε 4.10) and at 275 mμ (log ε 3.95), whereas *cis*-α, α'-dimethylstilbene[14] shows a maximum at 252 mμ (log ε 3.94). The proton magnetic resonance spectrum of IX exhibited a multiplet (20 hydrogens) at 2.85 τ, a singlet (2 hydrogens) at 4.80 τ[*4] and a singlet (6 hydrogens) at 8.25 τ. Chemically, IX did not discolor a solution of potassium permanganate in acetone at room temperature after one hour, whereas *cis*-stilbene did. All these results are consistent with the tricyclohexane structure (IXa). The stereochemistry of this compound is not yet known. The yield was 6.7%.

Consequently, it may be suggested that the cyclopropenylketone Ib dimerizes preferentially to the cyclobutane derivative, IX. Further irradiation caused an α-cleavage and produced a biradical of a tricyclohexane, which then rearranged to a benzene derivative.

In an attempt to produce a cyclopropenyl radical, Breslow[16] obtained a dimer, bis-cyclopropenyl. This dimer rearranges to benzene derivatives on

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[10] W. Dilthey and G. Hurtig, *Ber.*, **67**, 2004 (1934).

[11] N. Obata and I. Moritani, *Tetrahedron Letters*, in press.

[12] L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," John Wiley & Sons, New York (1958).

[13] S. G. Beech, J. H. Turfull and W. Wilson, *J. Chem. Soc.*, **1952**, 4686.

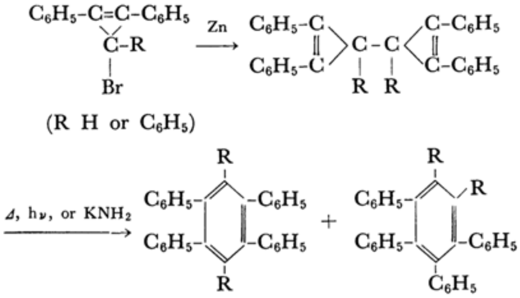
[14] H. Suzuki, This Bulletin, **33**, 396 (1960).

[*4] This absorption was identified as a tertiary proton in the tricyclohexane structure. Though similar proton appeared at a higher field (6.73—7.82 τ)[15] in methyl *trans*, *cis*-1, 2-diphenylcyclopropane-1-carboxylate, the deshielding effect might be more effective in IX because of the rigid ring system.

[15] J. K. Blatchford and M. Orchin, *J. Org. Chem.*, **29**, 839 (1964).

[16] R. Breslow, P. Gal, H. W. Chang and L. J. Altman, *J. Am. Chem. Soc.*, **87**, 5139 (1965).

heating, by irradiation or by treatment with potassium amide.



From a structural consideration, the ketones Ia and Ib in the present experiment are also capable of taking such a dimerization route, because one of the common photoreactions of the ketone is the α-cleavage.17) When a carbon-carbon bond on one side of a calbonyl group is preferentially cleaved, a cyclopropenyl radical is produced; it may dimerize as above, or it may abstract a hydrogen from the solvent. However, this was not the case in the ketones Ia and Ib. In a hydrocarbon fraction of the product none of the monomeric or dimeric hydrocarbons were detected other than a tricyclohexane and tetraphenylbenzene. Moreover, the isolation of a tricyclohexane as an intermediate clearly established that the reaction path was the preferential dimerization of the double bond in a cyclopropene skeleton. The α-cleavege followed it. A similar photodimerization of a cyclopropene derivative has recently been reported.18) Irradiation with ultraviolet light on 1, 3, 3-trimethylcyclopropene-1 in acetone in the presence of benzophenone results in the formation of two stereoisomeric dimers, tricyclo[3, 1, 0, $0^{2,4}$]hexanes.

There is an interesting possibility for this dimerization, that is, the carbonyl group may be absorbing most of the light, while the double bond is doing most of the reaction, as has been found in some other cases.19) In the present experiment, no evidence is available as a basis for deciding whether most of the light is absorbed by the carbonyl or by the double bond. However, the diphenylcyclopropene system absorbs the light at an appreciably longer wavelength with a high intensity.6,7) It is more likely, therefore, that the double bond in a diphenylcyclopropene is more easily excited than a carbonyl group and forms a cyclobutane ring. The cycloaddition of two double bonds under irradiation is well known and has been discussed recently by Hoffmann and Woodward.20)

In conclusion, the carbene reaction and photochemical reactions of the cyclopropene derivatives did not give simply ring-expanded materials as have been observed in many reactions. Cyclopropenylcarbene split into two olefinic compounds. Ultraviolet light caused a dimerization of olefin in the cyclopropene ring. Tricyclohexane derivatives were intermediates for the transformation of cyclopropenylketone to a benzene derivative.

Experimental*5

The Reaction of 3-Benzoyl-1, 2-diphenylcyclopropene (Ia) with Hydrazine Hydrate, 3, 4, 6-Triphenylpyridazine (IIIa).—A mixture of 1.07 g. (3.6 mmol.) of 3-benzoyl-1, 2-diphenylcyclopropene and 1.08 g. (21 mmol.) of hydrazine hydrate in 20 ml. of ethanol was heated under reflux for 15 hr. After the solution had cooled down, a mixture of yellow and white crystals, m. p. 135—175°C, was obtained. Repeated recrystallization of a mixture from ethanol-benzene gave white crystals, 3, 4, 6-triphenylpyridazine (IIIa), m. p. 171—172°C (reported 171°C)21); 0.75 g. (66.8%).

Found: C, 85.49; H. 5.17; N, 9.12; mol. wt. 299, Calcd. for $C_{22}H_{16}N_2$: C, 85.69; H, 5.23; N, 9.09%; mol. wt. 308.4.

In the infrared region, two characteristic peaks of IIIa were observed at 1560 cm^{-1} and 1580 cm^{-1}. The ultraviolet maximum in ethanol was 269 mμ (log ε 4.3) reported 273 mμ (log ε 4.4).22) A three-hour reaction caused a recovery of the starting material. The same material was prepared from ω-desylacetophenone and hydrazine hydrate.21) A mixed melting point determination of two samples showed no depression. The infrared and ultraviolet spectra of two samples were superimposable, also. The attempted recrystallization of yellow crystal gave a material which melted at 167—178°C, and which showed peaks at 3300 cm^{-1} (νN–H), 1635 cm^{-1} and 1590 cm^{-1} in the infrared spectrum. The ultraviolet spectrum of this impure yellow material showed broad maxima at 250 mμ and 310 mμ.

The Reaction of 3-Acetyl-1, 2-diphenylcyclopropene (Ib) with Hydrazine Hydrate, 3, 4-Diphenyl-6-methylpyridazine (IIIb).—A solution of hydrazine hydrate (0.23 g. (4.4 mmol)), and 3-acetyl-1, 2-diphenylcyclopropene (Ib) (0.46 g. (1.9 mmol.)) in 4 ml. of ethanol was heated under reflux for 20 hr. After the solution had cooled down, yellow crystal, m. p. 135—149°C, was obtained. This compound could not be purified by repeated recrystallization from ethanol or benzene. The evaporation of the mother liquid gave white crystals, 2, 4-diphenyl-6-methylpyridazine (IIIb), m. p. 122—123°C (petroleum ether); 0.15 g.

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17) O. L. Chapman, in W. A. Noyes, Jr., G. S. Hammond and J. N. Pitts, Jr., ed., "Advances in Photochemistry," Vol. I, Interscience Publishers, New York (1963), p. 323; R. Srinivasan, ibid., p. 83.

18) H. H. Stechl, *Chem. Ber.*, **97**, 2681 (1964).

19) Z. J. Barneis, D. M. S. Wheeler and T. H. Kinsle, *Tetrahedron Letters*, **1965**, 275; H. Morison, ibid., **1964**, 3653.

20) R. Hoffmann and R. B. Woodward, *J. Am. Chem. Soc.*, **87**, 2047 (1965); see also G. W. Griffin, A. F. Vellturo and K. Furukawa, ibid., **83**, 2725 (1961).

*5 All melting points were uncorrected. The IR spectrum was recorded by the use of EPI-S2. The UV spectrum was recorded by the use of EPS-2U. The NMR spectrum was recorded by the use of JNM-4H-100. The molecular weight was determined by the use of a vapor pressure osmometer.

21) A. Smith, *Ann.*, **289**, 316 (1896).

22) C. F. H. Allen and J. A. Vanallan, *J. Am. Chem. Soc.*, **73**, 5850 (1951).

(36.3%). Moreover, a solution of the yellow crystals in ether was gradually discolored in two days and 3, 4-diphenyl-6-methylpyridazine was obtained quantitatively. The structure of IIIb was established by the following observation.

Found: C, 82.75; H, 5.78; N, 11.35; mol. wt. 242. Calcd. for $C_{17}H_{14}N_2$: C, 82.90; H, 5.73; N, 11.67%; mol. wt. 246.3.

The characteristic infrared absorptions were at 1565 cm^{-1} and 1580 cm^{-1}. The ultraviolet maximum in ethanol was at 242 mμ (log ε 4.1). The NMR showed a multiplet (11 hydrogens) at 2.80 τ and a singlet (3 hydrogens) at 7.13 τ. Characteristic IR peaks of the impure yellow crystals, m. p. 150—156°C, were shown at 3300 cm^{-1} (νN–H), 1630 cm^{-1} and 1590 $cm.^{-1}$

2, 4-Dinitrophenylhydrazone of Ia and Ib.—The preparation of materials has already been described.⁶⁾ The characteristic infrared absorptions of 2, 4-dinitrophenylhydrazone of Ia, m. p. 193—194°C, were at 3250 cm^{-1} (νN–H) and 1825 cm^{-1} (νC=C in cyclopropene). The ultraviolet maxima of this compound in ethanol were at 228 mμ (log ε 4.25), 235 mμ (log ε 4.32), 296 mμ (log ε 4.25), 315 mμ (log ε 4.30) and 332 mμ (log ε 4.29). 2, 4-Dinitrophenylhydrazone of Ib, m. p. 210—211°C, showed characteristic IR peaks at 3300 cm^{-1} (νN–H) and 1830 cm^{-1} (νC=C in cyclopropene). The ultraviolet maxima of this compound in ethanol were at 228 mμ (log ε 4.33), 236 mμ (log ε 4.30), 295 mμ (log ε 4.24), 312 mμ (log ε 4.28) and 330 mμ (log ε 4.26).

3-Acetyl-1, 2-diphenylcyclopropene *p*-Toluenesulfonylhydrazone (IVb).—A solution of 3-acetyl-1, 2-diphenylcyclopropene (Ib) (0.14 g. (0.6 mmol.)) and *p*-toluenesulfonylhydrazine (0.16 g. (0.86 mmol.)) in 5 ml. of ethanol was heated under reflux for 0.5 hr. The product was then collected and recrystallized from benzene, m. p. 180—181°C (decomp.) The yield was 0.22 g. (93.0%).

Found: C, 71.86; H, 5.51. Calcd. for $C_{24}H_{22}N_2SO_2$: C, 71.61; H, 5.51%.

In the infrared spectrum the characteristic absorptions were observed at 3200 cm^{-1} (νN–H), 1820 cm^{-1} (νC=C in cyclopropene) and 1160 cm^{-1} (νSO_2). The ultraviolet maxima in ethanol were at 227 mμ (log ε 4.34), 234 mμ (log ε 4.32), 294 mμ (log ε 4.26), 302 mμ (log ε 4.36), 312 mμ (log ε 4.39) and 329 mμ (log ε 4.25).

At room temperature, a starting material was recovered after one day, whereas acetone and acetophenone reacted successfully.

The Reaction of 3-Benzoyl-1, 2-diphenylcyclopropene (Ia) with *p*-Toluenesulfonylhydrazone.—A solution of 3-benzoyl-1, 2-diphenylcyclopropene (Ia) (0.089 g. (0.30 mmol.)) and *p*-toluenesulfonylhydrazine (0.057 g. (0.32 mmol.)) in 5 ml. of ethanol was heated under reflux for 24 hr. After cooling, the precipitated material was found to be a starting ketone. After one week under reflux, however, no crystalline material was separated from the solution any more. The removal of the solvent gave a tarry material; *p*-toluenesulfonylhydrazone could not be obtained. In a separate experiment, the reaction was carried out in acetic acid at 90°C for 10 hr., but a tarry material resulted here also.

The Carbenic Decomposition of 3-Acetyl-1,2-diphenylcyclopropene *p*-Toluenesulfonylhydrazone (IVb) in the presence of Sodium Methoxide.—A solution of 3-acetyl-1, 2-diphenylcyclopropene *p*-toluenesulfonylhydrazone (IVb) (2.04 g. (5.1 mmol.)), in dry diglyme (40 ml.), was added drop by drop to a solution of sodium methoxide (0.31 g. (5.9 mmol.)), in dry diglyme (40 ml.), over a period of two hours at 120°C, at which temperature nitrogen gas was evolved gradually. Nitrogen gas and the volatile material was collected in a gas buret, and the latter was analyzed by mass spectrometer. We observed a mother peak corresponding to the C_3H_4 fragment in the mass spectrum. After it had cooled down, the reaction mixture was poured into a large amount of water. The organic material was extracted with ether several times. The combined ether solution was washed successively with ten 30-ml. portions of water to remove most of the diglyme. After the solution had been dried with anhydrous magnesium sulfate, the ether was removed by evaporation and the residue was subjected to column chromatography. Activated alumina (100 g.) was used. Elution with petroleum ether resulted in 0.26 g. (28.4%) of diphenylacetylene (VII), m. p. 59—60°C (reported 61°C).²³⁾ Elution with ether gave 0.33 g. (26.1%) of 3, 4-diphenyl-6-methylpyridazine (IIIb), m. p. 123—123.5°C (petroleum ether). In a separate experiment, *p*-toluenesulfonylhydrazone (IVb) was decomposed in the presence of copper powder at 120°C. The result was the same; the yields of VII and IIIb were 24.3 and 11.1% respectively.

The Photochemical Transformation of 3-Benzoyl-1, 2-diphenylcyclopropene (Ia).—3-Benzoyl-1, 2-diphenylcyclopropene (Ia) (0.602 g. (2.03 mmol.)), was dissolved in dry tetrahydrofuran (400 ml.) and irradiated by a high-pressure mercury lamp. The reaction was followed by a study of the ultraviolet spectrum. After the solution had been irradiated one and a half hours, the characteristic ultraviolet peaks near 300 mμ present in the staring ketone disappeared. The tetrahydrofuran was evaporated, and the residue was subjected to column chromatography. Activated alumina (90 g.) was used. Elution with petroleum ether gave 0.098 g. (25.3%) of 1, 2, 4, 5-tetraphenylbenzene (VIII), m. p. 260—261°C (petroleum ether) (reported 262—263°C).¹⁰⁾

Found: C, 93.86; H, 5.84. Calcd. for $C_{30}H_{22}$: C, 94.20; H, 5.80%.

The ultraviolet maxima in ethanol were at 252 mμ (log ε 4.65) and 282 mμ (log ε 4.24).

The same material was prepared from 3, 4-diphenylcyclopentadienon and diphenylacetylene at 275°C.¹⁰⁾ A mixed melting point determination of the two samples showed no depression. The infrared and ultraviolet spectra of the two samples were also superimposable. Elution with benzene, followed by that with ether, resulted in a glassy material (0.32 g.) which was not studied further.

The Photochemical Transformation of 3-Acetyl-1, 2-diphenylcyclopropene (Ib).—3-Acetyl-1, 2-diphenylcyclopropene (Ib) (0.78 g. (3.3 mmol.)) was dissolved in dry tetrahydrofuran (350 ml.) and irradiated by a high-pressure mercury lamp at 65°C. After two hours of irradiation, most of the solvent was removed by evaporation; and the separated solid was collected

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23) L. F. Fieser, "Experiments in Organic Chemistry," Maruzen Co., Tokyo, Japan (1963), p. 181.

from the oily residue. The recrystallization of the solid material from ligroin-benzene resulted in 0.052 g. (7.6%) of 1, 2, 4, 5-tetraphenyl-3, 6-diacetyl-tricyclo[3, 1, 0, $0^{2,4}$]hexane (IX), m. p. 285—287°C (with decomp.)

Found: C, 87.13; H, 6.10; mol. wt. 451. Calcd. for $C_{34}H_{28}O_2$: C, 87.15; H, 6.02%; mol. wt. 468.6.

In the infrared region, IX exhibited its characteristic absorptions at 1700 cm^{-1} and at 1020 cm^{-1}. The ultraviolet maxima in ethanol were at 226 mμ (log ε 4.21) and a shoulder at 275 mμ (log ε 3.74). The NMR showed a multiplet (10 hydrogens) at 2.85τ, a singlet (1 hydrogen) at 4.80, and a singlet (3 hydrogens) at 8.25 τ.

The concentration of the mother liquid of recrystallization gave a material melting at 260—261 °C, 1, 2, 4, 5-tetraphenylbenzene (VIII). The combined residue of recrystallization was subjected to column chromatography. From the hydrocarbon fraction, additional portions of VIII were obtained. The yield of VIII was 0.133 g. (20.3%).

The Photolysis of 1, 2, 4, 5-Tetraphenyl-3, 6-diacetyl-tricyclo[3, 1, 0, $0^{2,4}$]hexane (IX).—Tricyclohexane (IX) (25 mg. (0.053 mmol.)) was dissolved in dry tetrahydrofuran (300 ml.), and the solution was irradiated by a high-pressure mercury lamp for 4.5 hr. The temperature of the solution was kept at 50°C during the photolysis. Tetrahydrofuran was removed, and the residue was subjected to column chromatography. Activated alumina (30 g.) was used. Elution with petroleum ether gave 8.9 mg. (43.4%) of 1, 2, 4, 5-tetraphenylbenzene (VIII). Elution with ether resulted in a glassy material, but this was not studied further.