Diphenylcyclopropenone[1,2]

Ronald Breslow, Theo Eicher, Adolf Krebs, Ruth A. Peterson, and Judd Posner

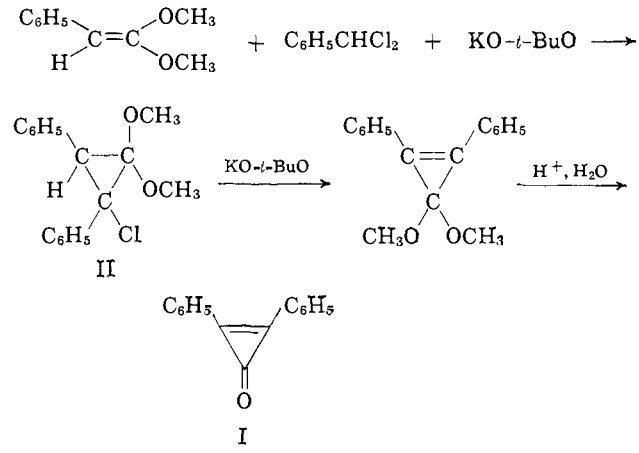
Contribution from the Department of Chemistry, Columbia University, New York, New York 10027. *Received November 19, 1964*

Diphenylcyclopropenone may be synthesized by a variety of methods; the best procedure involves elimination of HBr from α,α′-dibromodibenzyl ketone, but several syntheses involving carbenoids may also be used. The physical and chemical properties of diphenylcyclopropenone show that the ketone is strongly polarized, as expected for a derivative of the aromatic cyclopropenyl cation. On pyrolysis the compound is converted to diphenylacetylene and carbon monoxide, but under milder conditions a dimer of diphenylcyclopropenone is formed. With base, the ring opens at the carbonyl group, while catalytic hydrogenation causes a different cleavage, to dibenzyl ketone. Phenylmagnesium bromide adds normally to the carbonyl group, but hydroxylamine and diazomethane both afford unusual products; reaction of the ketone with pyridine proceeds by an unusual path as well. Diphenylcyclopropenone may be alkylated to yield ethoxydiphenylcyclopropenyl cation, and this undergoes nucleophilic substitution with dimethylamine to afford dimethylaminodiphenylcyclopropenyl cation.

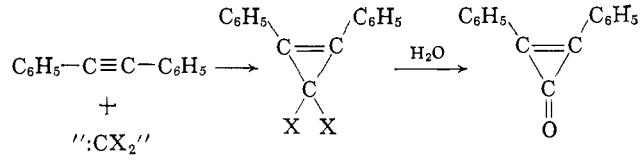
Diphenylcyclopropenone (I) was first synthesized in 1959, both in our laboratory[2a] and simultaneously by Vol'pin.[3] Since that time several publications[4] have appeared describing properties and reactions of this interesting substance. In the present paper we report the details of some of our investigations.

1. Synthesis. Our first[2a] synthesis of diphenylcyclopropenone was based on the addition of a carbene to a ketene acetal reported by McElvain.[5] The product is a chlorocyclopropanone ketal, but we felt that ready elimination of HCl should be possible[6] in the case of II to afford a diphenylcyclopropene derivative. Acidic work-up of the reaction produces diphenylcyclopropenone in an 80% yield, but the relative difficulty in preparing phenylketene dimethyl acetal makes this an unattractive synthetic method.

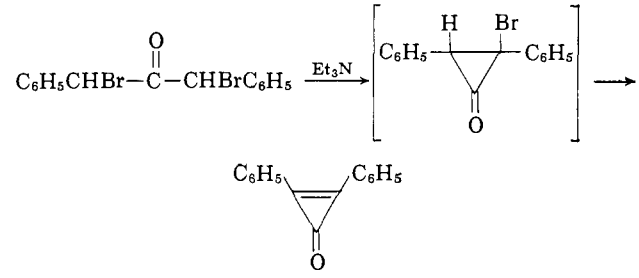
A more convenient procedure is that reported by Vol'pin.[3] Reaction of diphenylacetylene with bromoform and potassium *t*-butoxide affords a 20–30% yield of the ketone, which we have confirmed. We find that



a comparable yield is obtained with the carbenoid[7] from methyl trichloroacetate and sodium methoxide, but only a 6% yield is obtained with a 20% excess of sodium trichloroacetate as the carbene source[8] and none with sodium tribromoacetate or chlorodifluoroacetate.



The best procedure[2b] on a preparative scale is elimination of HBr from α,α′-dibromodibenzyl ketone. It has been established[9] that the Favorskii reaction of α-halo ketones proceeds through an intermediate with the symmetry of a cyclopropanone; we find that treatment of dibromodibenzyl ketone with triethylamine causes elimination of HBr from the intermediate cyclopropanone to produce diphenylcyclopropenone in 45% over-all yield from dibenzyl ketone.



Bromination of dibenzyl ketone affords not only the previously described[10] stereoisomer of m.p. 114°, but also an isomer of m.p. 96°. Since each shows a single strongly shifted aliphatic hydrogen signal in the n.m.r. (at τ 4.3 and 4.4, respectively, compared with 6.4 for

(1) Abstracted in part from the Ph.D. Theses of R. Peterson, 1962, and J. Posner, 1964; support of this work by the National Science Foundation, the Petroleum Research Fund of the American Chemical Society, the Sloan Foundation, and the California Research Corp. is gratefully acknowledged.

(2) For preliminary reports of some of these results, *cf.* (a) R. Breslow, R. Haynie, and J. Mirra, *J. Am. Chem. Soc.*, **81**, 247 (1959); (b) R. Breslow, J. Posner, and A. Krebs, *ibid.*, **85**, 234 (1963).

(3) (a) M. E. Vol'pin, Yu. D. Koreshkov, and D. N. Kursanov, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, **3**, 560 (1959); (b) D. N. Kursanov, M. E. Vol'pin, and Yu. D. Koreshkov, *J. Gen. Chem. USSR*, **30**, 2855 (1960).

(4) For example (a) Yu. G. Borodko and Ya. K. Syrkin, *Dokl. Akad. Nauk SSSR*, **136**, 1335 (1961); (b) B. E. Zaitsev, Yu. D. Koreshkov, M. E. Vol'pin, and Y. N. Sheinker, *ibid.*, **139**, 1107 (1961); M. Battiste, *J. Am. Chem. Soc.*, **86**, 942 (1964).

(5) S. M. McElvain and P. L. Weyna, *ibid.*, **81**, 2579 (1959).

(6) *Cf.* S. F. Darling and E. W. Spanagel, *ibid.*, **53**, 1117 (1931).

(7) W. E. Parham and E. E. Schweizer, *J. Org. Chem.*, **24**, 1733 (1959).

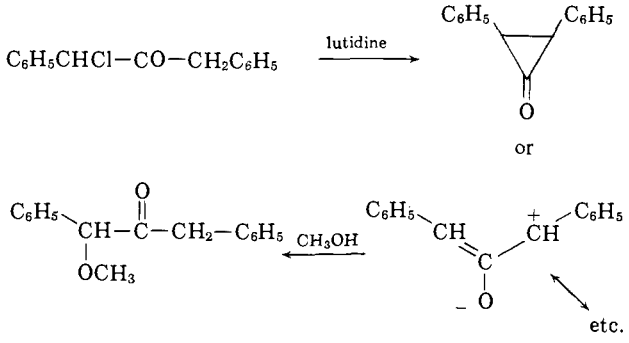
(8) W. M. Wagner, *Proc. Chem. Soc.*, **229** (1959).

(9) For a review, *cf.* A. Kende, *Org. Reactions*, **11**, 261 (1960).

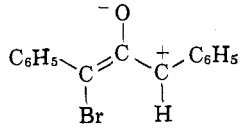
(10) P. Ruggli, H. Dahn, and J. Wigmann, *Helv. Chim. Acta*, **29** 113 (1946), and previous references.

dibenzyl ketone) they are both α,α'-dibromo ketones. The n.m.r. spectrum of the crude mixture shows that the *meso* and *dl* compounds are present in roughly a 1:1 ratio; the yield of cyclopropenone from this 1:1 mixture was nearly the same as that from the 90% pure m.p. 114° isomer. Diphenylcyclopropenone could also be prepared from α,α'-dichlorodibenzyl ketone, but in lower yield.

When α-chlorodibenzyl ketone is treated with 2,6-lutidine, an intermediate is produced which can be captured with furan[11] or with methanol[12]; the intermediate may be formulated as diphenylcyclopropanone or as a delocalized species.[11-13] Evidence that a delocalized intermediate must at least be in equilibrium



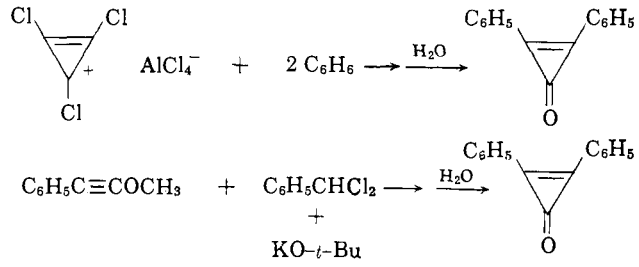
with the cyclopropanone is also found in studies[13] of the stereochemistry of the Favorskii reaction in polar media. However, in our reaction neither concerted nor stepwise loss of HBr from the delocalized intermediate (III) seems likely. Loss of the proton in the nodal plane of the π-system to afford an enolate carbene, or of the similarly situated bromine to afford a cation carbene, should not occur under our mild conditions; formation of a σ-bond by elimination should



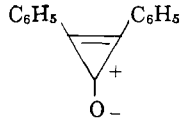
III

also require much more vigorous conditions. Accordingly, it seems that the bromocyclopropanone must be the intermediate in our case. It is interesting that approximately the same yield of cyclopropenone is obtained in aqueous dioxane solution: elimination of HBr is faster than cleavage of the cyclopropanone in either a Favorskii reaction or a solvolysis *via* III. However, treatment of the dibromo ketone with 2,6-lutidine in methanol produces no detectable cyclopropenone, although bromide ion is produced and diphenylcyclopropenone is stable under these conditions. Triethylamine in methanol affords an 8% yield of the cyclopropenone. Pyridine cannot be used since it reacts with the cyclopropenone (*vide infra*).

Two other syntheses of diphenylcyclopropenone should be mentioned. Recently, West has reported the reaction between trichlorocyclopropenyl cation and benzene.[14] We have found that the ketone may also be produced by reaction of phenylmethoxyacetylene with phenylchlorocarbene.[15] Neither of these seems to be an attractive preparative scheme.



2. Properties. In the infrared spectrum diphenylcyclopropenone shows the two strong bands at 1850 and 1640 cm.$^{-1}$ which are apparently characteristic of the cyclopropenone system. On the basis of solvent shifts, the 1850-cm.$^{-1}$ band has been assigned[16] to the C=C stretch in the cyclopropene system; disubstituted cyclopropenes generally show a weaker band in this region. The 1640-cm.$^{-1}$ absorption has been assigned[16] to C=O stretching. Since cyclopropanone probably has its carbonyl frequency[17] at 1825 cm.$^{-1}$, a shift to 1640 cm.$^{-1}$ would represent considerable weakening of the C=O bond. The stretched dipolar form could be stabilized because of the special aromatic stability of cyclopropenyl cations, but these unusual assignments must be considered only tentative.[18]



Good evidence for strong polarization of diphenylcyclopropenone is its dipole moment. We find[19] 5.14 D., while 5.08 D. has been reported,[3] but comparison of either value with the 3.0 D. for benzophenone, the 4.3 D. of tropone, and the 5.03 D. of trimethylamine oxide indicate that diphenylcyclopropenone is indeed very strongly polarized. Polarization is also reflected in the high basicity of diphenylcyclopropenone and other cyclopropenone derivatives; the ketone is half protonated[20] at $H_0 = -2.5 \pm 0.3$, and it readily yields salts with acids.[3] This basicity is used to assist in isolation of the ketone. The ultraviolet spectrum, $\lambda\lambda_{max}$ (in CH_3CN) 297 mμ (log ϵ 4.46), 285 (4.41), 227 (4.32), and 220 (4.34) with a shoulder at 310 (4.30), resembles that of simple diphenylcyclopropenes[21]; however, the spectra of arylcyclopropenyl cations are also similar.[21]

3. Reactions. On being heated at 160° for 14 hr., diphenylcyclopropenone decarbonylates to afford an 80% yield of diphenylacetylene. At 190° the decarbonylation is rapid, $t_{1/2}$ ~5 min., but at 145–150°, after 36 hr., only 20% of diphenylacetylene is formed

(11) A. W. Fort, *J. Am. Chem. Soc.*, **84**, 4979 (1962).
(12) A. W. Fort, *ibid.*, **84**, 2620 (1962).
(13) H. O. House and W. F. Gilmore, *ibid.*, **83**, 3980 (1961); *cf.* G. Stork and I. Borowitz, *ibid.*, **82**, 4307 (1960).
(14) S. Tobey and R. West, *ibid.*, **86**, 4215 (1964).
(15) R. Breslow, L. J. Altman, A. Krebs, E. Mohacsi, I. Murata, R. Peterson, and J. Posner, *ibid.*, **87**, 1326 (1965).
(16) A. Krebs, *Angew. Chem., Intern. Ed. Engl.*, **4**, 10 (1965).
(17) W. B. DeMore, H. O. Pritchard, and N. Davidson, *J. Am. Chem. Soc.*, **81**, 5874 (1959).
(18) R. Breslow, H. Höver, and H. Chang. *ibid.*, **84**, 3168 (1962), and earlier publications.
(19) Dielectric constant measurements were performed by Mr. Tibor Mahr of this department, and the dipole moment was calculated by the method of E. Guggenheim, *Trans. Faraday Soc.*, **45**, 714 (1949).
(20) A. Kende, private communication.
(21) R. Breslow and H. Chang, *J. Am. Chem. Soc.*, **83**, 2367 (1961).

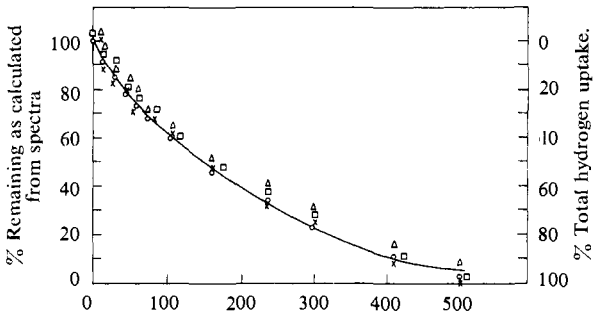
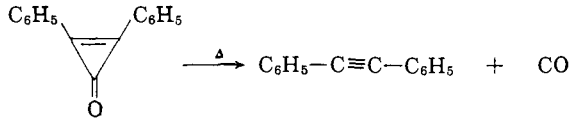
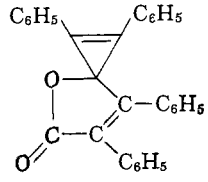


Figure 1. Spectral studies during hydrogenation of diphenylcyclopropenone in *p*-dioxane: ⊙, hydrogen uptake; ×, 1850-cm.$^{-1}$ infrared peak; △, 1640-cm.$^{-1}$ infrared peak, and ■, ultraviolet λ_{max} 298 mμ.

although decomposition of the ketone is complete. In addition to diphenylacetylene, this lower temperature pyrolysis affords a 40% yield of a dimer of diphenylcyclopropenone. The spectroscopic data, with a

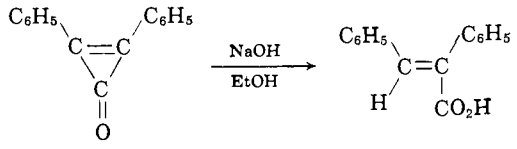


carbonyl band in the infrared at 1745 cm.$^{-1}$, aromatic hydrogens in the n.m.r., and a typical diphenylcyclopropene ultraviolet spectrum, are consistent with structure IV for this dimer. However, efforts to obtain definitive chemical evidence on the structure are incomplete and IV must be regarded as provisional. In any case, pyrolysis of the dimer does not afford diphenylacetylene, so these two thermal products arise from different pathways.

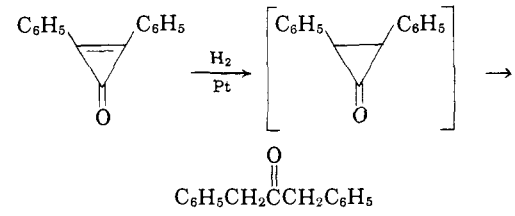


IV

Diphenylcyclopropenone is hydrolyzed with aqueous base to *cis*-1,2-diphenylacrylic acid.[3,22] The reaction is relatively rapid, $t_{1/2}$ in 0.1 *N* NaOH in ethanol at 24° being only about 5 min.; dialkylcyclopropenones are much more stable.[15,22]

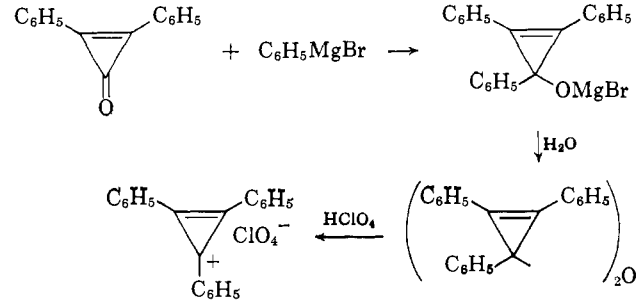


Catalytic hydrogenation of diphenylcyclopropenone has been reported[3] to yield diphenylcyclopropanol. We have repeated this reaction and find that 2 moles of hydrogen are indeed taken up, as reported, but the product is dibenzyl ketone, in 75% yield. Over a longer time dibenzyl ketone is further reduced to the alcohol. Apparently the intermediate diphenylcyclopropanone is reduced more easily than the starting material, since both ultraviolet and infrared assays of remaining diphenylcyclopropenone as a function of H_2 absorbed



show this as an apparent direct 2-mole reduction (Figure 1). In particular, after 1 mole of H_2 has been absorbed one has 0.5 mole of starting cyclopropenone and 0.5 mole of dibenzyl ketone. We considered the possibility that our observed cyclopropane hydrogenolysis, in contrast to what had been reported, could be due to traces of acid in our system; however, our results were identical when the reduction was run with $NaHCO_3$ present. The failure to reduce a cyclopropanone carbonyl might also be ascribed to its presence, in ethanol, as the hemiketal. However, our results were the same when purified dioxane was the solvent. Hydrogenolysis may well proceed *via* the open intermediate related to III, but it is interesting that this or the cyclopropanone are reduced more rapidly than they react with ethanol in the normal fashion.

Diphenylcyclopropenone reacts with phenylmagnesium bromide to afford a 50% yield of triphenylcyclopropenyl cation[21] after appropriate work-up. Since the yield is not affected by base treatment after hydrolysis of the Grignard complex, the intermediate in solution is not triphenylcyclopropenol (which would cleave) but probably the dimeric ether.[21] However,

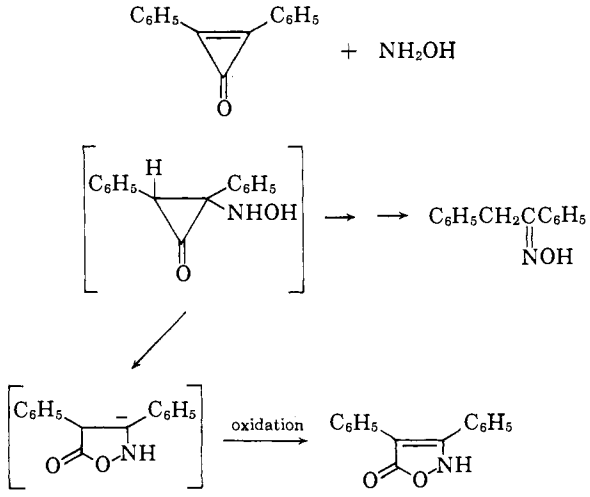


this does not seem to be a good general synthetic procedure since it does not work well with some aliphatic Grignard reagents.

It has been reported[3] that diphenylcyclopropenone gives a (not characterized) 2,4-dinitrophenylhydrazone. In our hands this material is ill-defined and gives poor analytical values for a simple derivative. In order to explore carbonyl derivatives in a more tractable series, we have examined the reaction of diphenylcyclopropenone with hydroxylamine. Two unusual products are obtained: deoxybenzoin oxime (31%) and 3,4-diphenylisoxazolone[23] (61%). Both products arise from an oxidation, although the results were unaffected by the exclusion of O_2. Only symbolic mechanisms are warranted, but it seems apparent that the first step involves conjugate addition of hydroxylamine to the carbon–carbon double bond. Controls show that neither diphenylacetylene nor 3,4-diphenylisoxazole is the precursor of deoxybenzoin oxime under these conditions, so direct attack on the

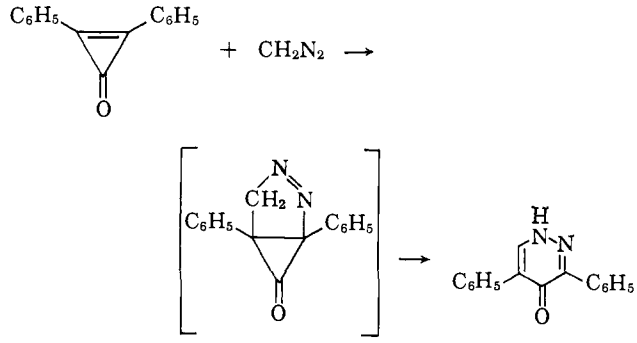
(22) R. Breslow and R. Peterson, *J. Am. Chem. Soc.*, 82, 4426 (1960).

(23) E. P. Kohler and A. H. Blatt, *ibid.*, 50, 504 (1928).



cyclopropenone is likely as the first step in formation of both products.

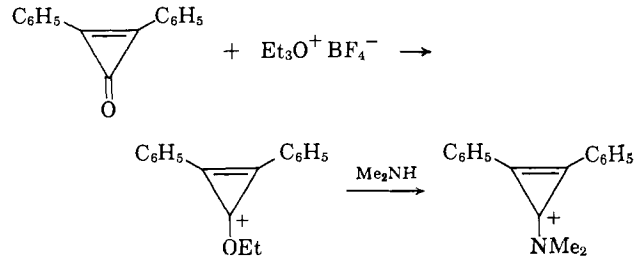
When diphenylcyclopropenone is treated with diazomethane 3,5-diphenylpyridazone-4 is formed.[24] The structure of this compound was proved by conversion to known[25] 3,5-diphenylpyridazine (prepared from known[26] 3,5-diphenylpyridazone-6). When the cyclo-



propenone is treated with diazomethane and $AlCl_3$, 3,5-diphenyl-4-methoxypyridazine is formed. Thus, even when diphenylcyclopropenone is coordinated with a Lewis acid, addition of diazomethane across the carbon–carbon double bond occurs rather than attack at the carbonyl group. Treatment of the pyridazin-4-one under the same conditions also affords the methoxy compound.

In the course of examining the reaction of α,α'-dibromodibenzyl ketone with bases (*vide supra*) it was found that diphenylcyclopropenone reacts readily with pyridine. Two moles of diphenylcyclopropenone is incorporated per mole of pyridine, and it seems likely that one of the diphenylcyclopropenones has become a diphenylacrylic ester residue since hydrolysis affords *cis*-1,2-diphenylacrylic acid.[27] The most likely structures based on the spectra and mechanistic considerations are diphenylacrylic esters of diphenylpyrrocolinols, but attempts at degradative structure proof have so far been fruitless.

Finally, in the course of some other work diphenylcyclopropenone has been converted into two interesting cyclopropenyl cations. Alkylation with triethyloxonium fluoroborate produces ethoxydiphenylcyclopropenyl fluoroborate. This reacts with dimethylamine to form 1,2-diphenyl-3-dimethylaminocyclopropenyl fluoroborate. The ethoxy cation hydrolyzes readily, but the amino cation is very stable; in fact, it can be recrystallized undecomposed from hot water.



Experimental

1. Synthesis of Diphenylcyclopropenone. A. From Dibenzyl Ketone. To a solution of 70 g. ($^1/_3$ mole) of commercial dibenzyl ketone in 250 ml. of glacial acetic acid, a solution of 110 g. ($^2/_3$ mole) of bromine in 500 ml. of acetic acid was added with stirring over 15 min. After the addition was complete, the mixture was stirred for an additional 5 min. and then poured into 1 l. of water. Solid Na_2SO_3 was added in small portions until the initial yellow color of the solution was discharged, and the mixture was allowed to stand for 1 hr. The slightly yellow mixture of *meso*- and *dl*-α,α'-dibromodibenzyl ketone was collected and air dried. Recrystallization from ligroin (*ca.* 1 l.) afforded 97 g. of white needles, m.p. 79–97°; an additional 11 g., m.p. 79–83°, was obtained by concentrating the mother liquors, and the two were combined.

This mixture of isomers (108 g.) was dissolved in 500 ml. of methylene chloride and the solution was added with stirring over 1 hr. to 100 ml. of triethylamine in 250 ml. of methylene chloride at room temperature. The mixture was stirred for an additional 30 min., extracted with two 150-ml. portions of 3 *N* HCl (discarded), and the organic phase was transferred to a flask and cooled in an ice bath. A cool solution of 50 ml. of H_2SO_4 in 25 ml. of water was slowly added. A slightly pink precipitate of diphenylcyclopropenone bisulfate separated and this was collected on a sintered glass funnel and washed with two 100-ml. portions of methylene chloride. The solid was then returned to the flask along with 250 ml. of methylene chloride and 500 ml. of water, and 5 g. of solid Na_2CO_3 was added in small portions. The organic layer was collected and the aqueous solution was extracted with two 150-ml. portions of methylene chloride. The combined organic layers were dried over $MgSO_4$ and evaporated to dryness. The impure diphenylcyclopropenone was recrystallized by repeated extractions with boiling cyclohexane (total 1.5 l.), the solution being decanted from a reddish, oily impurity. On cooling, the solution deposited white crystals, 29 g., and an additional 1 g. was obtained by concentrating the mother liquors to 150 ml. The combined 30 g. of diphenylcyclopropenone, m.p. 119–120°, represents an over-all yield of 45% based on dibenzyl ketone.

The mixture of stereoisomers of α,α'-dibromodibenzyl ketone could be resolved by fractional crystallization from cyclohexane into its components.

(24) *Cf.* also P. T. Izzo and A. S. Kende, *Chem. Ind.* (London), 839 (1964), for an independent report of this reaction.
(25) G. K. Almstroem, *Ann.*, **400**, 131 (1913).
(26) J. Druey and B. Ringier, *Helv. Chim. Acta*, **34**, 195 (1951).
(27) More than 1 mole is obtained, suggesting drastic degradation, but under mild conditions 1 mole is produced.

Isomer A, m.p. 96–96.5°, had n.m.r. signals at τ 2.8 (area 5) and 4.4 (area 1).

Anal. Calcd. for $C_{15}H_{12}Br_2O$: C, 48.96; H, 3.29; Br, 43.44. Found: C, 48.75; H, 3.33; Br, 43.71.

Isomer B, m.p. 115–116° (lit.[10] m.p. 114°), had n.m.r. signals at τ 2.8 (area 5) and 4.3 (area 1).

Anal. Calcd. for $C_{15}H_{12}Br_2O$: C, 48.96; H, 3.29; Br, 43.44. Found: C, 48.67; H, 3.19; Br, 43.50.

N.m.r. comparison of the τ 4.3 and 4.4 areas showed that the two isomers were present equally in the original mixture.

Treatment of the pure isomer B with triethylamine in the standard way afforded diphenylcyclopropenone in the same yield as was obtained from the 1:1 mixture of isomers A and B.

When the mixture of A and B (1.7 g.) was treated with 5 ml. of triethylamine in 35 ml. of dioxane and 5 ml. of H_2O, diphenylcyclopropenone was obtained in similar yield (0.34 g., 36%). No cyclopropenone could be detected (infrared band at 5.4 μ) when the mixture of A and B was treated with NaH in benzene, *t*-BuOK in benzene, or dry pyridine.

A mixture of *meso*- and *dl*-α,α'-dichlorodibenzyl ketones was prepared by reaction of dibenzyl ketone with SO_2Cl_2 in glacial acetic acid. The unfractionated product, m.p. 48–80°, n.m.r. τ 2.9 (area 5) and 4.45 and 4.75 (area 1), was used directly.

Anal. Calcd. for $C_{15}H_{12}Cl_2O$: C, 64.53; H, 4.33; Cl, 25.42. Found: C, 64.48; H, 4.32; Cl, 24.91.

Reaction of 10 g. of this dichloro ketone with triethylamine under the standard conditions afforded 0.9 g. (12% yield) of diphenylcyclopropenone.

B. From Diphenylacetylene. Reaction[3] of 60.2 g. of diphenylacetylene (0.338 mole) and 106.4 g. of potassium *t*-butoxide (0.950 mole) in 500 ml. of hexane with 77.5 g. of bromoform (0.306 mole) at −11° under N_2 over 3 hr., followed by aqueous work-up afforded 17.0 g. (0.082 mole) of diphenylcyclopropenone, m.p. 119–121°.

Reaction of diphenylacetylene (0.112 mole) with sodium methoxide (0.420 mole) and methyl trichloroacetate (0.154 mole) in pentane at −4°, followed by aqueous work-up, afforded diphenylcyclopropenone (0.013 mole).

Reaction of diphenylacetylene (0.112 mole) with sodium trichloroacetate (0.136 mole) in dimethoxyethane at 80° for 18 hr. afforded diphenylcyclopropenone (0.006 mole).

C. From Phenylketene Dimethyl Acetal. An 11.05-g. mixture[5] of phenylketene dimethyl acetal and methyl orthophenylacetate (2:1 or 0.042 mole:0.021 mole as determined from the n.m.r. spectrum) and 25.2 g. of commercial potassium *t*-butoxide (0.225 mole) was placed in a flask with 50 ml. of dried benzene. The reaction mixture was very viscous so an additional 200 ml. of benzene was added during the course of the reaction to facilitate stirring. The reaction mixture was put under a nitrogen atmosphere and 14.0 g. of freshly distilled benzal chloride (0.087 mole) was added dropwise over a period of 1 hr. to the reaction mixture which was cooled in ice water. The reaction mixture was then heated at 70–80° for 19 hr. to facilitate the loss of hydrogen chloride. The reaction was worked up to yield 7.0 g. of diphenylcyclopropenone, m.p. 117–120° (80.5% based on the ketene acetal).

2. Reactions of Diphenylcyclopropenone. A. Pyrolysis. Diphenylcyclopropenone was heated in the melt under N_2 at 160–162°. Carbon monoxide was slowly evolved (from the intensities of the 1850- and 1640-cm.$^{-1}$ infrared bands, respectively, 88 and 86% of the ketone remained after 15 min.). After 14 hr. an 80% yield of diphenylacetylene was obtained. At 190–192°, only 10% diphenylcyclopropenone was undecomposed after 7 min. and 74% after 3 min. When diphenylcyclopropenone was held at 145–150° for 36 hr. (complete decomposition) only a 20% yield of diphenylacetylene was obtained together with a 40% yield of a *dimer* of the cyclopropenone, m.p. 181–182° dec., isolated by trituration of the crude product with ethanol.

Anal. Calcd. for $C_{30}H_{20}O_2$: C, 87.35; H, 4.89; mol. wt., 412.5. Found: C, 87.48, 86.96; H, 5.03, 4.73; mol. wt. (osmometer, 0.8% CCl_4 solution), 448.

In the infrared spectrum the compound showed weak bands at 3080, 3063, 3028, 1955, 1885, 1830, 1810, 1635, 1600, and 1580 cm.$^{-1}$, and others in the 1370- to 890-cm.$^{-1}$ region, with strong bands at 1745, 1500, 1450, 703, and 688 cm.$^{-1}$ The ultraviolet spectrum in 95% ethanol showed $\lambda\lambda_{max}$: 313 mμ (ϵ 28,600), 297 (39,300), 284 sh (35,200), 228 (38,400), 222 (37,300), and 198 (61,800). The n.m.r. spectrum shows only complex absorption in the region of τ 2 to 3. On pyrolysis the dimer affords no detectable diphenylacetylene. Some dimer (5–15%) was also formed at 160°. Formation of the dimer was increased in the presence of traces of alkali.

B. Basic Hydrolysis. As has been reported elsewhere,[3,22] heating diphenylcyclopropenone in aqueous sodium hydroxide solution affords *cis*-1,2-diphenylacrylic acid in high yield. The rate of this cleavage was determined by preparing a standard solution of diphenylcyclopropenone in 95% ethanol. A 1-ml. aliquot was diluted with 5 ml. of water; this was extracted with 1 ml. of CCl_4 and the CCl_4 solution was examined quantitatively in the infrared at 1850 and 1640 cm.$^{-1}$ as a standard. To another 1-ml. aliquot 0.10 ml. of 1 *N* aqueous NaOH was added, and the solution was allowed to stand at 24° for 5 min. before dilution and extraction. Only 53 (1850 cm.$^{-1}$) to 54% (1640 cm.$^{-1}$) of diphenylcyclopropenone was uncleaved. After 3 min. at 48–49° in such 0.1 *N* alcoholic NaOH, 75% of the ketone was hydrolyzed.

C. Hydrogenation. Platinum dioxide (0.223 g.) was prereduced in 50 ml. of absolute ethanol, and 0.4545 g. of diphenylcyclopropenone was added. Rapid uptake of hydrogen ceased after 126 ml. (26°, 763 mm.) corresponding to 2.1 moles/mole of ketone. The mixture was filtered, the ethanol was removed *in vacuo*, and the residue was taken up in CCl_4. The infrared spectrum and n.m.r. spectrum of this solution were identical in all detail with the spectra of *dibenzyl ketone*. Aliquots afforded 65% yields of the dinitrophenylhydrazone of dibenzyl ketone (melting point, mixture melting point, and infrared); in controls the authentic ketone gave 85% isolable yields of dinitrophenylhydrazone, so the yield of dibenzyl ketone from the reduction is 75%. When the reduction was performed in purified *p*-dioxane as solvent, a 70% yield of dibenzyl ketone was obtained.

A hydrogenation in *p*-dioxane was followed by with-

drawing samples periodically for spectroscopic assay. The results are presented in Figure 1.

D. Reaction with Phenylmagnesium Bromide. A Grignard reagent was prepared with 2.50 g. (0.159 mole) of bromobenzene in 15 ml. of ether, and to the ice-cold solution 1.029 g. (0.0050 mole) of diphenylcyclopropenone in 5 ml. of benzene was added dropwise with stirring. After 30 min. the mixture was quenched in cold aqueous KH_2PO_4 solution and the organic layer was combined with an additional ether extract. After drying and solvent stripping, 2.04 g. of sirupy residue remained; when this was dissolved in ether and treated with $HClO_4$ in acetic anhydride 0.899 g. (49% yield) of *triphenylcyclopropenyl perchlorate* was obtained, m.p. 238–240°, identical with an authentic sample (mixture melting point, infrared, and ultraviolet).

E. Reaction with Hydroxylamine. Hydroxylamine hydrochloride (3 g.) was dissolved in 18 ml. of H_2O with 12 ml. of 20% aqueous sodium acetate, and 1.0 g. (0.0048 mole) of diphenylcyclopropenone in 50 ml. of ethanol was added. The solution was refluxed for 30 min., the ethanol was removed by distillation, and the product was separated into neutral and acidic (10% $NaHCO_3$) fractions. The neutral fraction yielded 0.318 g. (31%) of *deoxybenzoin oxime*, m.p. 94–96°, (mixture melting point, infrared, and analysis) after crystallization from aqueous ethanol and alumina chromatography. The acidic fraction yielded 0.703 g. (61.5%) of *3,4-diphenylisoxazolone*,[23] m.p. 158–159.5° (mixture melting point, analysis, infrared, and ultraviolet). Controls established that neither diphenylacetylene (97% recovery) nor 3,4-diphenylisoxazolone (93% recovery) is converted to detectable amounts of deoxybenzoin oxime under the reaction conditions.

F. Reaction with Diazomethane.[24] An ethereal solution of diazomethane (*ca.* 0.020 mole) was mixed at 0° with 2.0 g. of diphenylcyclopropenone (0.010 mole) in benzene, with immediate precipitation of a yellow solid. After 15 hr., the solid was collected and dried, yielding 1.50 g., m.p. 336–338° after crystallization from pyridine.

Anal. Calcd. for $C_{17}H_{14}N_2O$: C, 77.84; H, 5.38; N, 10.68. Found: C, 77.31; H, 5.36; N, 11.03.

Further work showed this to be *3,5-diphenylpyridazone-4;* the above yield corresponds to 58%, and 20% of diphenylcyclopropenone was also recovered from the filtrate.

For proof of structure, 2.01 g. of the above pyridazone was heated in 20 ml. of $POCl_3$ for 30 min. on the steam bath. After aqueous work-up, the gummy product was suspended in 60 ml. of ethanol with 3 ml. of aqueous ammonia, and hydrogenated over 0.5 g. of Pd–C. One mole of H_2 was absorbed over 2 hr., and 1.39 g. (74% yield) of *3,5-diphenylpyridazine* was then isolated, m.p. 141–141.5° from aqueous ethanol. The compound was identical (mixture melting point and infrared) with an authentic sample, prepared according to the procedure of Almstroem[25] but with catalytic hydrogenation substituted for phosphorus–HI reduction.

When 3,5-diphenylpyridazone-4 was treated with diazomethane and $AlCl_3$ in ether, it afforded *4-methoxy-3,5-diphenylpyridazine*, m.p. 171–172.5°.

Anal. Calcd. for $C_{18}H_{16}N_2O$: C, 78.24; H, 5.84; N, 10.14; mol. wt., 276.3. Found: C, 78.05; H, 5.54; N, 10.89; mol. wt. (osmometer, benzene), 282.

This product was the only material isolated (50% yield with 7% of the above pyridazone) when diphenylcyclopropenone was treated with diazomethane and $AlCl_3$ in ether.

G. Reaction with Pyridine. When 3.0 g. (0.0145 mole) of diphenylcyclopropenone was heated for 1.5 hr. at reflux in 50 ml. of methanol with 1.2 g. (0.015 mole) of pyridine, a green precipitate formed. After cooling, 1.0 g. of product was collected, m.p. 185–187° (at first another crystalline form, m.p. 158–159°, had been obtained). Recrystallization from chloroform–ethanol gave m.p. 187–187.5°.

Anal. Calcd. for $C_{35}H_{25}NO_2$: C, 85.51; H, 5.13; N, 2.85; mol. wt., 490. Found: C, 85.57; H, 5.55; N, 2.71; mol. wt. (osmometer, benzene), 427.

In the infrared spectrum the compound shows absorption at 3030, 1730, 1640, 1500, and 705 $cm.^{-1}$; the n.m.r. spectrum shows signals in the τ 2.5–3.5 region. Hydrolysis with refluxing 20% ethanolic KOH for 12 hr. afforded *cis-1,2-diphenylacrylic acid*, m.p. 172–173° (1.4 moles/mole).

H. Reaction with Triethyloxonium Fluoroborate. A solution of 6.0 g. (0.029 mole) of diphenylcyclopropenone and 12.0 g. (0.055 mole) of triethyloxonium fluoroborate in 45 ml. of CH_2Cl_2 was allowed to stand for 1 hr., then 100 ml. of dry ether was added and the precipitated *1,2-diphenyl-3-ethoxycyclopropenyl fluoroborate* was washed with ether and absolute ethanol yielding 7.5–9.0 g. (80–96%), m.p. 195.5–196°.

Anal. Calcd. for $C_{17}H_{15}BF_4O$: C, 63.53; H, 4.70. Found: C, 62.65; H, 4.18.

In the n.m.r. spectrum the compound showed the expected aromatic multiplet at τ 2.0, and a methyl triplet at 8.3, in a ratio of 10:3 (the CH_2 signal was obscured by the CH_2Cl_2 solvent). The compound was very sensitive to moisture, and was converted quantitatively to diphenylcyclopropenone on shaking with cold water.

A solution of 14.0 g. (0.0435 mole) of the ethoxycyclopropenium fluoroborate in 30 ml. of CH_2Cl_2 was treated with 2.0 g. (0.045 mole) of dimethylamine in 30 ml. of CH_2Cl_2, added over 5 min. After 30 min., 100 ml. of ether was added, and 9.0 g. (65%) of crude *1,2-diphenyl-3-dimethylaminocyclopropenyl fluoroborate* was collected, m.p. 231–234°. The analytical sample, recrystallized repeatedly from acetonitrile–ethanol, showed m.p. 236–236.5°.

Anal. Calcd. for $C_{17}H_{16}BF_4N$: C, 63.58; H, 5.02; N, 4.36. Found: C, 64.42; H, 5.30; N, 4.40.

In the n.m.r. spectrum the compound shows a multiplet at τ 2.2 and a sharp singlet at 6.25 in the ratio of 10:6. In the infrared spectrum there were bands at 3130, 1900, 1580, 1410, 1230, 1050, 770, and 680 $cm.^{-1}$ The compound was not sensitive to moisture, and it could be recrystallized undecomposed from hot water.