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Cyclopropene Derivatives. II.* The Reaction of Diazoketone with Triple Bond

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The additions of some keto-carbene to a triple bond were studied. Since keto-carbene rearranges easily to a ketene derivative (Wolff rearrangement), the carbenic addition will always be in competition with the rearrangement. In the case of benzoylphenylcabene, the rearrangement is preferred, and no cyclopropene derivative is obtained. However, benzoyl and acetylcarbene, both having hydrogen instead of phenyl as a substituent, could be successfully added to diphenylacetylene and di-*n*-butylacetylene, thus giving 1, 2-disubstituted cyclopropene derivatives. Thus, it was found that the acylcyclopropenes were synthesized in a single step by the utilization of the carbenic addition of keto-carbene to a triple bond.

A very attractive way to synthesize cyclopropenylketone seems to be the addition of keto-carbene to a triple bond. It is well known, however, that the decomposition of diazoketone gives a ketene derivative, which is a product of Wolff rearrangement.[1] Actually, certain ketenes, such as diphenylketene, have already been prepared by this method.[2] Since, however, the intermediate of this Wolff rearrangement will presumably be keto-carbene,[3] the addition of keto-carbene to an olefinic bond will always be in competition with the Wolff rearrangement.

Another possible side reaction of keto-carbene will be the 1, 3-dipolar addition to an unsaturated bond. Huisgen and his co-workers[3,4] investigated this addition extensively. They studied the competition of the 1, 3-dipolar addition with the Wolff rearrangement and concluded that the rearrangement was much faster than the addition. In the presence of copper powder, however, they successfully directed the reaction to the 1, 3-dipolar addition route. Keto-carbene co-ordinated to copper, and its further rearrangement was prevented.

Several workers[5] have successfully investigated the addition of benzoylcarbene and acetylcarbene to an ordinary double bond and to isolated cyclopropane derivatives respectively. In general, however, a triple bond is less reactive toward electrophilic attack than is a double bond.[6] Since carbene is known as an electrophilic reagnet,[7] its addition to a triple bond will be more sluggish than to a double bond. In other words, the Wolff rearrangement will compete more strongly in the addition of keto-carbene to a triple bond.

In the present investigation, the addition of various keto-carbenes, phenylbenzoylcarbene, benzoylcarbene and acetylcarbene, to diphenylacetylene and di-*n*-butylacetylene was studied. The successful one-step synthesis of some acylcyclopropenes will here be reported.

Results and Discussion

The thermal decomposition of azibenzil (I) in diphenylacetylene produced 2, 3, 4-triphenyl-1-naphthyl diphenylacetate (IV) in a 46.2% yield. In the presence of copper powder, the yield of IV was 28.7%. The basic hydrolysis of IV gave 2, 3, 4-triphenyl-1-naphthol (V) and diphenylacetic acid (VI). No cyclopropene derivative (III) was detected among the products in this case. The formation of IV is undoubtedly due to the preferential rearrangement of I to diphenylketene (VII).

Smith and Hoehn studied the reaction of diphenylacetylene with diphenylketene and isolated the

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* Part I: I. Moritani and N. Obata, *Tetrahedron Letters,* **1965**, 2817.

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

[1] L. Wolff, *Ann.*, **325**, 129 (1902); F. Weygand, *Angew. Chem.*, **72**, 535 (1960).

[2] L. I. Smith and H. H. Hoehn, "Organic Syntheses," Coll. Vol. III, 356 (1955).

[3] R. Huisgen, H. Konig, G. Binsch and H. J. Strum, *Angew. Chem.*, **73**, 368 (1961).

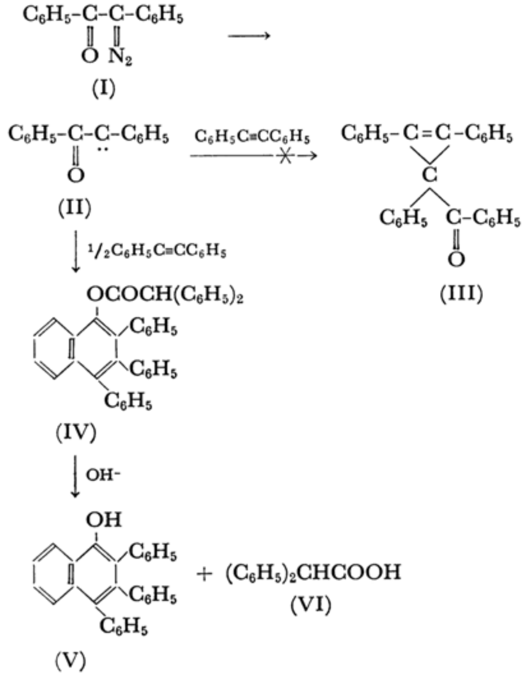
[4] R. Huisgen, ibid., **67**, 439 (1955); *Proc. Chem. Soc.*, **1961**, 357; *Angew. Chem.*, **75**, 604, 742 (1963); R. Huisgen, G. Binsch and L. Chosez, *Chem. Ber.*, **97**, 2628 (1964).

[5] K. B. Wiberg and T. W. Hutton, *J. Am. Chem. Soc.*, **76**, 5367 (1954); R. J. Bohrbacher and N. H. Cromwell, ibid., **79**, 401 (1957); P. Yates and T. J. Clark, *Tetrahedron Letters,* **1961**, 435; J. Novâk, J. Satuský, V. Šneberk and F. Šorm, *Collection Czechoslov. Chem. Communs.*, **22**, 1836 (1957).

[6] F. Bohlmann, *Angew. Chem.*, **69**, 82 (1957); M. Nakagawa, "Atarashii-Yuhkigosei-hannoh (New Synthetic Organic Reaction)," Kagaku Zohkan, 11, Kagaku Dohjin, Kyoto (1962), p. 35.

[7] P. S. Skell and R. M. Etter, *Chem. Ind.*, **1958**, 624; W. Kirmse, "Carbene Chemistry," Academic Press, New York (1964).

same material.8) In the present experiment, both materials, IV and V, showed satisfactory results of elemental analysis and molecular weights.

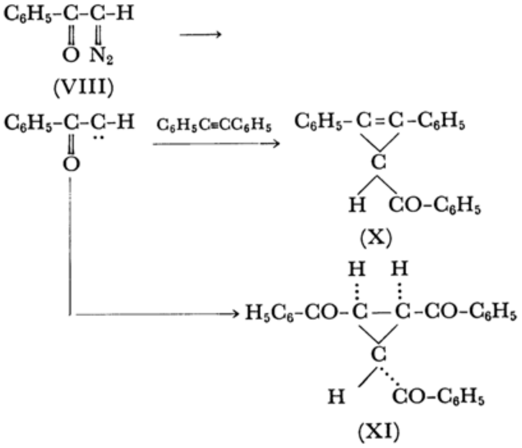


The structure of IV and V was further confirmed by the comparison of thier ultraviolet and proton magnetic resonance spectra with those of authentic 1, 2, 3-triphenyl-naphthalene. An attempt to transform V to a naphthalene derivative failed. *p*-Toluenesulfonate of V was treated with a large excess of Raney-nickel in ethanol,9) but the tosyl group would not be removed.

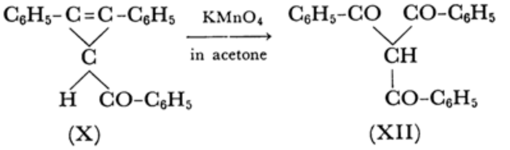
Apparently, phenylbenzoylcarbene (II) rearranged preferentially; no carbenic addition product was detected. One possible reason for this preferential rearrangement could be a steric factor. It may be expected, therefore, that the replacement of the bulky phenyl group by hydrogen might make the carbenic addition to a triple bond possible. Thus, the thermal decomposition of diazoacetophenone, *p*-methoxy-diazoacetophenone and diazoacetone was investigated.

The decomposition of diazoacetophenone (VIII) in a large excess of diphenylacetylene resulted in the formation of two pure materials, X and XI. The infrared and ultraviolet spectra of X exhibited all of the characteristic absorptions of diphenylcyclopropene derivatives.10) The results of the elemental analysis and the molecular weight determination were also in good agreement with the results for benzoyldiphenylcyclopropene.

Thus, compound X was identified as the desired cyclopropene derivative. Compound XI was found to be *trans*-1, 2, 3-tribenzoylcyclopropane on the basis of its melting point11) and its infrared spectrum. The proton magnetic resonance spectrum was superimposable upon the reported one.11c)



The structure of X was confirmed by the following observations. The permanganate oxidation of X produced tribenzoylmethane (XII) in a 57.1% yield. XII was identified by comparing it with an authentic sample.12)



The reaction of 1, 2-diphenylcyclopropenylcarboxylic acid chloride, prepared via a different route,13) with phenyl magnesium bromide gave an identical ketone (X).* Finally, the sodium borohydride reduction of X afforded phenyl-1, 2-diphenylcyclopropenyl carbinol in a very high yield.

The yields of X and XI were 1.2% and 7.8% respectively. The presence of copper powder markedly increased the yields, up to 8.1% for X and to 30.8% for XI.

Similarly, diazoacetophenone (VIII) was decomposed in di-*n*-butylacetylene, decyne-5, in the

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8) L. I. Smith and H. H. Hoehn, *J. Am. Chem. Soc.*, **63**, 1180 (1941).

9) G. W. Kenner and M. A. Murray, *J. Chem. Soc.*, **1949**, Supplt. 178.

10) 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).

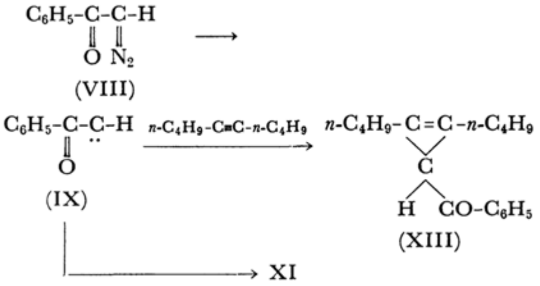
11) a) C. Grundmann, *Ann.*, **536**, 29 (1938); b) T. J. Clark and P. Yates, *J. Org. Chem.*, **27**, 286 (1962); c) J. A. Pople, W. G. Schneider and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., New York (1959), p. 289.

12) R. D. Abell, *J. Chem. Soc.*, **101**, 998 (1912).

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

* Breslow reported13) the synthesis of X utilizing diphenylcadmium instead of phenyl magnesium bromide. The same reaction as the Breslow's was followed, but we could not obtained X.

presence of copper powder; 3-benzoyl-1, 2-di-*n*-butylcyclopropene-1 (XIII) was thus obtained in a 21.1% yield. A small amount of XI, 1.8%, was also formed.



In the infrared region, compound XIII showed characteristic absorptions at 1667 cm⁻¹ ($\nu_{C=O}$), and 1900 cm⁻¹ ($\nu_{C=C}$). Its proton magnetic resonance spectrum is shown in Fig. 1. Aliphatic protons were separated nicely.

p-Methoxydiazoacetophenone (XIV) was also decomposed in diphenylacetylene in the presence of copper powder. The yield of 3-*p*-methoxybenzoyl-1, 2-diphenylcyclopropene-1 (XV) was 3.2%.

In a similar manner, diazoacetone (XVI) produced cyclopropene derivatives in both diphenyl acetylene and di-*n*-butylacetylene. The yields of XVII and XVIII was found to be 3.3% and 2.5% respectively.

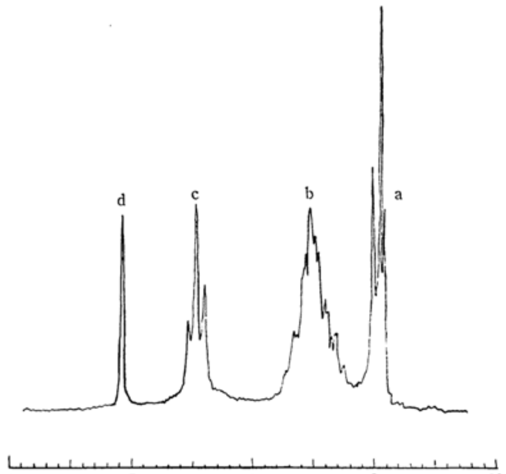
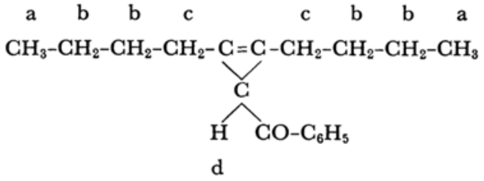


Fig 1. Proton magnetic resonance spectrum of 3-benzoyl-1, 2-di-*n*-butylcyclopropene-1.



All of the present results are summarized in Table I. The formation of *trans*-tribenzoylcyclopropane in a relatively large amount strongly suggests that the addition of acylcarbene to a triple bond is actually the case. It is known that the photodecomposition of pyrazolenine produces cyclopropene derivatives,⁽14⁾ while thermally pyrazolenine is simply rearranged to aromatized pyrazol.⁽15⁾ No example of its thermal decomposition to a cyclopropene derivative has yet been reported. Consequently, the intermediacy of pyrazolenine in the present study is practically out of the question.

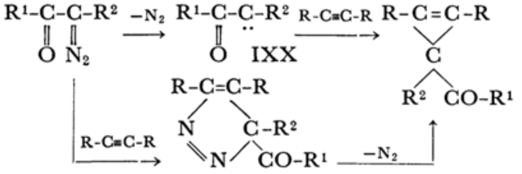
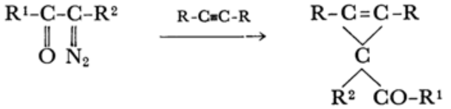


TABLE I. CYCLOPROPENE DERIVATIVES PRODUCED BY THE THERMAL DECOMPOSITION OF DIAZOKETONE IN THE PRESENCE OF COPPER POWDER AT 100°C



Run	Substituent		Acetylene	Solvent	Product, %	
	R¹	R²			Cyclopropene	XI
1	C_6H_5	C_6H_5	Diphenyl	Diglyme	—	—
2	C_6H_5	H	Diphenyl	Diglyme	8.1	30.8
3	C_6H_5	H	Di-*n*-butyl	Diglyme	21.1	1.8
4	*p*-$CH_3OC_6H_4$	H	Diphenyl	Diglyme	3.2	—
5	CH_3	H	Diphenyl	Neat	3.3	—
6	CH_3	H	Di-*n*-butyl	Neat	2.5	—

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14) G. L. Closs and W. A. Boll, *J. Am. Chem. Soc.*, **85**, 3904 (1963); G. Ege, *Tetrahedron Letters*, **1963**, 1667.

15) W. Kirmse and L. Horner, *Ann.*, **614**, 1 (1958); R. Hüttel, J. Riedl, H. Martin and F. Franke, *Chem. Ber.*, **93**, 1425 (1960); R. Hüttel, K. Franke, H. Martin and J. Riedl, ibid., **93**, 1433 (1960).

In the case of phenylcarbene, no addition to a triple bond occurred, whereas other carbenes IXX (R^2=H; R^1=C_6H_5, p-$CH_3OC_6H_4$, CH_3) added to a triple bond and produced yield. As is shown in Runs 2 and 3, the change in substituents on acetylene from the phenyl group to the *n*-butyl group resulted in a big increase in the yield of cyclopropene derivatives. This is understandable because of the difference in basicity between these two acetylenes. Substitution on carbene by more electron-releasing substituents, such as *p*-methoxybenzoyl and acetyl, instead of benzoyl reduced the yields of addition products. This is reasonable because of the electrophilic nature of the reacting carbene intermediate.

Experimental*

The Reaction of Azibenzil with Diphenylacetylene, 2, 3, 4-Triphenyl-1-naphthyl Diphenylacetate (IV).—A solution of azibenzil, m. p. 79—80°C with decomposition (reported m. p. 79°C (decomp.)16)), 7.5 g. (0.034 mol.), in 25 ml. of digylme was added, drop by drop, to a solution of diphenylacetylene, 10.1 g. (0.057 mol.), in 5 ml. of diglyme at 140°C. The addition was completed after one and a half hours. The reaction mixture was then kept at 140°C for an additional 30 min. After it had cooled, the mixture was poured into a large amount of water. The organic material was extracted with ether three times. The combined ethereal solution (ca. 300 ml.) was washed successively with ten 50 ml. portions of water in order to remove 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 (250 g.) was used for this. Each fraction was analyzed by infrared and ultraviolet spectroscopy. Elution with petroleum ether afforded 8.65 g. (0.049 mol.) of recovered diphenylacetylene. Elution with benzene gave 4.4 g. (46.2%) of 2, 3, 4-triphenyl-1-naphthyl diphenylacetate, m. p. 169—170°C (chloroform) (reported m. p. 168—169°C8)).

Found: C, 89.02; H, 5.34. Calcd. for $C_{42}H_{30}O_2$: C, 89.01; H, 5.34%. Mol. wt.: Found: 558, by freezing point-depression method in benzene. Calcd. for $C_{42}H_{30}O_2$: 556.7.

The characteristic infrared absorptions were 1760 cm^{-1} ($\nu_{C=O}$) and 1125 cm^{-1} (ν_{C-O}). The ultraviolet maxima in acetonitrile were 235 mμ (log ε 4.76) and 292 mμ (log ε 4.11). The NMR spectrum showed a multiplet (15 hydrogens) at 2.50—3.25τ and a singlet (1 hydrogen) at 5.02 τ.

In the presence of copper powder at 100°C, IV was obtained in a 28.7% yield.

2, 3, 4-Triphenyl-1-naphthol (V).—The hydrolysis of IV with pottasium hydroxide in a 50% water-ethanol mixture gave 2, 3, 4-triphenyl-1-naphthol, m. p. 162—163°C (ethanol) (reported m. p. 163°C8)), in a 81% yield and diphenylacetic acid, m. p. 147—148°C (water) (reported m. p. 144—145°C17)), in 74% yield. A mixed-melting-point determination of resultant diphenylacetic acid with an authentic material showed no depression.

The same naphthol derivative was also obtained by the reduction of diphenylacetate with litium aluminum hydride.

Found: C, 90.36; H, 5.42; O, 4.17; mol. wt., 326. Calcd. for $C_{28}H_{20}O$: C, 90.29; H, 5.42; O, 4.29%; mol. wt., 372.4.

The ultraviolet maxima in ethanol were 243 mμ (log ε 4.73), 260 mμ (log ε 4.58) and 310 mμ (log ε 3.95). The NMR spectrum showed a multiplet (19 hydrogens) at 1.65 —3.95τ, and a sharp singlet (1 hydrogen) at 4.61τ.

1, 2, 3-triphenylnaphthalene was prepared by following the known route18); m. p. 151.5—152.5°C. (ethanol-benzene) (reported m. p. 151°C18)). Its UV and NMR spectra were very similar to those of V.

p-Toluenesulfonate of V was prepared by Tipson's method19); m. p. 171—172°C (ethanol). The *p*-toluenesulfonate (0.15 g.) thus obtained was treated with Raney nickel (5 g.) in ethanol (20 ml.) at the reflux temperature for 10 hr.9) After the mixture had been worked up as usual the starting *p*-toluenesulfonate was obtained. Five days' refluxing gave the same results.

Found: C, 79.76; H, 4.91; S, 5.85. Clacd. for $C_{35}H_{26}O_3S$: C, 79.82; H, 4.97; S, 6.08%.

The Reaction of Diazoacetophenone with Diphenylacetylene, 3-Benzoyl - 1, 2-diphenylcyclopropene (X).—A solution of diazoacetophenone, m. p. 46.5—47.5°C (reported m. p. 47—48°C20)); 10.1 g. (0.069 mol.), in dried diglyme (40 ml.) was added, drop by drop, to a solution of diphenylacetylene (20.0 g. (0.11, mol.)) in dried diglyme (10 ml.) over a period of one and a half hours at 140°C. After the mixture had been worked up as in the former case, the reaction products were separated by alumina-column chromatography. After the recovered diphenylacetylene had been completely eluted out by petroleum ether, the eluent was changed to benzene. In relatively later fractions 3-benzoyl-1, 2-diphenylcyclopropene-1, 0.25 g. (1.2%); m. p. 152—153°C (ethanol), was obtained. After the eluent had been changed from benzene to ether, *trans*-1, 2, 3-tribenzoylcyclopropane, 0.55 g. (7.8%); m. p. 216—217°C (reported m. p. 215—217°C11a,b)), was obtained in later fractions.

In a separate experiment, a mixture of 20.1 g. of diphenylacetylene, 9.95 g. of diazoacetophenone and 4.4 g. of copper powder was brought to reaction at 100°C. The yield of X was 1.62 g. (8.1%) and XI was 2.52 g. (30.8%).

The structure of X was identified on the basis of the following observations.

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* Melting points are uncorrected. The molecular weights were determined by a vapor pressure osmometer unless otherwise stated. Diglyme (diethyleneglycol dimethyl ether) was dried over lithium aluminum hydride and distilled under reduced pressure.

16) C. D. Nenitzescu and E. Solomonica, "Organic Syntheses," Coll. Vol. II, 496 (1943).

17) C. S. Marvel, F. D. Hager and E. C. Caudle, ibid., Coll, Vol. I, 224 (1941).

18) L. I. Smith and H. H. Hoehn, *J. Am. Chem. Soc.*, **63**, 1184 (1941).

19) R. S. Tipson, *J. Org. Chem.*, **9**, 235 (1944).

20) P. Yates and B. L. Shapiro, *J. Am. Chem. Soc.*, **81**, 212 (1959).

Found: C, 89.10; H, 5.61; mol. wt., 280. Calcd. for $C_{22}H_{16}O$: C, 89.16; H, 5.44%; mol. wt., 296.3.

The infrared characteristic absorptions as a KBr pellet were 3060 cm^{-1}, 3020 cm^{-1} and 2990 cm^{-1} (ν_{C-H}), 1845 cm^{-1} ($\nu_{C=C}$) and 1668 cm^{-1} ($\nu_{C=O}$). The ultraviolet maxima were 228 mμ (log ε 4.39), 235 mμ (log ε 4.41), 244 mμ (log ε 4.28), 294 mμ(sh) (log ε 4.31), 308 mμ (log ε 4.40) and 321 mμ(sh) (log ε 4.24). NMR showed a multiplet (2 hydrogens) at 1.82τ, a multiplet (13 hydrogens) at 2.50τ, and a singlet (1 hydrogen) at 6.15τ.

2, 4-Dinitrophenylhydrazone of X was also prepared; m. p. 193—194°C (ethanol-benzene), Its infrared and ultraviolet spectra showed the presence of a cyclopropene skeleton.

Found: N, 11.85. Calcd. for $C_{28}H_{20}O_4N_4$: N, 11.76%.

trans-Tribenzoylcyclopropane (XI) gave the following results:

Found: C, 81.34; H, 5.21. Calcd. for $C_{24}H_{18}O_3$: C, 81.34; H, 5.12%.

NMR exhibited a multiplet (15 hydrogens) at 1.75—2.80τ, a triplet (1 hydrogen) at 5.77τ, and a doublet (2 hydrogens) at 6.28τ.

The Oxidation of 3-Benzoyl-1, 2-diphenylcyclopropene, Tribenzoylmethane (XII).—Ketone X (0.230 g. (0.00077 mol.)) was dissolved in 10 ml. of acetone, and an acetone solution of potassium permanganate was then added to it drop by drop. The addition of permanganate was stopped when the solution did not discolor. After the filtration of manganese-(IV) oxide, the reaction mixture was poured into a large amount of water, and the organic material was extracted with benzene three times. The combined benzene solution was then washed with water and dried over anhydrous magnesium sulfate. The evaporation of benzene gave a white solid material, tribenzoylmethane, m. p. 232—233°C (benzene) (reported 224—226°C[12]); 0.145 g. (57.1%).

Found: C, 80.13; H, 5.01. Calcd. for $C_{22}H_{16}O_3$: C, 80.47; H, 4.91%.

The same material was prepared from dibenzoylmethane and benzoyl chloride.[12] The mixed melting point of two samples showed no depression. The infrared spectra of the two samples were superimposable.

The Reaction of Diphenylcyclopropenecarboxylic Acid Chloride with Phenyl Magnesium Bromide, 3-Benzoyl-1, 2-diphenylcyclopropene (X).—A mixture of 1.20 g. (0.0049 mol.) of 1, 2-diphenylcyclopropenecarboxylic acid, m. p. 208—209°C (reported m. p. 209—211°C),[21] and a large excess of oxalyl chloride was heated under refluxing for 2 hr.[22] The excess oxalyl chloride was removed by distillation. To the residue benzene and petroleum ether were added, and then they were removed under reduced pressure. The residual white solid material was dissolved in 50 ml. of absolute ether. To this solution there was added, drop by drop, a solution of a Grignard reagent, prepared from 1.6 g. of bromobenzene and 0.36 g. of magnesium in 20 ml. of absolute ether, at 0°C. After this mixture had been worked up as usual, there was obtained a white solid, 3-benzoyl-1, 2-diphenylcyclopropene, m. p. 152—153°C (no melting point was reported in the literature[13]); 0.64 g. (44.1%). This sample showed no melting point depression when mixed with the sample obtained above.

An attempt to follow Breslow's procedure,[13] utilizing diphenyl cadmium instead of a Grignard reagent, failed; the material isolated was the original carboxylic acid, m. p. 208—209°C.

The Sodium Borohydride Reduction of X, Phenyl - 1, 2 - diphenylcyclopropenyl Carbinol.—Benzoylcyclopropene (X) (0.327 g. (0.0011 mol.)) was reduced with sodium borohydride (0.053 g.) in ethanol (10 ml.) at reflux temperature for 3 hr. Carbinol, m. p. 84—85°C (petroleum ether); 0.265 g. (81%), was obtained.

Found: C, 88.73; H, 6.41. Calcd. for $C_{22}H_{18}O$: C, 88.56; H, 6.08%.

The infrared characteristic absorptions were 3200 cm^{-1} (ν_{O-H}) and 1810 cm^{-1} ($\nu_{C=C}$). The ultraviolet maxima in ethanol were 224 mμ (log ε 4.39), 230 mμ (log ε 4.44), 237 mμ (log ε 4.35), 310 mμ (log ε 4.30), 320 mμ (log ε 4.39) and 337 mμ (log ε 4.22). The NMR spectrum showed a multiplet (15 hydrogens) at 2.27—2.95τ, a doublet (1 hydrogen) at 5.54τ (J=7 c. p. s.), doublet (1 hydrogen) at 7.57τ (J=7 c. p. s.) and a singlet (broad, 1 hydrogen) at 7.94τ.

3-Benzoyl-1, 2-di-*n*-butylcyclopropene-1 (XIII).—Decyne-5[23] (15.25 g. (0.11 mol.)) and copper powder (7.35 g.) were placed in a reaction flask, and to them there was added 7.35 g. (0.0503 mol.) of diazoacetophenone[20] in 20 ml. of diglyme at 100°C were a period of two hours. After this mixture had been worked up as above, *trans*-tribenzoylcyclopropane (XI) was separated (0.314 g. (1.8%)). A fraction eluted with petroleum ether containing 10% ether was collected and distilled. 3-Benzoyl-1, 2-di-*n*-butylcyclopropene (XIII) boiled at 131—132°C (3×10^{-1} mmHg) (n_D^{20} 1.5202).

Found: C, 83.99; H, 9.59; mol. wt., 268. Calcd. for $C_{18}H_{24}O$: C, 84.32; H, 9.44%; mol. wt., 256.4.

The infrared characteristic absorptions were 1900 cm^{-1} ($\nu_{C=C}$) and 1667 cm^{-1} ($\nu_{C=O}$).

3-*p*-Methoxybenzoyl-1, 2-diphenylcyclopropene-1 (XV).—To a mixture of diphenylacetylene (18.15 g. (0.102 mol.)) and copper powder (3.8 g.) in 10 ml. of diglyme there was added 9.9 g. (0.056 mol.) of *p*-anisyl-diazomethane[24] in 30 ml. of diglyme over a two-hour period at 100°C. After this mixture had been worked up as above, 0.590 g. (3.2%) of 3-*p*-methoxybenzoyl-1,2-diphenylcyclopropene (XV) was obtained, m. p. 137—138°C (ethanol).

Found: C, 84.40; H, 5.54. Calcd. for $C_{23}H_{18}O_2$: C, 84.64; H, 5.56%.

The characteristic infrared peaks were 1840 cm^{-1} ($\nu_{C=C}$) and 1665 cm^{-1} ($\nu_{C=O}$). The ultraviolet maxima in ethanol were 223 mμ (log ε 4.57), 234 mμ (log ε 4.40), 292 mμ (log ε 4.64), 308 mμ (log ε 4.56) and 324 mμ (log ε 4.35). The NMR spectrum showed a doublet (2 hydrogens) at 1.90τ, a multiplet (10 hydrogens) at 2.30—2.80τ, a doublet (1 hydrogen) at 3.12τ, a singlet (3 hydrogen) at 6.18τ, and a singlet (1 hydrogen) at 6.30τ.

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21) R. Breslow, R. Winter and M. Battiste, *J. Org. Chem.*, **24**, 415 (1959).

22) R. Breslow, J. Lockhart and A. Small, *J. Am. Chem. Soc.*, **84**, 2793 (1962).

23) E. A. Bride and G. F. Hennion, ibid., **59**, 1310 (1937).

24) A. C. Wilds and A. L. Meader, *J. Org. Chem.*, **13**, 763 (1948).

3-Acetyl-1, 2-diphenylcyclopropene-1 (XVII).—ω-Diazoacetone[24] (10.59 g. (0.110 mol.)) in 20 ml. of diglyme was added, drop by drop, to a mixture of 23.46 g. (0.132 mol.) of diphenylacetylene and 6.35 g. of copper powder in 10 ml. of diglyme at 100°C over the period of one hour. The reaction mixture was then treated in a manner similar to that described previously. From the fraction eluted out by an ether-benzene mixture, 3-acetyl-1,2-diphenylcyclopropene-1, m. p. 101—102°C (petroleum ether), was obtained in 3.3% yield.

Found: C, 87.12; H, 6.14; mol. wt., 230. Calcd. for $C_{17}H_{14}O$: C, 87.15; H, 6.14%; mol. wt., 234.3.

The infrared characteristic absorptions were 1840 cm^{-1} ($\nu_{C=C}$) and 1685 cm^{-1} ($\nu_{C=O}$). The ultraviolet maxima in ethanol were 226.5 mμ (log ε 4.37), 234 mμ (log ε 4.32), 283 mμ (log ε 4.24), 294 mμ (log ε 4.35), 318 mμ (log ε 4.38) and 330 mμ (log ε 4.34). The NMR spectrum exhibited a singlet (1 hydrogen) at 7.18τ, a singlet (3 hydrogens) at 8.25τ, and a multiplet (10 hydrogens) at 2.25—2.80τ.

2, 4-Dinitrophenylhydrazone of XVII melted at 210—211°C (decomp.) (an ethanol-benzene mixture).

Found: C, 66.96; H, 4.43. Calcd. for $C_{23}H_{18}O_4N_4$: C, 66.60; H, 4.38%.

p-Toluenesulfonylhydrazone of XVII was also prepared; m. p. 180—181°C (benzene).

Found: C, 71.86; H, 5.51. Calcd. for $C_{24}H_{22}O_2N_2S$: C, 71.61; H, 5.51%.

The Sodium Borohydride Reduction of XVII.—Ketone XVII (0.230 g.) was reduced by sodium borohydride (0.096 g.), in ethanol at the reflux temperature. Methyl-1, 2-diphenylcyclopropenyl carbinol, m. p. 78—79°C (petroleum ether), was obtained in a 96.1% yield.

Found: C, 85.99; H, 6.78. Calcd. for $C_{17}H_{16}O$: C, 86.40; H, 6.83%.

The characteristic infrared peaks were 3200 cm^{-1} (ν_{O-H}), 1810 cm^{-1} ($\nu_{C=C}$) and 1075 cm^{-1} (ν_{C-O}). The ultraviolet maxima were 224 mμ (log ε 4.39), 230 mμ (log ε 4.44), 237 mμ (log ε 4.35), 310 mμ (log ε 4.30), 320 mμ (log ε 4.39), and 337 mμ (log ε 4.22). The NMR spectrum exhibited multiplet (10 hydrogens) at 2.25—2.90τ, a multiplet (1 hydrogen) at 6.12τ, a doublet (1 hydrogen) at 7.75τ, a broad singlet (1 hydrogen) at 8.20τ, and a doublet (3 hydrogens) at 8.80τ.

3-Acetyl-1, 2-di-*n*-butylcyclopropene-1 (XVIII).—A solution of ω-diazoacetone[24] (9.20 g. (0.11 mol.)) in 20 ml. of diglyme was added, drop by drop, to a mixture of 27.35 g. (0.197 mol.) of decyne-5 and 6.38 g. of copper powder at 100°C over a two-hour. After the usual treatment of the reaction mixture, fractions were eluted by a petroleum ether - ether mixture, collected, and distilled. 3-Acetyl-1, 2-di-*n*-butylcyclopropene-1, b. p. 77—78°C/0.3 mmHg; 0.485 g. (2.5%), was thus obtained.

Found: C, 79.91; H, 11.30. Calcd. for $C_{13}H_{22}O$: C, 80.35; H, 11.41%.

The infrared spectrum showed characteristic absorptions at 1895 cm^{-1} ($\nu_{C=C}$) and 1685 cm^{-1} ($\nu_{C=O}$). The NMR spectrum exhibited a triplet (4 hydrogens) at 7.58τ, a singlet (1 hydrogen) at 7.84τ, a singlet (3 hydrogens) at 8.16τ, a multiplet (8 hydrogens) at 8.52τ, and a triplet (6 hydrogens) at 9.06τ.