was extracted with saturated sodium bicarbonate. The bicarbonate solution was heated until free from ether, then cooled and acidified with dilute sulfuric acid. The white precipitate of diphenylacetic acid was removed and crystallized from aqueous ethanol. It weighed 1.13 g., and melted at 147° alone or when mixed with an authentic specimen.

The ethereal solution was washed with water and dried over sodium sulfate. The solvent was evaporated and the residue was crystallized once from a mixture of chloroform and ethanol and twice from petroleum ether (b. p. 90–100°). 2,3,4-Triphenyl-α-naphthol (3.0 g.) melted at 163°.

Anal. Calcd. for $C_{28}H_{20}O$: C, 90.29; H, 5.42. Found: C, 90.38; H, 5.16.

2,3,4-Triphenyl-α-naphthyl Acetate III.—The naphthol II (93 mg.) was warmed for ten minutes on the steam-bath with acetic anhydride (1 cc.) and a drop of sulfuric acid. Ice was added and the solid (110 mg.) was removed and crystallized from a mixture of chloroform and ethanol. The acetate III was white and melted at 194°.

Anal. Calcd. for $C_{30}H_{22}O_2$: C, 86.92; H, 5.36. Found: C, 87.21; H, 5.46.

Oxidation of the Naphthol II.—The naphthol II (1.26 g., 0.0033 mole) was refluxed for twenty-five hours with a solution of potassium permanganate (2.1 g.) and potassium hydroxide (0.5 g.) in water (100 cc.). The manganese oxides were removed by filtration and the filtrate was acidified with dilute hydrochloric acid. The precipitated acids were removed and steam distilled. The distillate was extracted with ether, the ethereal solution was dried and evaporated. The residue consisted of benzoic acid, m. p. and mixed m. p. 121°. The residue in the distilling flask was extracted with ether, and the ethereal solution was dried and evaporated. The residue consisted of *o*-benzoylbenzoic acid hydrate, m. p. and mixed m. p. 93–95°.

Summary

1. Diphenylketene reacts with diphenylacetylene to produce 2,3,4-triphenyl-α-naphthyl diphenylacetate, I. This ester, when hydrolyzed, gives diphenylacetic acid and the primary product of the ketene–acetylene reaction, 2,3,4-triphenyl-α-naphthol II.

2. It follows that when diphenylketene reacts with arylacetylenes, a hydrogen atom attached to an acetylenic carbon atom is not required.

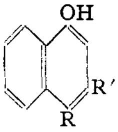
MINNEAPOLIS, MINNESOTA
RECEIVED DECEMBER 30, 1940

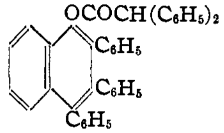
[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

The Reaction between Diphenylketene and Arylacetylenes. VI. Mechanism[1]

BY LEE IRVIN SMITH AND HARVEY H. HOEHN[2]

Any mechanism for the reaction between diphenylketene and arylacetylenes must account for the formation of I,[3] II and III from phenylacetylene, *p*-tolylacetylene and diphenylacetylene,





I $R = R' = C_6H_5$ III

II $R = C_6H_5$; $R' = p\text{-}CH_3C_6H_4^-$

respectively. The mechanism must also explain why the group originally associated with the monoarylacetylene appears in the 3-position of the resulting naphthols I and II[4]; why disubstituted, as well as monosubstituted, acetylenes undergo the reaction[1]; why an α-naphthol, rather than the β-isomer is formed[3,5]; and it must not demand that the ketene should first combine with a monoarylacetylene to give a derivative of diphenylacetic acid,[6] the usual product of the reaction between the ketene and any reagent containing an active hydrogen atom.

The addition of arylacetylenes to diphenylketene resembles a Diels–Alder reaction in that no catalyst is required and elevated temperatures are not necessary to bring about the reaction. There is a 1,4-conjugated system in diphenylketene, and although one of the double bonds is in the benzene ring, if the assumption is made that this can react, then a diene synthesis would lead to naphthols. However, this mechanism, as shown in the formulas, would lead to the β-naphthols V and VII via the two intermediates IV and VI, regardless of the way in which the acetylene added. In one case the aryl groups would be oriented in the 1,3-positions (V), and in the other case, they would occupy the 1,4-positions (VII), but in both products the hydroxyl group

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(1) Paper V, THIS JOURNAL, **63**, 1180 (1941).

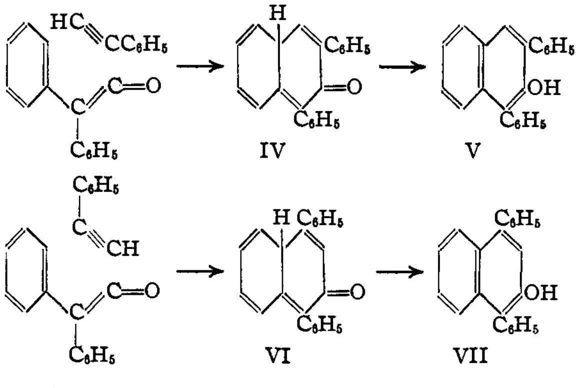
(2) Abstracted from a thesis by Harvey H. Hoehn, presented to the Graduate Faculty of the University of Minnesota, in partial fulfillment of the requirements for the Ph.D. degree, June, 1940.

(3) Paper I, Smith and Hoehn, THIS JOURNAL, **61**, 2619 (1939).

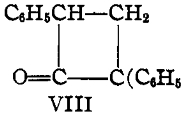
(4) Paper II, Smith and Hoehn, *ibid.*, **63**, 1175 (1941).

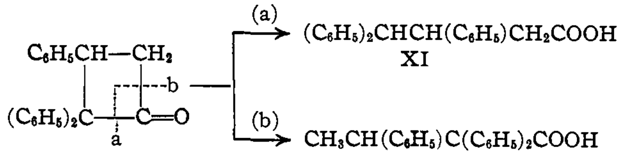
(5) Paper IV, Smith and Hoehn, *ibid.*, **63**, 1178 (1941).

(6) Paper III, Smith and Hoehn, *ibid.*, **63**, 1176 (1941).



would occupy the β-position. The same considerations would apply to the products derived in this manner from diarylacetylenes; these also would be β-naphthols. Since the products are actually α-naphthols, the reaction cannot be a Diels–Alder synthesis of the sort pictured here.


VIII

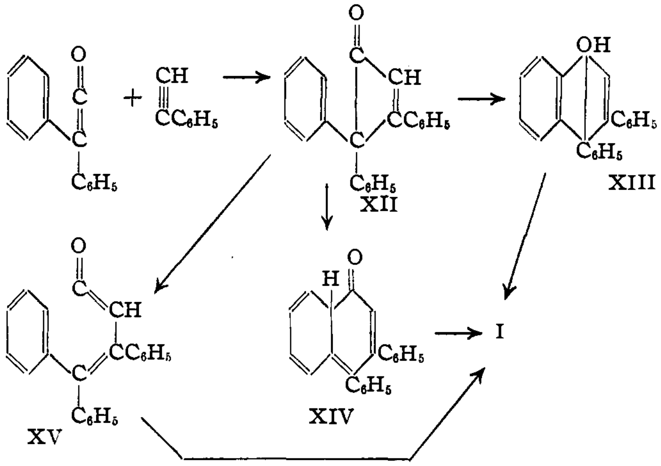


IX

Staudinger and Suter,[7] who studied the reaction between diphenylketene and styrene, formulated the reaction product as VIII although they recognized the possibility that the alternative formula IX might be the correct one. A few years later, Staudinger and Rheiner[8] concluded that IX was the correct structure. These authors hydrolyzed the cyclobutanone to an acid which they regarded as α,α,β-triphenylbutyric acid, X. Quite recently, Bergmann and Bergmann[9] have synthesized both acids X and XI and they have shown that the acid melting at 178° and resulting from the cleavage of the cyclobutanone IX is in reality β,γ,γ-triphenylbutyric acid XI—that is, action of alkali upon the cyclobutanone IX results in the rupture of bond a rather than bond b. It has been shown recently that other ethylenic compounds likewise react with diphenylketene to produce cyclobutanone derivatives of the type of IX and that, moreover, these compounds are cleaved by alcoholic alkali just as IX is, the bond between the carbonyl group and the carbon carrying the two phenyl groups (corresponding to a in formula IX) being broken.[10,11,12]

Agre, who studied the reaction between diphenylketene and cyclopentadiene[10] and other unsaturated compounds and who discovered that arylacetylenes reacted with the ketene,[13] stated that in analogy with the ethylenic compounds, the product of the reaction between diphenylketene and phenylacetylene should be the cyclobutenone XII. Actually, 2,2,3-triphenylcyclobutenone (XII) is not obtained but if it is regarded as the primary product, a mechanism can be formulated for the reaction between diphenylketene and arylacetylenes which is in accord with all the available facts concerning not only this reaction, but also the one between the ketene and ethylenes.

On this basis, the reaction can be written as follows:



The isomerization of XII to I might involve any one of the secondary intermediates XIII, XIV or XV, but which of these is involved, if any, it is not possible to say. The most important intermediate is the primary one XII because this formulation shows (a) that an α-naphthol will result; (b) that the aryl group in the acetylene will occupy the 3-position in this naphthol; (c) that both mono- and di-arylacetylenes should

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(7) Staudinger and Suter, *Ber.*, **53**, 1092 (1920).

(8) Staudinger and Rheiner, *Helv. Chim. Acta*, **1**, 8 (1924).

(9) Bergmann and Bergmann, *J. Chem. Soc.*, 727 (1938).

(10) Smith, Agre, Leekley and Prichard, THIS JOURNAL, **61**, 7 (1939).

(11) Lewis, Ramage, Simonsen and Wainwright, *J. Chem. Soc.*, 1837 (1937).

(12) Farmer and Farooq, *Chem. & Ind.*, 1079 (1937).

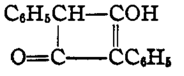
(13) C. L. Agre, Ph.D. Thesis, University of Minnesota, October, 1937.

give analogous products and (d) the bond in the cyclobutenone XII which is broken in the subsequent steps is the one which should be broken if there is any analogy between acetylenes and ethylenes in their reactions with diphenylketene. Indeed, if as has been stated, the bond in the cyclobutanone IX ruptures so readily because of the strain present in this ring, then the corresponding bond in the cyclobutenone XII should rupture much more readily—perhaps so readily that XII might be incapable of existence except momentarily.

Unfortunately attempts to obtain definite proof that the intermediate XII was actually involved were unsuccessful. It has been observed that the reaction mixture containing diphenylketene and phenylacetylene became very viscous after standing for several hours, and considerably before the reaction mixture solidified. If at this stage substance XII were present, then reduction of the reaction mixture should give 2,2,3-triphenylcyclobutanone IX which in turn could be prepared from the ketene and styrene. Accordingly, the reaction mixture was subjected to the action of hydrogen for eight hours under thirty-five pounds pressure in the presence of a platinum oxide catalyst, but the only product that could be isolated was the naphthol I.

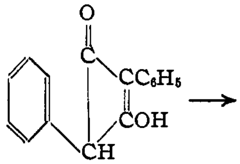
As another approach, an attempt was made to dehydrogenate the cyclobutanone IX in the hope of obtaining either the cyclobutenone XII or the naphthol I. As it was not possible to use a high temperature dehydrogenation, the only alternative was to try low temperature dehydrogenation in the presence of an active hydrogen acceptor. Accordingly a solution of the cyclobutanone IX in toluene was refluxed for three days with chloranil[14] but no hydroquinone was formed (tetrachlorohydroquinone is extremely sparingly soluble in toluene) nor did the yellow color of the solution fade in the slightest (both IX and I are colorless).

While it must be admitted, therefore, that the mechanism of the reaction has not been definitely established, yet the proposed mechanism accounts for all of the facts and serves as a useful working hypothesis even in the absence of definite proof. In this connection, it is noteworthy that Staudinger[15] postulated that one of the dimers of phenylketene (obtained by isomerizing the primary product XVIII with alkali) was 2,4-diphenylcyclobutenol-1-one-3 (XVI), but Lardy[16] observed that the absorption spectrum of phenylketene dimer was quite different from those of tetrasubstituted cyclobutane-1,3-diones. If the second step of the mechanism proposed here for the addition of arylacetylenes is applied to phenylketene dimer (XVI), the resulting product would be 1,3-dihydroxy-2-phenylnaphthalene (XVII). If this dimer is in reality XVII instead of XVI, then the proposed mechanism would acquire a high degree of probability, for XVIII can be converted into XVI (= XVII?). Experiments along these lines are under way and the results will be reported in a later paper.

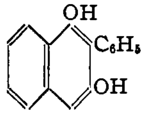


$$\begin{array}{ll} C_6H_5CH & —COH \\ O=C & —CC_6H_5 \end{array}$$

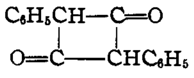
XVI



XVI



XVII



$$\begin{array}{ll} C_6H_5CH & —C=O \\ O=C & —CHC_6H_5 \end{array}$$

XVIII

Experimental Part

2,2,3-Triphenylcyclobutanone (IX).—Styrene (3.5 cc., 0.03 mole) and diphenylketene (5.82 g., 0.03 mole) were mixed and heated to 65° under nitrogen for a day. The product (8.0 g.) was crystallized from a mixture of chloroform and ethanol. It melted at 135–136°, in agreement with the value in the literature.[17]

Dehydrogenation.—The cyclobutanone IX (596 mg., 0.002 mole) and chloranil (492 mg., 0.002 mole) in toluene (15 cc.) was refluxed for thirty-six hours with no noticeable change. Since the theoretical amount of chloranil was used, the failure of the yellow color to fade, or of the solution to deposit any hydroquinone, indicated that no reaction had occurred.

Hydrogenation of the Phenylacetylene–Diphenylketene Reaction Mixture.—The ketene (2 cc.) and phenylacetylene (1.2 cc.) were placed under nitrogen in the bottle of an apparatus for catalytic reduction, and allowed to stand at room temperature for thirteen hours. The orange colored mixture was very viscous. Dry ethanol (50 cc.) was added and the color faded at once to light yellow. Platinum oxide catalyst (50 mg.) was added and the solution was subjected for eight hours to the action of hydrogen under thirty-five pounds pressure. The catalyst was removed and the alcohol was evaporated from the filtrate. The residue was taken up in petroleum ether (b. p. 60–68°). The cooled solution deposited light yellow needles which melted at 129–135°. When recrystallized from petroleum ether, the substance (560 mg.) was white

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[14] (a) Arnold and Collins, THIS JOURNAL, **61**, 1407 (1939); (b) Arnold, Collins and Zenk, *ibid.*, **62**, 983 (1940).

[15] Staudinger, *Ber.*, **44**, 533 (1911).

[16] Lardy, *J. chim. phys.*, **21**, 281 (1924).

[17] Staudinger, *Helv. Chim. Acta*, **7**, 3 (1929).

and melted at 142–143° alone or when mixed with 3,4-diphenyl-α-naphthol I.

Summary

1. A mechanism for the formation of aryl-α-naphthols, such as I and II, from diphenylketene and arylacetylenes, has been suggested. While not proved, this mechanism is in accord with all the available facts concerning this reaction. It explains why α- and not β-naphthols are formed, why the aryl group of the acetylene occupies the 3-position in the naphthol; why mono- as well as di-arylacetylenes undergo the reaction and it does not require that an active hydrogen be present in the acetylene.

MINNEAPOLIS, MINNESOTA
RECEIVED DECEMBER 30, 1940

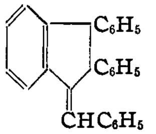
[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

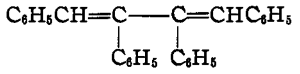
The Reaction between Lithium and Diphenylacetylene

BY LEE IRVIN SMITH AND HARVEY H. HOEHN

A study of the reaction between metallic lithium and diphenylacetylene was begun some years ago by Schlenk and Bergmann[1] and continued by Bergmann and Zwecker,[2] and by Bergmann and Schreiber,[3] who reported that an ethereal solution of the hydrocarbon $C_{14}H_{10}$, shaken with lithium for eight days at room temperature and then decomposed with alcohol, gave a white hydrocarbon $C_{28}H_{20}$ melting at 151°, together with a second hydrocarbon $C_{28}H_{22}$, melting at 183°. It was also reported[1] that 1,1-diphenyl-2,2-dichloroethylene as well as the analogous bromoethylene reacted similarly with lithium, giving the same hydrocarbon, m. p. 151°. Since it had been shown previously[4] that 1,1-diphenyl-2,2-dichloroethylene as well as 1,1-diphenyl-2-bromoethylene could be converted into diphenylacetylene by action of sodium hydroxide or sodium ethoxide, Schlenk and Bergmann proposed that the reaction between lithium and the 1,1-diphenyl-2,2-dihaloethylenes involved diphenylacetylene as an intermediate.

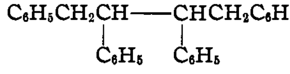
The 151° hydrocarbon on oxidation gave *o*-benzoylbenzoic and benzoic acids and it was assigned the structure 1,2,3-triphenylnaphthalene, VII, a structure which was consistent with the other reactions reported for it. The 183° hydrocarbon was reduced[3] to the known 1-benzyl-2,3-diphenylhydrindene, m. p. 115°, by action of phosphorus and hydriodic acid. This reaction was regarded as a simple reduction, and since the only compounds which could give 1-benzyl-2,3-diphenylhydrindene on simple reduction were 1-benzyl-2,3-diphenylindene, 1,2-diphenyl-3-benzyl indene and 1-benzal-2,3-diphenylhydrindene, and since the first two were known and were different from the 183° hydrocarbon, this hydrocarbon was regarded as 1-benzal-2,3-diphenylhydrindene (I)


I



$$C_6H_5CH{=}\underset{\displaystyle C_6H_5}{\underset{|}{C}}{-}\underset{\displaystyle C_6H_5}{\underset{|}{C}}{=}CHC_6H_5$$

II



$$C_6H_5CH_2\underset{\displaystyle C_6H_5}{\underset{|}{CH}}{-}\underset{\displaystyle C_6H_5}{\underset{|}{CH}}CH_2C_6H_5$$

III

In connection with work on the reaction between arylacetylenes and diphenylketene[5] it was necessary to repeat some of the work on the reaction between lithium and diphenylacetylene. It has been found that the white hydrocarbon $C_{28}H_{22}$, which melts at 183°, does not have the structure I, but is 1,2,3,4-tetraphenylbutadiene-1,3 (II), previously synthesized by Orechoff[6] and reported by him to melt at 183–184° and to be converted, by action of bromine in chloroform, into *yellow* 1-benzal-2,3-diphenylindene, which also melts at 184°. When the *white* 183° compound was heated to 250° with sulfur, hydrogen sulfide was evolved and tetraphenylthiophene, also white and melting at 184°, was produced. Action of bromine on an ethereal solution of the 183° hydrocarbon gave the yellow 1-benzal-2,3-diphenylindene, in agreement with the results of Orechoff and, finally, reduction of the white 183°

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(1) Schlenk and Bergmann, *Ann.*, **463**, 71 (1928).

(2) Bergmann and Zwecker, *ibid.*, **487**, 155 (1931).

(3) Bergmann and Schreiber, *ibid.*, **500**, 118 (1933).

(4) (a) Lipp, *Ber.*, **56**, 567 (1923); (b) Staudinger and Rathsam, *Helv. Chim. Acta*, **5**, 648 (1922).

(5) Smith and Hoehn, THIS JOURNAL, **61**, 2619 (1939); *ibid.*, **63**, 1180, 1181 (1941).

(6) Orechoff, *Ber.*, **47**, 89 (1914).