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

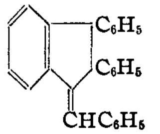
[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

The Reaction between Lithium and Diphenylacetylene

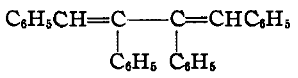
BY LEE IRVIN SMITH AND HARVEY H. HOEHN

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)

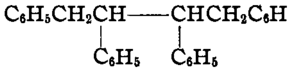


I



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

II



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

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).

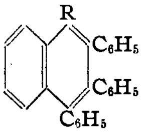
[5] Smith and Hoehn, THIS JOURNAL, **61**, 2619 (1939); *ibid.*, **63**, 1180, 1181 (1941).

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

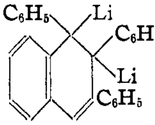
hydrocarbon with sodium and alcohol produced 1,2,3,4-tetraphenylbutane (III).

Hence it seems clear that this 183° hydrocarbon must be II, but in view of the ease with which bromine converts II into the indene, it is readily comprehensible that Bergmann and Schreiber[3] should have obtained 1-benzyl-2,3-diphenylhydrindene by action of red phosphorus and hydriodic acid upon a solution of II in acetic acid.

It also has been reported[1,2,3] that two lithium derivatives were formed in the reaction between diphenylacetylene and lithium. The evidence for this was based upon the products obtained by carbonating the reaction mixture. Two products were reported; a monocarboxylic acid $C_{29}H_{20}O_2$, melting at 258°, assigned structure IV, and a substance $C_{30}H_{20}O_3$, melting at 270°, and considered to be 1,2,3 - triphenyl - 1,2 - dihydronaphthalene-1,2-dicarboxylic anhydride. The two lithium derivatives, then, were represented as V and VI,

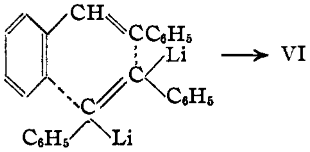


IV R = COOH
V R = Li
VII R = H



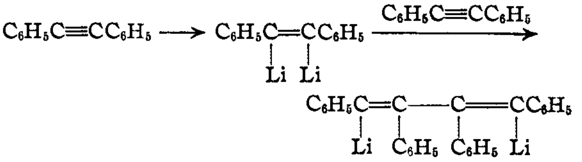
VI

and since carbonation of the mixture of V and VI gave a product containing about 75% of the anhydride, the mixture of lithium derivatives was supposed to consist largely of VI. In order, however, to explain the formation of 1,2,3-triphenylnaphthalene from this mixture by alcoholysis, it was postulated that the dihydronaphthalene corresponding to VI was so unstable that it dehydrogenated spontaneously to the triphenylnaphthalene. The formation of the monolithium derivative V of the naphthalene was explained as a direct action of the metal upon the naphthalene, the latter arising from a direct dimerization of diphenylacetylene. The dilithium derivative VI was supposed to arise by addition of a dilithium derivative of diphenylacetylene to a partially reduced diphenylacetylene. Thus



However, 1,2,3,4 - tetraphenyl - 1,4 - dilithiobutadiene VIII is the true intermediate in the formation of the lithium compounds which give rise to 1,2,3-triphenylnaphthalene on alcoholysis. When an ethereal solution of diphenylacetylene was shaken with excess lithium for an hour, the reaction mixture turned deep red, became distinctly warm and deposited a bright red granular precipitate. Continued action of the metal resulted in disappearance of the red precipitate. The solution became brown and a brown, sticky precipitate separated. If the reaction mixture was decomposed while the red precipitate was present, an excellent yield of 1,2,3,4-tetraphenylbutadiene, m. p. 183°, resulted, but if decomposition was delayed until after the red precipitate was replaced by the brown one, then an excellent yield of 1,2,3-triphenylnaphthalene, VII, m. p. 151°, was obtained. Moreover, when excess metal was avoided, and exactly 1 mole of hydrocarbon was used for two atoms of lithium, then the only product obtained on alcoholysis was the tetraphenylbutadiene, regardless of the duration of the experiment. This result showed that the lithium derivative V of the naphthalene was not formed by elimination of lithium hydride from 1,2,3,4-tetraphenyl-1,4-dilithiobutadiene VIII.

The formation of VIII from diphenylacetylene and lithium is analogous to the known dimerizing addition of alkali metals to certain ethylenes, but as in the ethylenic series, it may be supposed to occur in stages rather than directly, although evidence on this point is lacking.



$$C_6H_5C\equiv CC_6H_5 \longrightarrow C_6H_5\underset{\text{Li}}{C}=\underset{\text{Li}}{C}C_6H_5 \xrightarrow{C_6H_5C\equiv CC_6H_5} C_6H_5\underset{\text{Li}}{C}=\underset{C_6H_5}{C}-\underset{C_6H_5}{C}=\underset{\text{Li}}{C}C_6H_5$$

VIII

Before the entire mechanism of the reaction between lithium and diphenylacetylene can be determined, it is necessary to establish the nature of the metallic derivative or derivatives which give rise to triphenylnaphthalene VII. Here, also, it has not been possible to duplicate the results previously reported.[1,2,3] Carbonation of the brown organolithium mixture which gives VII led to a product from which the only substance that could be isolated was a compound melting at 264–265° with evolution of a gas, and analyzing perfectly for $C_{28}H_{19}COOH$ (IV). This 265° substance probably was the compound reported[1,2,3] to melt at 258° with evolution of a gas, and to be one of the products obtained when the mixture of lithium derivatives was carbonated. Yet the 265° substance, after it was once precipitated, was insoluble in sodium carbonate, sodium hydroxide or in Claisen alkali—most unusual properties for an acid to possess.

Attempts to brominate 1,2,3-triphenylnaphthalene VII, using conditions similar to those used for bromination of naphthalene itself, produced no bromo derivative. Nitration of the hydrocarbon gave a mononitro compound which had the proper composition, but reduction of the nitro-compound gave a very unstable amine and it was not possible to convert this to the known 2,3,4-triphenyl-α-naphthol.[7]

Experimental Part[8]

Reaction between Lithium and Diphenylacetylene. A.—The hydrocarbon (8.9 g., 0.005 mole) was dissolved in ether (20 cc.), lithium (shavings, 1 g.) was added, the cork stopper was wired in place and the mixture was placed on the shaking machine for two hours. After fifteen minutes, the flask was distinctly warm and a considerable amount of red granular solid had separated. After two hours, the temperature had fallen to that of the room. The mixture was poured into cold dry ethanol (100 cc.) and the white solid was removed and crystallized twice from a mixture of benzene and petroleum ether (b. p. 28–38°). The white needles (5.9 g.) melted at 182.5–183°. Orechoff[6] reports the m. p. of 1,2,3,4-tetraphenylbutadiene as 183–184°.

Anal. Calcd. for $C_{28}H_{22}$: C, 93.81; H, 6.19. Found: C, 93.93; H, 6.26.

B. A duplicate of experiment A, except that the mixture was shaken for twenty-eight hours. The mixture was decomposed as above, and the white solid was dissolved in a mixture of ethanol and chloroform. After filtering the hot solution, most of the chloroform was evaporated from the filtrate and the residue was cooled. The white needles (6.3 g.) melted at 151°.

Anal. Calcd. for $C_{28}H_{20}$: C, 94.33; H, 5.67. Found: C, 94.25; H, 5.76.

C. The hydrocarbon (1.58 g., 0.01 mole) in dry ether (2 cc.) was shaken with lithium shavings (75 mg., 0.01 gram atom = 70 mg.) for one week. The reaction mixture was composed of a bright red granular precipitate and a deep red ethereal solution. Decomposition, isolation and purification as described under A above resulted in 1.1 g. of tetraphenylbutadiene, m. p. 183°. Thus the time factor has no effect unless an excess of the metal is used.

Tetraphenylthiophene.—Tetraphenylbutadiene (1.4 g.) and sulfur (160 mg.) were heated to 250° for four hours in an open tube. The light yellow reaction mixture was taken up in benzene, filtered and the filtrate was evaporated. The residue was dissolved in a mixture of chloroform and petroleum ether; the cooled solution deposited white needles (850 mg.) of tetraphenylthiophene melting at 184°.

Anal. Calcd. for $C_{28}H_{20}S$: C, 86.56; H, 5.19. Found: C, 86.51; H, 5.36.

1,2,3,4-Tetraphenylbutane.—Tetraphenylbutadiene (356 mg.) was dissolved in amyl alcohol (10 cc.) and during the course of three hours, sodium (1 g.) was added in small pieces to the boiling solution. Water was added and the solvent alcohol was removed by steam distillation. The white solid was removed from the cooled residue and crystallized from a mixture of alcohol and chloroform. It weighed 175 mg. and melted at 179–180°.[9] A mixture with tetraphenylbutadiene (m. p. 183°) was completely liquid at 168°.

1 - Benzal - 2,3 - diphenylindene.—Tetraphenylbutadiene (560 mg.) was added to a solution of bromine (0.2 cc.) in ether (20 cc.). The reaction mixture became light yellow and hydrogen bromide was evolved. After standing at room temperature for several days, the solvent was evaporated and the residue was crystallized from a mixture of chloroform and ethanol. The substance contained no halogen. It formed yellow needles (400 mg.) which melted at 184°. Orechoff[6] obtained the same yellow substance, m. p. 184°, by subjecting the diene in hot chloroform to the action of bromine.

Carbonation Experiment.—Diphenylacetylene (5 g.) in ether (70 cc.) was shaken with lithium shavings (1 g.) for four days. (At this time the mixture had deposited the sticky brown precipitate which on alcoholysis, gives 1,2,3-triphenylnaphthalene.) More ether was added and a rapid current of carbon dioxide was passed into the solution until the color became light yellow. The mixture was poured over ice and the aqueous layer was separated, warmed to remove dissolved ether, then cooled and acidified with dilute sulfuric acid. The light tan solid was removed, dried, and its solution in hot benzene was filtered. The solvent was evaporated from the filtrate and the residue was crystallized first from acetic acid and then from a mixture of benzene and petroleum ether (b. p. 60–68°). The white product (700 mg.) softened at 261° and melted at 265° with gas evolution. This product was insoluble in, and unchanged by the action of sodium carbonate, sodium hydroxide or Claisen alkali. Although this substance has the composition required by the acid IV, it is still to be determined whether or not the substance really is an acid.

Anal. Calcd. for $C_{29}H_{20}O_2$: C, 86.96; H, 5.04. Found: C, 86.89; H, 5.00.

Nitration of 1,2,3-Triphenylnaphthalene, m. p. 151°.—The hydrocarbon (360 mg.) was dissolved in acetic acid (5 cc.). Nitric acid (0.1 cc.) and a drop of sulfuric acid were added and the solution was heated at 90° for thirty minutes. The light yellow solution was cooled and the solid (175 mg.) was removed and crystallized twice from acetic acid. The product formed fine needles which were only slightly yellow and which melted at 200–201°.

Anal. Calcd. for $C_{28}H_{19}O_2N$: C, 83.76; H, 4.77. Found: C, 83.62; H, 4.83.

Reduction of the Nitro Compound.—The nitro-1,2,3-triphenylnaphthalene (400 mg.) in acetic acid (7 cc.) and

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(7) Smith and Hoehn, THIS JOURNAL, **63**, 1180 (1941).

(8) Microanalyses by E. E. Renfrew and E. E. Hardy.

(9) Wallis and Adams, THIS JOURNAL, **55**, 3850 (1933), report the m. p. as 178°.

water (3 cc.) was refluxed with zinc (20 mesh) for three hours. The nitro compound slowly dissolved and at the end a clear solution resulted. This was poured over ice and the white precipitate was removed and crystallized twice from ethanol. The product (150 mg.) formed pink needles which melted at 189–190° to a dark reddish liquid. The material was not analytically pure, however.

Anal. Calcd. for $C_{25}H_{21}N$: C, 90.53; H, 5.70. Found: C, 89.53; H, 5.99.

Summary

1. The first step in the reaction between lithium and diphenylacetylene is the formation of 1,2,3,4-tetraphenyl-1,4-dilithiumbutadiene-1,3.

2. The compound resulting from alcoholysis of the first lithium derivative is 1,2,3,4-tetraphenylbutadiene, and not 1-benzal-2,3-diphenylhydrindene as has been previously reported.

3. The relative amounts of metal and hydrocarbon determine the nature of the final product formed whenl ithium reacts with diphenylacetylene. When the molar ratio of hydrocarbon and metal is 1:1, the final product is the tetraphenylbutadiene. When excess metal is used, the final product is a hydrocarbon which appears to be 1,2,3-triphenylnaphthalene.

4. Carbonation of the metallic derivative which corresponds to 1,2,3-triphenylnaphthalene leads to a substance previously reported as a monocarboxy derivative of this hydrocarbon, and having this composition. Yet this substance shows surprising properties for an acid, for it is not soluble in sodium carbonate, sodium hydroxide or Claisen alkali.

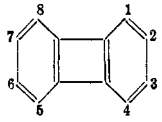
MINNEAPOLIS, MINNESOTA RECEIVED JANUARY 2, 1941

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF TRINITY COLLEGE]

Biphenylene

BY WARREN C. LOTHROP

The history of the interesting hydrocarbon biphenylene (I)[1] is a series of repeated failures in its preparation and of only one isolated and irreproducible success. The earliest report is that of Hosaeus,[2] who carried out a Wurtz reaction with *o*-dibromobenzene but obtained biphenyl as the only hydrocarbon. An internal Ullmann reaction[3] in which 2,2′-diaminobiphenyl was diazotized and treated with copper, gave carbazole, while attempted dehydration of 2-hydroxybiphenyl not unexpectedly also failed.[4]



I

Dobbie, Fox and Gauge[5] in a series of articles claimed the preparation of the hydrocarbon in 100% yield by the intramolecular Wurtz reaction of freshly cut sodium on 2,2′-dibromobiphenyl. They reported analyses of a compound very similar to biphenyl and based their proof on its method of synthesis and its oxidation in part to phthalic acid. In their last paper they reported failure to obtain anything but resins from a corresponding reaction on 2,2′-diiodobiphenyl but did describe several reactions of their new hydrocarbon. These indicated a strained central ring, since bromine opened it to give the starting material, 2,2′-dibromobiphenyl, while dilute nitric acid formed dibenzofuran among other products.

Nierenstein[6] at this time found that a zinc dust distillation of purpurotannin gave a hydrocarbon identical with that of Dobbie, Fox and Gauge. This seemed strange, since to purpurotannin was ascribed a substituted dibenzofuran structure while Hoffmeister[7] had found that dibenzofuran itself did not yield biphenylene on such treatment.

Attempts by other workers[8] to repeat the original preparation of the compound from 2,2′-dibromobiphenyl[5] failed completely, so that doubts of the possible existence of a compound containing a cyclobutadiene ring could be rea-

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[1] The nomenclature is that of *Chemical Abstracts*, Third Decennial Index, p. 3730, but the numbering in the diagram is suggested as more comparable to that used in other hydrocarbons.

[2] Hosaeus, *Monatsh.*, **14**, 323 (1893).

[3] Niementowski, *Ber.*, **34**, 3331 (1901).

[4] Cullinane, Morgan and Plummer, *Rec. trav. chim.*, **56**, 627 (1937).

[5] Dobbie, Fox and Gauge, *J. Chem. Soc.*, **99**, 683, 1615 (1911); **103**, 36 (1913).

[6] Nierenstein, *Ann.*, **386**, 318 (1911); "The Natural Organic Tannins," Churchill, 1934.

[7] Hoffmeister, *Ann.*, **159**, 213 (1871).

[8] (a) Mascarelli and Gatti, *Gazz. chim. ital.*, **63**, 661 (1933); (b) Mascarelli, Gatti and Longo, *ibid.*, **63**, 654 (1933); (c) Schwechten, *Ber.*, **65**, 1605 (1932).