benzene and petroleum ether (b. p., 90–100°), when it formed white needles (6.2 g., 77%) which melted at 153–154°.

Anal. Calcd. for $C_{23}H_{18}O$: C, 88.99; H, 5.85. Found: C, 88.90; H, 5.93.

3-*p*-Tolyl-4-phenyl-α-naphthyl Acetate III.—The naphthol II (200 mg.) was boiled for a few minutes in acetic anhydride (2 cc.) containing sulfuric acid (1 drop). The cooled solution was poured over ice and the solid was removed and crystallized from ethanol. The acetate (210 mg.) was white and melted at 131–132°.

Anal. Calcd. for $C_{25}H_{20}O_2$: C, 85.19; H, 5.73. Found: C, 84.89; H, 5.93.

3-*p*-Tolyl-4-phenyl-1,2-naphthoquinone IV.—The naphthol II (620 mg., 0.002 mole) was dissolved in acetic acid (20 cc.), lead tetraacetate (1.52 g., 0.004 mole) was added and the solution was refluxed for one hour. Half of the acetic acid was distilled off and hydrochloric acid (1 cc.) and ethanol (30 cc.) were added to the residue. The hot solution was filtered and a little water was added to the filtrate. On cooling, bright red crystals of the quinone (350 mg.) separated. After crystallization from ethanol, the substance melted at 226–227°.

Anal. Calcd. for $C_{23}H_{16}O_2$: C, 85.15; H, 4.97. Found: C, 84.85; H, 5.12.

Phenazine.—When a solution of the quinone IV (30 mg.) and *o*-phenylenediamine (20 mg.) in ethanol (10 cc.) was heated on the steam-bath for thirty minutes, yellow needles of the phenazine separated. The product was removed from the cooled mixture and crystallized from ethanol, when it melted at 283–284°.

Anal. Calcd. for $C_{29}H_{20}N_2$: C, 87.84; H, 5.09. Found: C, 85.43; H, 5.08.

Permanganate Oxidation of IV.—The quinone IV (1.24 g., 0.004 mole) was refluxed for fourteen hours with a solution of potassium permanganate (6.28 g., 0.04 mole) and potassium hydroxide (3 g.) in water (100 cc.). The manganese oxides were removed from the cooled mixture, and the filtrate was concentrated to 75 cc., cooled to 0° and acidified with dilute sulfuric acid. The yellow precipitate was removed, dried and suspended in ether (20 cc.) and allowed to stand for a short time. The mixture was filtered and the ether was evaporated from the filtrate. The residue, a yellow oil, crystallized when inoculated with *o*-benzoylbenzoic acid. This solid (180 mg.) was again suspended in ether and processed as before with the addition of a little Norit. Evaporation of the ether left white needles which melted at 90–91°; when mixed with *o*-benzoylbenzoic acid hydrate (m. p. 95°) the substance softened at 91° and melted at 94–95°.

The insoluble material from the above treatments with ether was refluxed for thirty hours with methanol (20 cc.) containing sulfuric acid (2 cc.). The hot solution was filtered and the filtrate was concentrated and cooled. The solid was removed and shaken with saturated aqueous sodium carbonate. The insoluble material was crystallized from methanol. It weighed 80 mg. and melted at 140–141°, alone, or when mixed with an authentic specimen of methyl terephthalate.

Summary

1. Diphenylketene reacts with *p*-tolylacetylene to produce 3-*p*-tolyl-4-phenyl-α-naphthol, II, whose structure has been proved by oxidation to *o*-benzoylbenzoic and terephthalic acids.

2. It follows that when diphenylketene reacts with a monoarylacetylene, the aryl group in the 3-position of the resulting 3,4-diaryl-α-naphthol is supplied by the acetylene.

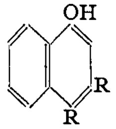
MINNEAPOLIS, MINNESOTA RECEIVED DECEMBER 2, 1940

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

The Reaction between Diphenylketene and Arylacetylenes. III. Phenyldiphenylacetylacetylene[1]

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

In the previous papers,[1,3] it has been shown that diphenylketene and arylacetylenes react to produce a 3,4-diarylnaphthol (I), and that the aryl group supplied by the acetylene occupies the 3-position in this naphthol.



I

$(C_6H_5)_2CHCO(C_4H_4N)$

II

$(C_6H_5)_2CHCOC{\equiv}CC_6H_5$

III

Diphenylketene reacts with many compounds containing an active hydrogen atom to give compounds containing the diphenylacetyl group; even pyrrole behaves in this way, forming diphenylacetylpyrrole[4] (II). It was conceivable, therefore, that the first step in the reaction between diphenylketene and a monoarylacetylene would be a reaction of this type, leading to the initial formation of phenyldiphenylacetylacetylene III (from phenylacetylene). This acetylenic ketone would then be cyclized to the naphthol I under the conditions used.

To test this hypothesis, phenyldiphenylacetyl-

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(1) Paper II, THIS JOURNAL, **63**, 1175 (1941).

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

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

(4) Staudinger and Suter, *Ber.*, **53**, 1104 (1920).

acetylene (III) has been synthesized. Since Grignard reagents have been shown to react normally at the carbonyl group of diphenylketene,[5] phenylethynylmagnesium bromide was added to diphenylketene. An excellent yield of the ketone III was produced. The ketone formed a semicarbazone, and when reduced catalytically gave 1,1,4-triphenylbutanone-2 (IV). The butanone IV was also synthesized by an independent method. Condensation of benzaldehyde with 1,1-diphenylacetone produced the ethylenic ketone V, which on reduction gave the butanone IV.

$$C_6H_5CHO + CH_3COCH(C_6H_5)_2 \longrightarrow \underset{\text{V}}{C_6H_5CH{=}CHCOCH(C_6H_5)_2} \longrightarrow \underset{\text{IV}}{C_6H_5CH_2CH_2COCH(C_6H_5)_2}$$

When the acetylenic ketone III was refluxed for some time in acetic acid containing zinc chloride, it underwent no change. It follows, therefore, that in the formation of the naphthol I from diphenylketene and phenylacetylene, an intermediate of the type of III is not involved.

Both ketones—III and V—crystallized nicely and had sharp melting points, 97–98° and 62°, respectively, but after standing for a year the analytical samples of both contained a yellow liquid. The semicarbazone of III, however, remained unchanged during this time.

Experimental Part[6]

Phenyldiphenylacetylacetylene (III).—Phenylacetylene (5.5 cc.) in ether (10 cc.) was added slowly to a solution of ethylmagnesium bromide [prepared from ethyl bromide (4 cc.), magnesium (1.2 g.), and ether (20 cc.)]. The reaction mixture was refluxed for four hours, and the acetylenic Grignard reagent separated as a light brown lower layer. Diphenylketene (9.7 g.) in ether (10 cc.) was slowly added, and after stirring and refluxing the mixture for an hour it was poured into saturated iced ammonium chloride (200 cc.). The ether layer was separated and the aqueous layer was thoroughly extracted with ether. The combined ether solutions were washed with bicarbonate and then with water. Most of the ether was evaporated and petroleum ether (b. p. 28–38°) was added to the residue. The chilled solution deposited light yellow needles (12 g.) of the ketone III which melted at 88-96°. After several crystallizations from aqueous ethanol, the substance was white and melted at 97–98°. The losses on crystallization were quite large.

Anal. Calcd. for $C_{22}H_{16}O$: C, 89.15; H, 5.45. Found: C, 89.46; H, 5.72.

After standing in a closed bottle for a year, the analytical sample had changed, for the most part, into a light lemon yellow oil.

Semicarbazone.—The ketone (200 mg.), sodium acetate (0.5 g.) and semicarbazide hydrochloride (0.5 g.) were warmed on a water-bath for one hour in ethanol (20 cc.) and water (3 cc.). The semicarbazone (195 mg.) was white, and melted at 197–198° after several crystallizations from aqueous methanol.

Anal. Calcd. for $C_{23}H_{19}ON_3$: C, 78.18; H, 5.39. Found: C, 76.92; H, 5.63.

1,1-Diphenylacetone.—The following directions are a modification of those of Stoermer.[7] Ethyl lactate (30 g.) was dropped slowly into a solution of phenylmagnesium bromide [prepared from bromobenzene (80 g.), magnesium (12.3 g.) and ether (300 cc.)]. The mixture was decomposed with ice and acetic acid and thoroughly extracted with ether. The combined ether solutions were washed with dilute sodium hydroxide, followed by water. Most of the ether was evaporated, and when low boiling petroleum ether was added to the residue, 1,1-diphenylpropylene glycol (22 g.), melting at 95°, separated.

The glycol (11.5 g.), hydrochloric acid (5 drops) and water (55 cc.) were heated in a sealed tube for three hours at 180°. The product from two such experiments was extracted with ether and the ether was evaporated. 1,1-Diphenylacetone (21 g.) remained. The substance melted at 41–61°, but this wide range is due to the dimorphic nature of the ketone.

Benzaldiphenylacetone (V).—The above ketone (20 g.), benzaldehyde (20 cc., freshly distilled) and sodium hydroxide (5 cc., 40%) and some ethanol were stirred for two hours at room temperature. The product was removed from the chilled mixture and crystallized from ethanol. The ketone V (21 g.) was white and melted at 112° in agreement with the value in the literature.[8]

1,1,4-Triphenylbutanone-2 (IV). A. From III.—The acetylenic ketone (500 mg.) was dissolved in ethanol (30 cc.), platinum oxide catalyst was added and hydrogen under 1 atm. pressure was passed into the mixture. The catalyst was removed and the filtrate was concentrated. Addition of water to the cooled solution precipitated the ketone IV which was removed and crystallized from aqueous alcohol. It formed white needles (300 mg.) which melted at 62°.

Anal. Calcd. for $C_{22}H_{20}O$: C, 87.95; H, 6.72. Found: C, 87.59; H, 6.66.

After standing for a year in a closed bottle, most of the ketone had changed to a light yellow oil, but by chilling the solution of this oil in dilute ethanol, white needles (m. p. 58–59°) could still be obtained.

B. From V.—The ethylenic ketone V (298 mg.), platinum oxide catalyst (20 mg.) and acetic acid (30 cc.) were subjected to the action of hydrogen under 35 lb. pressure. After removal of the catalyst, the filtrate was diluted with water and set aside in a refrigerator. The long white needles (210 mg.) melted at 57–59° alone or when mixed with a specimen prepared by reduction of III.

Attempted Cyclization of III.—The acetylenic ketone III (200 mg.) was dissolved in acetic acid (15 cc.), freshly fused zinc chloride (300 mg.) was added and the solution was refluxed for one hour. Dilution with water gave

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(5) Gilman and Heckert, THIS JOURNAL, **42**, 1010 (1920).

(6) Microanalyses by J. W. Opie and C. O. Guss.

(7) Stoermer, *Ber.*, **39**, 2302 (1906).

(8) Staudinger, *Helv. Chim. Acta*, **7**, 3 (1929).

light yellow crystals which melted at 94–95°. When mixed with III (m. p. 97–98°), the substance melted at 94–96°.

Summary

1. Phenyldiphenylacetylacetylene III has been synthesized and its structure has been proved.

2. This ketone cannot be cyclized to the naphthol I, from which it follows that the ketone III is not an intermediate in the formation of the naphthol from diphenylketene and phenylacetylene.

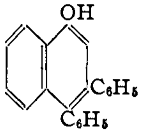
MINNEAPOLIS, MINNESOTA
RECEIVED DECEMBER 13, 1940

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

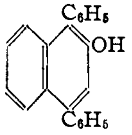
The Reaction between Diphenylketene and Arylacetylenes. IV. Synthesis of 1,4-Diphenyl-β-naphthol[1]

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

In the first paper of this series[3] it was shown that diphenylketene and phenylacetylene reacted to form 3,4-diphenyl-α-naphthol, I. Before the structure of the reaction product was definitely known, however, an isomeric naphthol, 1,4-diphenyl-β-naphthol (II) had to be considered because it was possible to write a reaction between the ketene and the acetylene which led to the β (II) rather than to the α (I) naphthol.



I

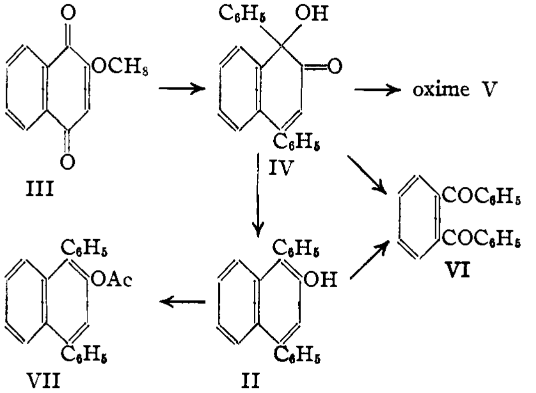


II

In order to reach a decision, 1,4-diphenyl-β-naphthol (II) was synthesized. This substance was not identical with the product of the reaction between diphenylketene and phenylacetylene, but because the synthesis of II presented some interesting features, a description of it is presented at this time.

The starting material was 2-methoxy-1,4-naphthoquinone (III). The methoxyquinone reacted with phenylmagnesium bromide to give a good yield of 1-hydroxy-2-keto-1,4-diphenyldihydronaphthalene (IV), which formed an oxime V and which, on oxidation, gave *o*-dibenzoylbenzene (VI).

This is an interesting reaction between a 1,4-quinone and a Grignard reagent, for the reagent adds largely 1,2 to both carbonyl groups. The simultaneous cleavage of the methoxyl group by the reagent is not surprising, since the methoxyl group of III is more like an ester group than an ether group. Thus III is converted into the hydroxyquinone by dilute alkali and, conversely, the hydroxyquinone can be converted into III by the action of methyl alcohol containing a little mineral acid.



Reduction of the ketol IV by zinc and acetic acid gave the naphthol II, which formed an acetate (VII) and which, on oxidation, gave *o*-dibenzoylbenzene (VI).

Experimental Part[4]

2-Methoxy-1,4-naphthoquinone (III) (41 g.) was prepared from 1-amino-2-naphthol-4-sulfonic acid (87.5 g.) essentially as described by Fieser and Fieser.[5] The crude product was heated with dilute sodium hydroxide (2.5%, 375 cc.) until solution was complete (ten minutes). The deep red solution was filtered while hot, the cooled filtrate was acidified with dilute sulfuric acid and the precipitate (41 g.) was removed. The hydroxyquinone (35 g.) was dissolved in methanol (350 cc.), hydrochloric acid (25 cc.) was added and the mixture was refluxed for thirty minutes. 2-Methoxy-1,4-naphthoquinone (30 g.) was obtained from the cooled reaction mixture. It melted at 181–183°.

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(1) Paper III, THIS JOURNAL, 63, 1176 (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) Smith and Hoehn, THIS JOURNAL, 61, 2619 (1939).

(4) Microanalyses by C. O. Guss.

(5) Fieser and Fieser, THIS JOURNAL, 57, 494 (1935).