JOURNAL OF THE
AMERICAN CHEMICAL SOCIETY

VOLUME 63 MAY 6, 1941 NUMBER 5

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

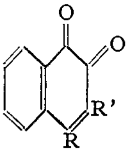
The Reaction between Diphenylketene and Aryl Acetylenes. II. *p*-Tolylacetylene[1]

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

In the first paper of this series[1] it was shown that diphenylketene and phenylacetylene, when mixed and allowed to stand at room temperature, react to form 3,4-diphenyl-α-naphthol I.

I R = R' = C_6H_5
II, R = C_6H_5; R' = *p*-$CH_3C_6H_4$—

III, R and R' as in II



IV, R and R' as in II

In order to elucidate the mechanism of this reaction, it first was necessary to determine which of the three aryl groups present in the reactants occupied the 3-position in the product I.

To decide this point, *p*-tolylacetylene has been added to diphenylketene. When equimolecular amounts of the reactants were mixed and allowed to stand overnight in a nitrogen atmosphere, there was produced a white crystalline substance melting at 153–154° having the composition $C_{23}H_{18}O$ (II). Like its homolog I, substance II reacted with acetic anhydride to form a monoacetate (III) and with lead tetraacetate to form a bright red orthoquinone (IV). When oxidized by alkaline permanganate, II gave a mixture of *o*-benzoylbenzoic acid and terephthalic acid.

It follows, therefore, that when diphenylketene and a monoarylacetylene react, the 3,4-diaryl-α-naphthol produced contains in the 3-position the aryl group that was present in the acetylene.

Experimental Part[3]

1-*p*-Tolyl-1-chloroethylene.—Phosphorus pentachloride (188 g.) was placed in a Claisen distilling flask (250 cc.) fitted with a dropping funnel and a drying tube. The flask was surrounded by a bath of ice and salt, and *p*-tolyl methyl ketone (110 g.) was slowly (one hour) dropped onto the solid pentachloride. The reaction mixture was allowed to stand for an hour, then the cooling bath was removed and the mixture was allowed to stand for twelve hours longer. Phosphorus oxychloride was removed by distillation under reduced pressure and the residue was distilled through a small column of the Fenske type. The product, an oil (85 g., 68.5%), boiled at 81–83° under 10 mm.

***p*-Tolylacetylene.**—The above chloroethylene (85 g.) was refluxed for twenty-four hours with potassium hydroxide (50 g.) in dry ethanol (100 cc.). The mixture was poured into ice water (1000 cc.), the oil was separated and the aqueous layer was extracted with ether. The oil and the ether extracts were combined and dried over potassium hydroxide. The ether was removed and the residue was distilled. *p*-Tolylacetylene (31 g., 65%) boiled at 79–82° under 31–33 mm.

3-*p*-Tolyl-4-phenyl-α-naphthol II.—The acetylene (3.0 g.) and diphenylketene (5.1 g.) were mixed in a flask under nitrogen and the mixture was allowed to stand at room temperature for twenty-four hours. The solid product was removed and crystallized from a mixture of

---

(1) First paper, Smith and Hoehn, THIS JOURNAL, 61, 2619 (1939).

(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) Microanalyses by C. O. Guss and E. E. Renfrew.

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.

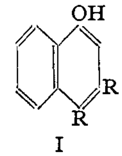
MINNEAPOLIS, MINNESOTA RECEIVED DECEMBER 2, 1940

[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-

---

[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).