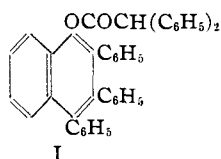


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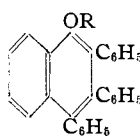
The Reaction between Diphenylketene and Arylacetylenes. V. Diphenylacetylene¹BY LEE IRVIN SMITH AND HARVEY H. HOEHN²

In a previous paper³ it was shown that the 3,4-diaryl- α -naphthol formed when diphenylketene reacts with an arylacetylene contains in the 3-position the aryl group that was supplied by the acetylene. In order to gain further insight into the mechanism of this reaction, it was necessary to determine whether or not the acetylenic hydrogen atom of the hydrocarbon played any role in the reaction, *i. e.*, whether or not a diarylacetylene would react with the ketene.

When diphenylketene and diphenylacetylene were heated together for a day in a sealed tube at 80°, the orange color of the reaction mixture faded and a lemon yellow solid was formed. The crude yellow product gave a positive test for phenols (Folin), but after several crystallizations from ethanol, a white solid melting at 168–169° was obtained. This solid had the composition C₄₂H₃₀O₂; it gave a negative phenol test and was not soluble in Claisen alkali. The composition of the material showed that it was derived from two molecules of the ketene and one of the acetylene, and assuming the first product of the reaction to be 2,3,4-triphenyl- α -naphthol (II), in analogy with the other products derived from the ketene and aryl acetylenes,^{3,4} the most likely structure for the addition product was I, 2,3,4-triphenyl- α -naphthyl diphenylacetate, resulting from the action of a second molecule of the ketene upon the primary product II. This supposition was proved correct, for the substance I, on hydrolysis with alcoholic potassium hydroxide, gave



I



II, R = H; III, R = Ac

diphenylacetic acid and 2,3,4-triphenyl- α -naphthol, II. The naphthol II formed an acetate, III, and, when the naphthol was oxidized, the products were *o*-benzoylbenzoic and benzoic acids.

Hence it follows that the addition of an aryl-

acetylene to diphenylketene does not require that there be a hydrogen atom attached to one of the acetylenic carbon atoms, for this hydrogen atom, if present, is not involved in the reaction in any way.

Experimental Part⁵

Stilbene Dibromide.—Stilbene (60 g.) was dissolved in ether (1000 cc.) and bromine (18 cc.) was rapidly (ten minutes) added to the well stirred solution. The product was removed and washed with ether until it was white. The substance melted at 243–244° and weighed 87 g.

Diphenylacetylene.—Stilbene dibromide (80 g.) was refluxed for twenty-four hours with a solution of potassium hydroxide (120 g.) in dry ethanol (200 cc.). The product, precipitated by addition of water (1000 cc.), was crystallized from ethanol. It weighed 36 g. and melted at 60–61°.

2,3,4-Triphenyl- α -naphthyl diphenylacetate I.—Since a difficultly separable mixture of this substance and the naphthol II resulted when the acetylene and the ketene were mixed in molecular proportions, it was better to use an excess of ketene, thus converting all of the product into I, and then hydrolyze this to the naphthol II. Diphenylketene (7.76 g., 0.04 mole) and diphenylacetylene (3.56 g., 0.02 mole) were mixed in an atmosphere of carbon dioxide and the mixture was warmed to 70–80° for three days. The color of the ketene disappeared after two days, and at the end of the reaction the white solid was removed and suspended in petroleum ether (b. p. 60–68°). The suspension was filtered and the residue (11 g.), which melted at 161–164°, was crystallized twice from a mixture of chloroform and ethanol. The product (9.3 g.) formed white plates which melted at 168–169°. The Folin test was negative and the substance was insoluble in Claisen alkali.

Anal. Calcd. for C₄₂H₃₀O₂: C, 89.01; H, 5.34. Found: C, 89.11; H, 5.38.

When equimolecular quantities of the reactants were used, the product melted at 145–156° after crystallization from ethanol-chloroform, and gave a positive Folin test. It required many crystallizations, accompanied by much loss of material, to obtain pure I from this mixture. Attempts to isolate the other component of the mixture, presumably II, were unsuccessful.

2,3,4-Triphenyl- α -naphthol II.—The ester I (5.7 g., 0.01 mole) was refluxed for thirty-six hours with a solution of potassium hydroxide (25 g.) in methanol (200 cc.) and water (50 cc.). Hydrolysis was very slow, but could be followed readily since the ester was not completely soluble in the amount of solvent used. At the end of the reaction the clear light yellow solution contained no suspended material. The solution was diluted with water, acidified with dilute sulfuric acid and thoroughly extracted with ether. The ether solution, after washing with water

(1) Paper IV, *THIS JOURNAL*, **63**, 1178 (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) Paper II, *THIS JOURNAL*, **63**, 1175 (1941).(4) Smith and Hoehn, *THIS JOURNAL*, **61**, 2619 (1939).

(5) Microanalyses by C. O. Guss, E. E. Hardy and E. E. Renfrew.

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.

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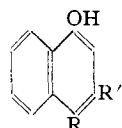
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The Reaction between Diphenylketene and Arylacetylenes. VI. Mechanism¹

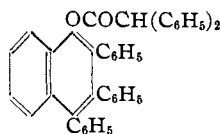
BY LEE IRVIN SMITH AND HARVEY H. HOEHN²

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 $R = R' = C_6H_5$

II $R = C_6H_5$; $R' = p-CH_3C_6H_4-$



III

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 II⁴; why disubstituted, as well as monosubstituted, acetylenes undergo the reaction¹; why an α -naphthol, rather than the β -isomer is formed⁵; 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

(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).