

in the present experiments. Quite satisfactory results were obtained, and accordingly the effect of omitting the solvent from some other typical Michael reaction mixtures was studied. Here, too, rather good yields were obtained. The experiments are summarized in Table I, and the experimental procedure is described below.

A mixture of one-half mole of each of the reactants was stirred by hand and treated with two or three drops of a solution of 1 g. of sodium in 20 ml. of ethanol (or methanol if a methyl ester was involved). In most cases the ensuing reaction was exothermic, and external cooling was used to keep the temperature of the mixture below 50°. Completion of reaction was recognized when the temperature of the mixture began to fall, and when a further rise was not caused by the addition of one drop more of the catalyst solution. The mixture was then neutralized with acetic acid. Solid products were crystallized from alcohol; liquid products were washed with water, if necessary after dilution with carbon tetrachloride, and then distilled under reduced pressure. Distillation was usually preceded by decomposition; acrid pyrolysis products condensable in a liquid air trap were formed. This decomposition involved by-products, however, whose presence was also indicated

by non-volatile residues from the first distillations, for re-distillation of the products was accompanied by no decomposition and no distillation residues.

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### Summary

When attempts are made to condense benzyl cyanide with methyl acrylate (or acrylonitrile) in alcoholic solutions, alcohol addition takes place rather than a Michael reaction, and methyl  $\beta$ -methoxypropionate (or  $\beta$ -ethoxypropionitrile) is formed.  $\gamma$ -Carbethoxy- $\alpha$ -phenylbutyronitrile (or  $\alpha$ -phenylglutaronitrile) can be obtained, however, if the reaction is carried out without a solvent. Other Michael additions of benzyl cyanide to various  $\alpha,\beta$ -unsaturated compounds also proceed well in the absence of a solvent.

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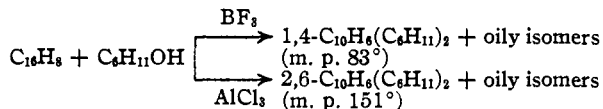
[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

## The Dialkylation of Naphthalene. II. The Synthesis of 2,6-Diphenylnaphthalene

BY CHARLES C. PRICE AND ARTHUR J. TOMISEK

Two crystalline dicyclohexylnaphthalenes have been reported from the alkylation of naphthalene. The lower melting isomer (m. p. 83°), obtained by alkylation with cyclohexanol using boron fluoride as a catalyst,<sup>1</sup> was shown to be the 1,4-isomer by dehydrogenation to 1,4-diphenylnaphthalene (m. p. 133°). The higher melting isomer (m. p. 151°) obtained by Bodroux<sup>2</sup> by alkylation with cyclohexanol and by Pokrovskaya and Stepentseva<sup>3</sup> with cyclohexene, in each instance using aluminum chloride as a catalyst, was dehydrogenated by Pokrovskaya and Stepentseva to a high-melting diphenylnaphthalene<sup>3</sup> (m. p. 230°) of unknown structure. This material has now been shown to be identical with a sample of synthetic 2,6-diphenylnaphthalene. Thus, as in the dialkylation of benzene,<sup>4</sup> orientation in the dialkylation of naphthalene using

boron fluoride differs from that using aluminum chloride.



The synthesis of 2,6-diphenylnaphthalene was accomplished by the series of reactions shown.

The Friedel-Crafts condensation of biphenyl with phenylsuccinic anhydride gave a mixture from which the acid (I) was isolated as the principal product by repeated fractional crystallization. This product (I) was shown to have been formed by condensation of phenylsuccinic anhydride in the 4-position of biphenyl by oxidation to *p*-phenylbenzoic acid. The other phenyl group was assigned the position  $\beta$  to the carboxyl group. Had it been in the alternative  $\alpha$  position, the diphenylnaphthalene obtained as the final product would have been the known 2,7-isomer, m. p. 143°. The orientation of the condensation thus corresponds to that observed for the con-

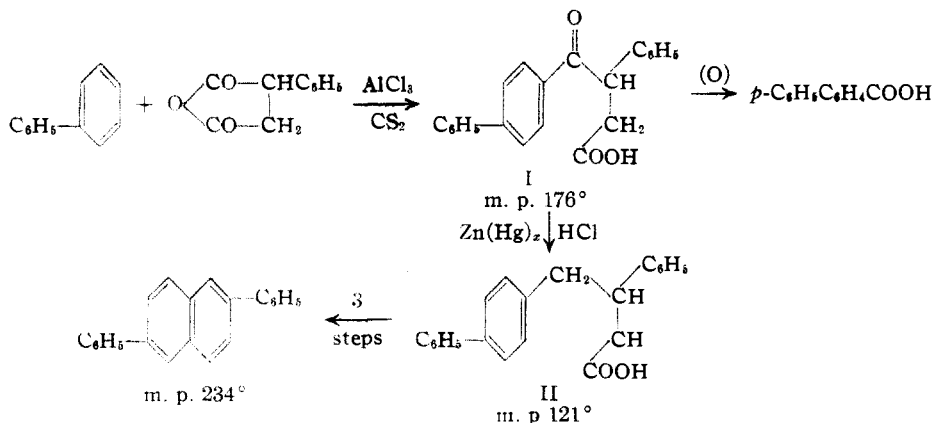
(1) Price, Shafer, Huber and Bernstein, *J. Org. Chem.*, **7**, 517 (1942).

(2) Bodroux, *Ann. chim.*, [10] **11**, 511 (1929).

(3) Pokrovskaya and Stepentseva, *J. Gen. Chem.*, (U. S. S. R.), **9**, 1953 (1939).

(4) McKenna and Sowa, *This Journal*, **59**, 470 (1937).

(5) Hey and Lawton, *J. Chem. Soc.*, 375 (1940).



denation of toluene and phenylsuccinic anhydride under similar conditions.<sup>6</sup>

### Experimental<sup>7</sup>

Phenylsuccinic acid<sup>8</sup> (130 g., 0.742 mole) was converted to the anhydride by refluxing for one hour with acetyl chloride<sup>9</sup> (275 g., 3.5 moles). The reaction mixture was then fractionally distilled, yielding the anhydride in 80% yield, b. p. 190–194° (6 mm.), m. p. 53–54°. Some 12% of the acid was recovered from the residue in the distilling flask.

**$\beta$ -Phenyl- $\beta$ -(*p*-phenylbenzoyl)-propionic Acid (I).**—A solution of 35.2 g. (0.2 mole) of phenylsuccinic anhydride, 46.2 g. (0.3 mole) of biphenyl and 40 g. (0.32 mole) of aluminum chloride in 200 cc. of carbon disulfide was boiled under reflux with mechanical stirring for one hour. The bright green color of the reaction mixture faded during hydrolysis with dilute hydrochloric acid. The solvent and excess biphenyl were next removed by steam distillation and the residue of solid acids was collected by filtration. The powdered mixture of acids was digested with warm concentrated sodium hydroxide for an hour. The sodium salt of the condensation product was insoluble and separated as shiny white plates; filtration thus separated the product from phenylsuccinic acid. The sodium salt so obtained was then digested with concentrated hydrochloric acid and the product crystallized from benzene three times. About three-fourths of the crude acid was recovered as pure  $\beta$ -phenyl- $\beta$ -(*p*-phenylbenzoyl)-propionic acid, m. p. 175.5–176°.

*Anal.* Calcd. for  $\text{C}_{22}\text{H}_{18}\text{O}_3$ : C, 79.98; H, 5.49. Found: C, 80.05; H, 5.41.

About 2 g. of this acid was oxidized by warming for

(6) Desai and Wali, *Proc. Indiana Acad. Sci.*, **6A**, 135 (1937); see also Wali, Khalil, Bhatia and Ahmad, *Proc. Indian Acad. Sci.*, **14A**, 139 (1941).

(7) Microanalyses by Miss Theta Spoor.

(8) Lapworth and Baker, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., second edition, 1941, p. 451.

(9) Alexander, *Ann.*, **258**, 75 (1890).

several hours with excess alkaline potassium permanganate solution. The acid recovered after two recrystallizations from ethyl alcohol-isoamyl alcohol-water melted at 215°, corresponding to *p*-phenylbenzoic acid.

**$\beta$ -Phenyl- $\gamma$ -*p*-xenylbutyric Acid (II).**—The keto acid (5 g.) was reduced by boiling for twenty-four hours under reflux with 20 cc. of concentrated hydrochloric acid, 5 cc. of water, 5 cc. of glacial acetic acid, 4 cc. of benzene and 20 g. of amalgamated zinc pellets. An ether extract of the reaction mixture was washed with water and evaporated, leaving a waxy crystalline solid residue. Recrystallization from alcohol-water gave colorless needles of  $\beta$ -phenyl- $\gamma$ -*p*-xenylbutyric acid, m. p. 120.5–121°.

*Anal.* Calcd. for  $\text{C}_{22}\text{H}_{20}\text{O}_2$ : C, 83.51; H, 6.37. Found: C, 83.66; H, 6.41.

**2,6-Diphenyl-naphthalene.**—The butyric acid above (9 g.) was converted to the acid chloride by means of thionyl chloride (9 cc.). The acid chloride was cyclized by treating with aluminum chloride (8 g.) in 75 cc. of carbon disulfide. The crude tetralone was reduced by the same procedure as that employed for the keto acid (I). A portion of the crude oily diphenyltetralin (2 g.) was heated with 4 g. of selenium at 290–320° for eighteen hours. After cooling, the residue was extracted thoroughly with hot benzene. The extract was evaporated and the residue recrystallized from alcohol to yield 0.4 g. of 2,6-diphenyl-naphthalene, m. p. 233–234°. A mixture with a sample of diphenyl-naphthalene, m. p. 233–234°, obtained by dehydrogenation of dicyclohexyl-naphthalene,<sup>1</sup> also melted at 233–234°.

### Summary

2,6-Diphenyl-naphthalene (m. p. 233–234°) has been synthesized and found to be identical with the diphenyl-naphthalene first obtained by Pokrovskaya and Stepentseva from the dehydrogenation of the crystalline dicyclohexyl-naphthalene, m. p. 151°.

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