Dehydration of Hydro-2,4-xyloin

(a) **With Sulfuric Acid.**—A mixture of 1 g. of the hydroxyloin, 60 ml. of concentrated sulfuric acid, and 45 ml. of water was heated in a steam-bath for forty-five minutes. The product was purified by recrystallization from methanol; m. p. 145–146°.

Anal. Calcd. for $C_{36}H_{40}O_2$: C, 85.67; H, 7.99; mol. wt., 536. Found: C, 85.85; H, 8.29; mol. wt. (ebullioscopic in chloroform), 460, 512.

A Zerewitinoff determination showed that the compound had no active hydrogen. It is probably the tetraxylyldioxane.

A mixture of 1 g. of this compound, 50 ml. of glacial acetic acid and 15 ml. of hydriodic acid (sp. gr. 1.50) was heated for four hours on the steam-bath. By suitable manipulation the product was resolved into two solids. One, after being recrystallized from methanol, melted at 201–203°.

Anal. Calcd. for $C_{36}H_{42}$: C, 91.08; H, 8.92. Found: C, 91.06; H, 8.71.

The other solid melted at 70–71° after repeated recrystallization from methanol.

Anal. Calcd. for $C_{18}H_{22}$: C, 90.69; H, 9.31. Found: C, 90.86; H, 9.23.

These two compounds were not examined further.

(b) **With a Mixture of Acetic and Hydrochloric Acids.**—A mixture of 1 g. of the hydroxyloin, 24 ml. of glacial acetic acid and 6 ml. of concentrated hydrochloric acid was heated under reflux for four hours. The product was crystallized from glacial acetic acid; m. p. 53–54°.

Anal. Calcd. for $C_{18}H_{22}O$: C, 85.67; H, 7.99. Found: C, 85.39; H, 7.67.

This compound failed to form an acetate or benzoate and appeared to be the desoxy-2,4-xyloin.

Di-(2,4-xylyl)-methyl Ether.—An attempt was made to prepare di-(2,4-xylyl)-carbinol by adding 21.4 g. of ethyl formate to a two-fold excess of 2,4-xylylmagnesium bromide. The chief product, isolated by conventional procedures, was 17 g. of **di-(2,4-vinyl)-methyl ether** melting at 180–185°. After recrystallization from isopropyl alcohol it melted at 184–185.5°.

Anal. Calcd. for $C_{34}H_{30}O$: C, 88.26; H, 8.28. Found: C, 88.21; H, 8.38.

A viscous oil was isolated also. Although it failed to crystallize, it gave the reaction expected of the **di-(2,4-xylyl)-carbinol.** Coops, Nauta, Ernsting and Faber[5] reported a melting point of 101° for this compound. When 20 g. of this oil was treated with concentrated hydrochloric acid according to the procedure of Reid[6] for di-(*o*-tolyl)-methyl chloride, a 70% yield of **di-(2,4-xylyl)-methyl chloride** was obtained, m. p. 85–88°. The chloride was recrystallized from low-boiling petroleum ether; m. p. 85–86°.[6]

The chloride was made from the dixylylmethyl ether in a similar manner; yield 63%.

Di-(2,4-xylyl)-acetonitrile.—The procedure was similar to that used by Newman[7] in the preparation of α-naphthonitrile. A mixture of 8.5 g. of di-(2,4-xylyl)-methyl chloride, 3.54 g. of cuprous cyanide and 5 ml. of pyridine (dried over calcium oxide) was heated at 240–250° for twenty-four hours. The nitrile weighed 6.9 g. and melted at 110–113°. It was recrystallized from methanol; m. p. 112–113.5°.

Anal. Calcd. for $C_{18}H_{18}N$: C, 86.69; H, 7.68. Found: C, 86.97; H, 7.63.

Di-(2,4-xylyl)-acetic Acid.—A mixture of 2 g. of di-(2,4-xylyl)-acetonitrile, 6 g. of potassium hydroxide, 1 ml. of water and 60 ml. of diethylene glycol was heated under reflux for four hours. The acid, isolated in the usual way, was recrystallized from a mixture of benzene and low-boiling petroleum ether; m. p. 181–182°.

Anal. Calcd. for $C_{18}H_{20}O_2$: C, 80.56; H, 7.51. Found: C, 80.71; H, 7.75.

(5) Coops, Nauta, Ernsting and Faber, *Rec. trav. chim.*, **59**, 1109 (1940).

(6) Reid, THIS JOURNAL, **61**, 3238 (1939).

(7) Newman, "Organic Syntheses," **21**, 89 (1941).

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Metalation of Cumene by Ethylpotassium[1]

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The metalation of cumene by ethylpotassium (prepared *in situ* from diethylmercury and potassium) proceeds laterally to some extent. This was established by carbonation of the metalation products and isolation of phenyldimethylacetic acid. The reference sample of phenyldimethylacetic acid was prepared in accordance with the procedure of Ziegler and co-workers[2] by carbonation of the product obtained from the cleavage of 2-phenyl-isopropyl methyl ether with sodium–potassium alloy.

$$C_6H_5CH(CH_3)_2 \xrightarrow[(3)\ HOH]{(1)\ (C_2H_5)_2Hg + K;\ (2)\ CO_2} C_6H_5C(CH_3)_2(CO_2H)$$

On the basis of a recent report by Morton and co-workers[3] on the metalation of cumene by amylsodium it is possible that some of the unidentified acids in the carbonation mixture may contain the *o*- and *p*-isopropylbenzoic acids. In this connection, we have observed that the *p*-isopropylbenzoic acid can be conveniently prepared in 49% yield by carbonation of *p*-isopropylmagnesium bromide.

Experimental

A mixture of 2.6 g. (0.01 mole) of diethylmercury, 1.37 g. (0.035 g. atom) of potassium and 25 cc. of cumene was stirred at room temperature, in an atmosphere of dry nitrogen, for ten hours. The mixture was then carbonated by Dry Ice, and the base-soluble material was precipitated from a dilute basic solution by the addition of hydrochloric acid. Fractional crystallization of the crude acid mixture from petroleum ether (b. p. 60–68°) first gave 0.3 g. (19%) of acid melting at 65–68°. Further recrystallization yielded 0.15 g. of an acid melting at 76–77°. This acid was shown, by the method of mixed melting points, to be identical with phenyldimethylacetic acid prepared in 58% by Ziegler's[2] procedure.

(1) Paper LXIII in the series "The Relative Reactivities of Organometallic Compounds." The preceding paper with Jones is in *J. Org. Chem.*, **10**, 505 (1945).

(2) Ziegler and Theilmann, *Ber.*, **56**, 1740 (1923); Ziegler, Crössmann, Kleiner and Schäfer, *Ann.*, **473**, 1 (1929).

(3) Morton, Massengale and Brown, THIS JOURNAL, **67**, 1620 (1945).

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Flocculation of Suspensions by Immiscible Liquids

BY EARL K. FISCHER, EDMUND N. HARVEY, JR., AND AGNES S. DYER

The mechanism of the flocculation of solid particles dispersed in water-immiscible liquids