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 $C_{34}H_{39}O$: 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°.[5]

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.

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

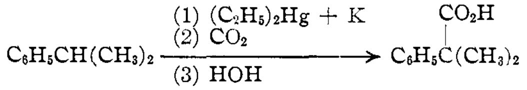
[6] Reid, THIS JOURNAL, **61**, 3238 (1939).

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

Metalation of Cumene by Ethylpotassium[1]

BY HENRY GILMAN AND LEO TOLMAN

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.



$$C_6H_5CH(CH_3)_2 \xrightarrow[\text{(3) HOH}]{\substack{\text{(1) } (C_2H_5)_2Hg\, +\, K \\ \text{(2) } CO_2}} C_6H_5\overset{\overset{\displaystyle CO_2H}{|}}{C}(CH_3)_2$$

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.

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[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 has long been the subject of theoretical and experimental investigation. Evidence has accumulated showing that water and surface-active substances added to such solid-in-liquid dispersions profoundly modify the extent of flocculation as evidenced by sedimentation volumes[1,2,3,4] and plastic-flow properties.[4,5]

A recent study by Kruyt and Van Selms[6] on the plasticity of starch, quartz and glass bead suspensions in organic media as influenced by added water came to the attention of the authors while work indicating similar conclusions was in progress in this Laboratory. Experiments involving different systems with added liquids other than water are reported briefly in this note pending a more detailed investigation.

A thoroughly dried powder of "hydrophilic" surface properties, such as titanium dioxide, may be dispersed in a non-polar hydrocarbon oil and maintained in a deflocculated state provided the system is kept free of moisture. It was observed that immiscible polar compounds other than water, when added in small relative quantities, cause flocculation of the dispersed particles. Experiments showed marked differences in the extent of flocculation with different liquids. It was inferred that the immiscible reagent formed a bridge between adjacent particles and that the force necessary to separate the solid particles would be essentially that required to increase the liquid–liquid interface so formed. The tension at the interface between reagent and suspending liquid should, therefore, be related to the extent of flocculation which is measurable as the yield value of a bulk dispersion in a rotational viscometer.

In these experiments, titanium dioxide of a "water-dispersible" pigment grade was dried for ten days at 110° and ground on a three-roll mill in a mixture of equal parts by weight of a pharmaceutical mineral oil and isobutylene polymer to give a solids content of 30% by weight. The particle size (d_3) of the pigment was 0.18 μ as calculated from adsorption measurements with nitrogen at $-198°$ by the Brunauer–Emmett–Teller procedure. The viscosity of the oil mixture was 13.6 poises at 30°. Flocculating reagents (see caption to Fig. 1) were mixed with portions of this dispersion and the plastic viscosity and yield values were measured in absolute units on a rotational viscometer.[7] Interfacial tension measurements of the various added reagents against the dispersion medium were made on a Cenco–du Nouy tensiometer at 30°.

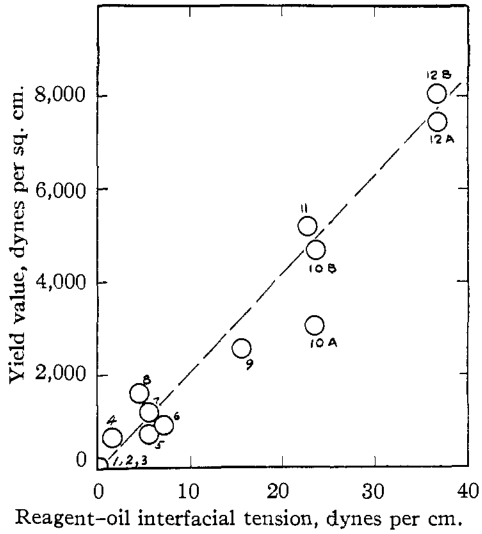

Fig. 1.—Variation of yield value of titanium dioxide-non-polar oil suspensions on addition of polar liquids: 1, control (no reagent); 2, octyl alcohol, 1.2%; 3, 2-ethylbutyl alcohol, 1.0%; 4, propyl alcohol, 3%; 5, 2,3-butanediol, 3%; 6, furfuryl alcohol, 3%; 7, methanol, 3%; 8, ethanol, 3%; 9, ethylene glycol, 3%; 10, glycerol, A, 2.2%, B, 0.6%; 11, formamide, 2.0%; 12, water, A, 0.6%, B, 1.4%. Water content calculated to form unimolecular film, 0.26%. (All percentages by weight on dispersed phase; all measurements made at 30°.)

The curve (Fig. 1) shows the unmistakable upward trend of yield value with increasing interfacial tension as predicted, despite difficulties in maintaining anhydrous conditions and in preventing evaporation of appreciably volatile reagents during experimental manipulation.

These experiments indicate that rigorous drying or removal of contaminants would serve to reduce the numerous cases of flocculation attributed to "poor wetting" of a solid surface by a liquid. Further, the plotted data suggest that surface-active agents promote deflocculation (and hence increase the mobility) of a solid–liquid system by lowering the liquid-liquid interfacial tension, thus weakening or removing the bridge between particles. In the opposite case, that of a solid with hydrophobic surface properties dispersed in a water-miscible liquid, the addition of a substance immiscible with the suspending liquid increases the extent of flocculation, as is implicit in several previously reported experiments[5] showing that certain reagents may increase the yield value of solid-in-liquid suspensions.

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