Four alloys of compositions immediately surrounding the $Mg_4Na_4Pb_3$ peak in the ternary diagram were analyzed thermally in order to define the compound region; the experimental data are given below.

THERMAL ANALYSIS OF $Mg_4Na_4Pb_3$ REGION OF Mg–Na–Pb SYSTEM

Atom %[a]			Temperature breaks					
			Primary		Secondary		Tertiary	
Mg	Na	Pb	Temp., °C.	Time, min.	Temp., °C.	Time, min.	Temp., °C.	Time, min.
36.36	36.36	27.27 ($Mg_4Na_4Pb_3$)	600.7	23	383.8	<1[b]		
37.50	37.50	25.00 ($Mg_3Na_3Pb_2$)	589.8	7	559.9	7		
35.00	35.00	30.00 ($Mg_7Na_7Pb_6$)	583.0	9	476.8	3	407.9	<1[b]
34.20	39.00	26.80	596.5	16	555.2	<1[b]	350.0	<1[b]
38.30	34.00	27.70	596.9	22	531.7	<1[b]	398.9	3

[a] The metals used were Dow extruded bar magnesium of over 99.9% purity, du Pont sodium and Asarco lead of over 99.95% purity. [b] These small breaks are of doubtful validity.

The cooling curve for $Mg_4Na_4Pb_3$ showed a long, flat, sharp break at 600.7° and a very short break at 383.8°. The latter is attributed to a slight deviation from theoretical in the composition of the alloy. The four alloys surrounding the compound had lower initial breaks of shorter duration and, in all but one instance, more definite secondary breaks.

The compound $Mg_4Na_4Pb_3$ is a brittle alloy, gray in color, and of more pronounced crystallinity than the other alloys in its region. Moist air corrodes the compound rapidly. It reacts vigorously with water or acid; in the reaction with acid, the evolved hydrogen is ignited. The approximate density of the alloy is 4.5–4.7 g./cc.

The compound was difficult to polish because of rapid oxidation, even when immersed in mineral oil. Microscopic examination of a polished surface disclosed three phases, with the main phase of $Mg_4Na_4Pb_3$ present to an extent greater than 99%.

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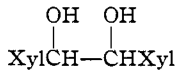
A Synthesis of Di-(2,4-xylyl)-acetic Acid

BY REYNOLD C. FUSON AND M. L. WARD[1]

In a search for a convenient route to di-(2,4-xylyl)-acetaldehyde and the corresponding acid an attempt was made to reduce 2,4-xylaldehyde bimolecularly and to dehydrate the resulting hydrobenzoin (I). It is interesting that this relatively unhindered aldehyde did undergo bimolecular reduction with the binary mixture, Mg-MgI_2.[2] The product proved to be a mixture of the two glycols previously reported by Law.[3] Dehydration of the hydroxyloin, however, yielded a compound which was not the desired aldehyde and which appeared to be the desoxyxyloin (II).



$$\overset{OH}{XylCH}-\overset{OH}{CHXyl}$$

I

XylCOCH$_2$Xyl

II

A synthesis of the dixylylacetic acid was carried out according to the scheme

$$XylMgBr \xrightarrow{HCO_2C_2H_5} (Xyl)_2CHOH \longrightarrow (Xyl)_2CHCl \longrightarrow (Xyl)_2CHCN \longrightarrow (Xyl)_2CHCO_2H$$

Experimental

Bimolecular Reduction of 2,4-Xylaldehyde.—The mixture obtained by treatment of the aldehyde with the binary mixture, Mg-MgI_2, was separated by the use of hot high-boiling petroleum ether, which dissolved the isohydroxyloin whereas the hydroxyloin was almost completely insoluble. The isohydroxyloin, after repeated recrystallization, melted at 129–130°. The hydroxyloin melted at 153–154°. A by-product was 2,4-xylic acid, m. p. 123–124°.[4]

Another by-product, isolated from the hydroxyloin fraction and crystallized from methanol, melted at 172–173°.

Anal. Calcd. for $C_{36}H_{42}O_4$: C, 80.26; H, 7.86. Found: C, 80.19; H, 8.28.

This compound was a bimolecular derivative and appeared to be a glycol; it formed an **acetate**, which after recrystallization from methanol melted at 126–127°.

Anal. Calcd. for $C_{44}H_{50}O_8$: C, 74.76; H, 7.13. Found: C, 74.71; H, 7.55.

The **acetate** of the hydroxyloin, purified by recrystallization from methanol, melted at 105–106°.

Anal. Calcd. for $C_{22}H_{26}O_4$: C, 74.55; H, 7.39. Found: C, 74.75; H, 7.39.

Reduction of Hydro-2,4-xyloin. (a) With Phosphorus and Iodine.—A mixture of 0.2 g. of hydro-2,4-xyloin, 0.3 g. of iodine, 0.6 g. of red phosphorus and 30 ml. of glacial acetic acid was heated under reflux for twenty-four hours and poured into water containing a small amount of sodium sulfite. The **1,2-di-(2,4-xylyl)-ethylene,** isolated by conventional methods, was recrystallized from methanol; m. p. 108–109.5°.

Anal. Calcd. for $C_{18}H_{20}$: C, 91.47; H, 8.53. Found: C, 91.48; H, 8.73.

(b) **With Hydrogen Iodide.**—A mixture of 0.3 g. of hydro-2,4-xyloin, 40 ml. of glacial acetic acid and 10 ml. of hydriodic acid (sp. gr. 1.50) was heated on a steam-bath for twelve hours. The solution developed a deep red color and droplets of oil appeared on the surface. The mixture was poured into water and the organic product taken up in ether. The **1,2-di-(2,4-xylyl)-ethane,** remaining after removal of the solvent by distillation, was purified by recrystallization from methanol; m. p. 71–72°.

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

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(1) Abbott Fellow, 1941–1942.

(2) Gomberg and Bachmann, THIS JOURNAL, **49**, 236 (1927); **52**, 4967 (1930).

(3) Law, *J. Chem. Soc.*, 748 (1907).

(4) Auwers and Kockritz, *Ann.*, **352**, 288 (1907).

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).

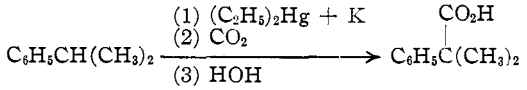
(6) Reid, THIS JOURNAL, **61**, 3238 (1939).

(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.



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

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