thallium is 147°, and distillation should be carried out at reduced pressure to avoid explosive decomposition. Some other physical, and some chemical properties are described.

AMES, IOWA. RECEIVED[14] DECEMBER 31, 1945

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[14] Original manuscript received November 16, 1942.

NOTES

Iodinated Dialkylaminoalkyl Pyridyl Ethers

BY ALFRED BURGER AND MARIE S. BAILEY

The substitution of the hydroxypyridine for hydroxyphenyl groups in halogenated derivatives of these ring systems has proved a valuable lead in improving bactericidal properties in a number of cases. We hoped, therefore, that replacement of the benzene ring in certain tuberculostatic halogenated dialkylaminoalkyl phenyl ethers[1] by pyridine would produce more highly active compounds. The few examples reported below did not support this expectation; none of the derivatives was tuberculostatic *in vitro*. An analogous basic ether of 5,7-diiodo-8-hydroxyquinoline, as well as 2,5-diiodo-6-hydroxy-nicotinic acid were also inactive.

Experimental

Diiodo-3-hydroxypyridine and triiodo-3-hydroxypyridine were prepared by the method of Binz and Maier-Bode.[2] Both phenols were methylated with diazomethane in ether–methanol solution.

Diiodo-3-methoxypyridine, obtained as colorless shiny crystals in a yield of 90%, melted at 100.5–101°.

Anal. Calcd. for $C_6H_5I_2NO$: N, 3.88. Found: N, 3.88.

Triiodo-3-methoxypyridine crystallized from dilute methanol as colorless, shiny needles, m. p. 113°. The yield was 99%.

Anal. Calcd. for $C_6H_4I_3NO$: N, 2.89. Found: N, 2.73.

2,5-Diiodo-6-hydroxynicotinic Acid.—A solution of 8.15 g. of iodine and 9 g. of potassium iodide in 20 cc. of water was added dropwise to a hot mechanically stirred solution of 10 g. of 6-hydroxynicotinic acid[3] in 125 cc. of 20% ammonium hydroxide. The reaction mixture was filtered from a greenish precipitate, and the filtrate acidified with acetic acid. The resulting brown precipitate was recrystallized three times from a 1:1 mixture of dioxane and ethanol. The shiny yellow needles melted at 242–249° (dec.).

Anal. Calcd. for $C_6H_3I_2NO_3$: N, 3.57. Found: N, 3.82.

Diiodo-3-(2-diethylaminoethoxy)-pyridine.—One and eight-tenths grams of diiodo-3-hydroxypyridine was dissolved in a mechanically stirred solution of 0.07 g. of sodium in 20 cc. of methanol. A solution of diethylaminoethyl chloride, prepared by dissolving 1 g. of diethylaminoethyl chloride hydrochloride in a solution of 0.1 g. of sodium in 10 cc. of methanol, was added, and the mixture refluxed for eighteen hours. The solvent was removed under reduced pressure, the oil dissolved in 75 cc. of ether, and washed with two 35-cc. portions of dilute sodium hydroxide solution and then with water. The ether solution was dried over anhydrous sodium sulfate, the ether distilled, and the residual oil converted to its **dihydrochloride** in acetone solution. Two recrystallizations from methanol furnished a colorless salt of m. p. 204–205°. The yield was 0.7 g. (26%).

Anal. Calcd. for $C_{11}H_{16}I_2N_2O \cdot 2HCl$: N, 5.40. Found: N, 5.50.

Diiodo-3-[(2-methylpiperidino)-3-propoxy]-pyridine Dihydrochloride was prepared in an analogous manner, using a 30% excess of 3-(2-methylpiperidino)-propyl chloride hydrochloride, and the corresponding amounts of the other reagents. The salt, obtained in a yield of 31% after crystallization from methanol, melted at 129–129.5°.

Anal. Calcd. for $C_{14}H_{20}I_2N_2O \cdot 2HCl$: N, 5.08. Found: N, 5.23.

5,7-Diiodo-8-[3-(2-methylpiperidino)-propoxy]-quinoline.—To a mechanically stirred solution of 0.6 g. of sodium in 20 cc. of methanol and 100 cc. of dioxane was added 5 g. of 5,7-diiodo-8-hydroxyquinoline and 3.25 g. of 3-(2-methylpiperidino)-propyl chloride. After boiling under reflux for nine hours, the mixture was worked up in the customary manner. The dihydrochloride crystallized from benzene and melted at 127–128.5°. The yield was 0.9 g. (11.4%).

Anal. Calcd. for $C_{18}H_{22}I_2N_2O \cdot 2HCl$: N, 4.59. Found: N, 4.58.

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UNIVERSITY OF VIRGINIA
CHARLOTTESVILLE, VIRGINIA
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[1] Burger, Wilson, Brindley and Bernheim, THIS JOURNAL, **67**, 1416 (1945).

[2] Binz and Maier-Bode, *Z. angew. Chem.*, **49**, 486 (1936).

[3] We are indebted to Dr. W. A. Lott for this material.

The Intermetallic Compound $Mg_4Na_4Pb_3$

BY GEORGE CALINGAERT, HYMIN SHAPIRO AND IVAR T. KROHN

In the course of a thermal investigation of the ternary system Mg–Na–Pb, the alloy $Mg_4Na_4Pb_3$ was found to be a compound with an open maximum. Melts were made in 200-g. batches under an atmosphere of nitrogen in a closed iron bomb fitted with a thermocouple well. The bomb was held at 725° for forty-five minutes with intermittent shaking. The alloy was then allowed to cool at the constant rate of 1° per minute, the rate of cooling being controlled by reduction of the heat input through a calibrated rheostat system. Temperature measurements were made on a Leeds and Northrup K-2 potentiometer, using thermocouples calibrated against the freezing point of lead. The cooling curves were interpreted after the manner of Tammann.[1]

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[1] Tammann, "A Textbook of Metallography," The Chemical Catalog Co., Inc., New York, 1925, p. 181.

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%.

CHEMICAL RESEARCH LABORATORY
ETHYL CORPORATION
DETROIT, MICHIGAN

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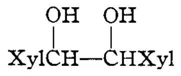
A Synthesis of Di-(2,4-xylyl)-acetic Acid

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, $Mg\text{-}MgI_2$.[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).



$$\overset{OH}{XylCH}\text{—}\overset{OH}{CHXyl}$$

I

$XylCOCH_2Xyl$

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, $Mg\text{–}MgI_2$, 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).