A New Synthesis of 6-Methyl-3-pyridinol

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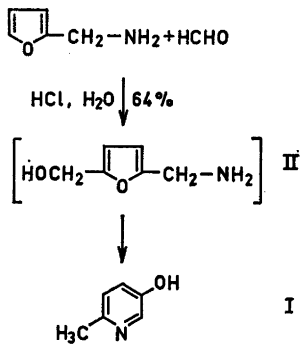
6-Methyl-3-pyridinol (I) has been prepared by interaction of furfurylamine and formaldehyde in acid aqueous solution (yield 64 %). Since it is known that 2-aminomethyl-5-hydroxymethyl-furan (II) under similar reaction conditions is transformed into I (yield 88 %) [1] it is reasonable to assume that II, or its equivalent, is an intermediate in the formation of I from furfurylamine and formaldehyde.



Experimental. Furfurylamine (97 g, 1.00 mole), and then 37 % formaldehyde solution (100 g, 1.23 mole) are added to a mixture of concentrated hydrochloric acid (230 ml) and water (325 ml) in such a way that the temperature does not exceed 0°. 3 N Hydrochloric acid (100 ml) is heated under reflux in a 1 liter flask fitted with a stirrer. The above solution of furfurylamine hydrochloride, formaldehyde and hydrochloric acid is added dropwise into this flask (4 h). During addition the reaction mixture is kept under gentle reflux, while the addend is kept below 0°. The reaction is complete, when all has been added. The mixture is cooled to about 80° and brought to pH 7.5–8.0 by cautious addition of sodium hydroxide pellets (about 110 g). The reaction product, which separates in a crude form on neutralization, may be isolated pure by continuous extraction with ether. The yield is about 70 g (64 %) of analytically pure product melting at 168–170° (Hershberg app., corr.) (Ref. 1 m.p. 169–171°).

1. Elming, N. and Clauson-Kaas, N. *Acta Chem. Scand.* **10** (1956) 1603.

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The Crystal Structure of $IrAl_3$

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In the course of phase analysis and crystal structure studies on the iridium-aluminium system a phase with the composition $IrAl_3$ has been studied.

A sample of $IrAl_3$ was prepared by arc-melting a mixture of iridium powder (L. Light & Co; about 99.98 %) and aluminium (E. Merck AG, at least 99.99 %) in

Table 1. The Guinier powder pattern of $IrAl_3$ ($CuK\alpha_1$ radiation).

hkl	$\sin^2\theta_{obs}$	$\sin^2\theta_{calc}$	I_{obs}	I_{calc}
002	0.03946	0.03945	st	72.3
100	0.04389	0.04387	st	52.3
101	0.05370	0.05374	vst	160.9
102	0.08325	0.08332	w	9.5
110	0.13161	0.13162	st	96.5
103	0.13258	0.13263	vst	131.2
004	0.15774	0.15779	vw	15.3
112	0.17115	0.17109	st	61.4
200	0.17555	0.17549	vw	8.2
201	0.18528	0.18535	m	34.0
104	0.20164	0.20167	vvw	5.7
202	0.21491	0.21494	vvw	3.1
203	0.26428	0.26425	m	54.4
114	0.28931	0.28941	m	46.1
105	0.29039	0.29042	vw	15.8
210	0.30700	0.30711	vw	9.2
211	0.31692	0.31697	m	41.4
204	—	0.33328	vvw	3.7
212	—	0.34656	vvw	4.4
006	0.35517	0.35503	w	11.8

an argon atmosphere. A slight excess of aluminium was used in order to counterbalance the loss by vaporization of this metal. The X-ray powder pattern showed the product to be a single phase.

Single crystals of $IrAl_3$ were obtained from the crushed melt. The Weissenberg data showed hexagonal symmetry and the unit-cell dimensions derived from a Guinier photograph (*cf.* Table 1) were:

$$a = 4.246 \text{ Å}, \quad c = 7.756 \text{ Å}$$

The single-crystal data were collected along an a-axis using CuK radiation. The multiple film technique was used and the intensities were estimated visually. The data obtained showed $IrAl_3$ to have a $D0_{18}$-type of structure. In this type of structure there is only one atomic parameter to be refined and this was done from successive ϱ_o and ϱ_c syntheses based on the $h0l$ reflexions. The following structure was thus derived:

Unit cell content: $2IrAl_3$
Space group: $P6_3/mmc$ (No. 194)

Ir in $2c$ $\frac{1}{3},\frac{2}{3},\frac{1}{4}$; $\frac{2}{3},\frac{1}{3},\frac{3}{4}$
Al_1 in $2b$ $0,0,\frac{1}{4}$, ; $0,0,\frac{3}{4}$
Al_2 in $4f$ $\frac{1}{3},\frac{2}{3},z = 0.575$; $\frac{2}{3},\frac{1}{3},\bar{z}$; $\frac{2}{3},\frac{1}{3},\frac{1}{2}+z$; $\frac{1}{3},\frac{2}{3},\frac{1}{2}-z$

Table 1 gives a comparison between calculated and observed powder intensity data.

The interatomic distances are given in Table 2. The environment of iridium consists of eleven aluminium atoms at distances between 2.45 and 2.80 Å and the average distance is 2.65 Å. These distances may be compared to the Os—Al distances in Os_4Al_{13}.[1] In this structure the Os—Al distances are in the range 2.46—2.86 Å and there are two kinds of osmium atoms. One has eleven aluminium neighbours at an average distance of 2.65 Å and the other ten at an average distance of 2.64 Å. Those average distances are thus practically the same in $IrAl_3$ and Os_4Al_{13} and this is in concordance with the very similar metallic radii found in the pure elements (r_{Os} = 1.353 Å and r_{Ir} = 1.357 Å).

Table 2. Interatomic distances in $IrAl_3$.

Atom	Neighbour	C.N.	Distance(Å)
Ir	Al_1	3	2.45
	Al_2	2	2.52
	Al_2	6	2.80
Al_1	Ir	3	2.45
	Al_2	6	2.80
Al_2	Ir	1	2.52
	Ir	3	2.80
	Al_1	3	2.80
	Al_2	1	2.71
	Al_2	3	2.71

The arc-melted $IrAl_3$ sample was also studied at lower temperatures by heat treatments in evacuated silica tubes followed by quenching in water. The $D0_{18}$ phase was thus found to be retained in specimens quenched from 950°C but not in such that were quenched from 850°C. The stability region of $IrAl_3$ ($D0_{18}$-type) obviously extends from approximately 900°C upwards.

Further studies on phases of this system are in progress.

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1. Edshammar, L.-E. *Acta Chem. Scand.* **18** (1964) 2294.

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On the Conversion of Cholest-5-ene-3β,7α-diol to 7α-Hydroxycholest-4-en-3-one in Rat Liver Homogenates

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The first step in the degradation of cholesterol to cholic acid is a hydroxylation at position C-7 to yield cholest-5-ene-3β,7α-diol.[1,2] Cholest-5-ene-3β-,7α-diol in turn is converted into 7α,12α-dihydroxycholest-4-en-3-one either by means of the intermediary formation of 7α-hydroxycholest-4-en-3-one or of cholest-5-ene-3β,7α,12α-triol.[2-4] Recently, Hutton and Boyd [5] reported studies on the conversion of cholest-5-ene-3β,7α-diol into 7α-hydrox-