

be determined directly by radioactive assay, as in the case of a compound which resists purification, both A_0 and X can be calculated by carrying out a second dilution with subsequent radioactive assay of the purified product. The specific activity, A_2 , of the product after the second dilution is related to A_1 by the equation

$$A_2(D_1 + D_2 + X - S) = A_1(D_1 + X - S) \quad (3)$$

$$X = (A_2 D_2) / (A_1 - A_2) - (D_1 - S) \quad (4)$$

where D_2 is the amount of diluent added during the second dilution, and S is the weight of samples used for assay after the first dilution. The yield, X , may be obtained from equation (4), while equation (1) may be solved directly for A_0 .

During a recent synthesis of chrysene-5,6- C_{14}^{14} , a product was obtained which resisted all attempts at purification. This sample was used to test the double dilution method, since its specific activity in microcuries per millimole was known from that of a previous radioactive reactant. The data were as follows: D_1 , 98.8 mg.; D_2 950 mg.; S , 6.7 mg.; A_1 , 141.7 microcuries per millimole, and A_2 , 16.32 microcuries per millimole. From these values, the yield X , 31.6 mg., and A_0 , 586 microcuries per millimole, were calculated. The value A_0 , as determined from radioactive assay of the previous reactant, was 595 microcuries per millimole.

It is obvious that the radioactivities A_0 , A_1 and A_2 may be expressed per unit weight, or per mole of compound, since the molecular weight of chrysene is a constant factor in equations (1), (2), (3) and (4). The difference in molecular weights of the radioactive and normal chrysene may be neglected, since the relative amount of chrysene-5,6- C_{14}^{14} present in the mixtures is so small that this difference is less than the experimental error.⁶

Since the least accurate data used in these calculations are the micro assays, it is apparent that the value of X will become inaccurate unless $A_1 \gg A_2$ and $(D_1 - S)$ is as small as possible. Thus, maximum accuracy results when D_1 approaches zero, and equation (3) becomes equivalent to equation (1).

(6) For an excellent discussion of the theory of isotope dilution, see H. Gest, M. D. Kamen and J. M. Reiner, *Arch. Biochem.*, **12**, 273 (1947).

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The Crystal Structure of Ferric Bromide

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The crystal structure of ferric chloride has been studied by several investigators. According to Wooster¹ it may be assigned a rhombohedral unit cell of the DO_3 type; the corresponding hexagonal cell has the lattice constants $a = 5.9$ and $c = 17.26$ with six molecules. This is a layer type structure with hexagonal close packing of halogens analogous to bismuth triiodide (C_3^1). Recently, Geierberger² has reviewed the work of Wooster

(1) N. Wooster, *Z. Krist.*, **83**, 35 (1932).

(2) Karl Geierberger, *Z. anorg. Chem.*, **258**, 361 (1949).

and others and suggests that the cell constants should be revised to $a = 6.05$ and $c = 17.38$ to be consistent with powder pattern data and the observed density. The latter values are in better agreement with results obtained for $FeCl_3$ in conjunction with the present work. Twenty lines were observed on a powder pattern which were assigned indices with $a = 6.06$ and $c = 17.47$ with a mean deviation of the calculated d 's from those observed of 0.15% (maximum deviation 0.3%).

It has been found possible to correlate powder pattern data for ferric bromide by assuming a similar type structure. Copper $K\alpha$ radiation was used with independent samples of ferric bromide prepared in conjunction with equilibrium studies reported previously.³ The planes observed correspond very closely with those found for ferric chloride under similar experimental conditions, and with those reported by Klemm and Krose⁴ for $ScCl_3$, $TiCl_3$ and VCl_3 . The latter have been classified by them as possessing a ferric chloride type structure.

Observed interplanar spacings are given in Table I and compared with those calculated for a hexagonal cell with $a = 6.42$ and $c = 18.40$.

TABLE I
INTERPLANAR SPACINGS IN FERRIC BROMIDE

$d_{\text{obsd.}}$	Estimated rel. intensity	Index	$d_{\text{calcd.}}$
6.1 (?)	0.5	0 0 3	6.133
3.19 (?)	0.5	1 1 0	3.210
3.061	4	0 0 6	3.067
2.837	10	1 1 3	2.844
2.215	8	1 1 6	2.218
1.850	7	3 0 0	1.853
1.725	7	1 1 9	1.721
1.590	5	3 0 6	1.586
1.551	5	2 2 3	1.553
1.536	2	0 0 12	1.534
1.422	4	2 2 6	1.422
1.265	4	2 2 9	1.263
1.191	4	4 1 3	1.190
1.182	4	3 0 12	1.181
1.147	2	1 1 15	1.146
1.129	2	4 1 6	1.128
1.045	2	4 1 9	1.043
0.977	2	2 2 15	0.975
0.927	1	6 0 0	0.927

Other high order reflections consistent with these lattice constants were observed between 2 2 15 and 6 0 0 but have not been listed because of the relatively large uncertainty in measurement of the spacings. The mean deviation of the calculated d 's from those observed is 0.15%, neglecting the first two values which were of such low intensity and large spacing as to be somewhat uncertain.

Assuming that the octahedra are not distorted appreciably the following distances have been calculated and are compared with corresponding values for ferric chloride, using constants for the latter as found in this Laboratory.

(3) N. W. Gregory and B. A. Thackrey, *THIS JOURNAL*, **72**, 3176 (1950).

(4) W. Klemm and E. Krose, *Z. anorg. Chem.*, **253**, 218 (1947).

	Fe-X	X-X in the layers	X-X in adjacent layer
FeCl ₃	2.48	3.50	3.59
FeBr ₃	2.63	3.70	3.77

The X-X distance between adjacent layers is consistent with the accepted values for the crystal radii of the bromide and chloride ions⁵ (Cl⁻ = 1.81; Br⁻ = 1.95). Using the normal crystal radii of the halogens, the ferric ion has available a calculated volume of radius 0.67 in FeCl₃ and 0.68 in FeBr₃. In view of the fact that the halogens are pulled somewhat closer together within the layers by the metal ions and that the radius ratio indicates anion-anion contact, these values appear consistent with the reported ionic radius of 0.60 for ferric ion.⁵

The author would like to acknowledge the generous permission of Professor E. C. Lingafelter for the use of X-ray equipment.

(5) L. C. Pauling, "Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1942.

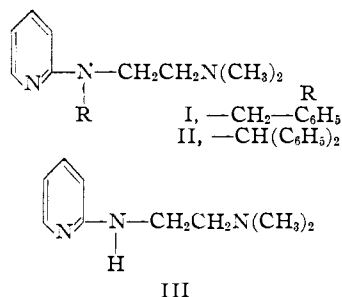
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Displacement of the Benzohydril Group by an Alkyl Group

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α -(Benzylamino)-pyridine condenses readily with 2-dimethylaminoethyl chloride in the presence of lithium amide to give the expected tertiary amine (I).² However, we have not yet succeeded in isolating II from an analogous reaction of α -(benzohydrilamino)-pyridine with the same chloride. Instead we find that the reaction mixture,

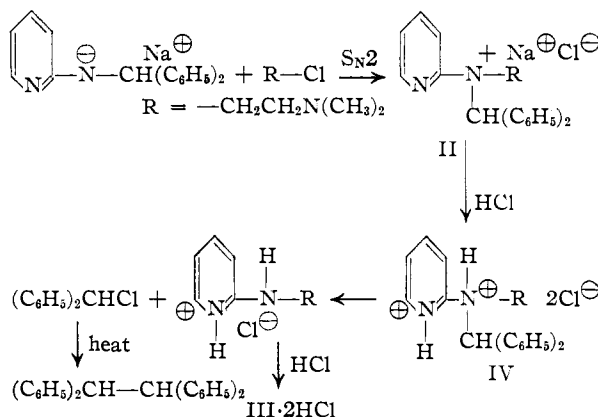


after treatment with hydrogen chloride, unexpectedly gives the dihydrochloride of III in 40% yield along with small amounts of benzohydril chloride³ and *sym*-tetraphenylethane.⁴ These results represent the over-all displacement of a benzohydril group by an alkyl group.

Experiments have been conducted in an attempt to establish a mechanism for the reaction. The sodamide catalyzed condensation between III and benzohydril bromide resulted in only unreacted III (54 to 74% recovery as the dihydrochloride), some benzohydril bromide and *sym*-

tetraphenylethane. Under the same experimental conditions and with the omission of III, benzohydril bromide decomposed to form a small amount of *sym*-tetraphenylethane.⁵ In another experiment it was established that treatment of α -(benzohydrilamino)-pyridine with sodamide will not displace the benzohydril group. Simply the sodium salt of the starting amine results, and 80% of the amine can be recovered.

With these experimental facts in mind, the following possible mechanism is proposed as an explanation of the unexpected formation of III during the attempted synthesis of II. In regard



to the decomposition of IV, it is not known whether there is a direct displacement on the benzohydril group by the chloride ion, or whether there is a spontaneous ionization of IV followed by the combination of the benzohydril carbonium ion with the chloride ion. Further, failure to isolate II or IV may be attributed to steric requirements. There may be insufficient space in II for the presence of the benzohydril group, which would cause it to be expelled as a carbonium ion, whereas there is sufficient space in I for the smaller benzyl group.

Experimental⁶

α -(Benzohydrilamino)-pyridine (V) Hydrobromide.—A mixture of 98.8 g. (0.4 mole) of benzohydril bromide and 37.6 g. (0.4 mole) of α -aminopyridine reacted very exothermically within a few minutes, and on cooling a reddish-brown resin formed. The resin was recrystallized once from absolute alcohol to give 77 g. (57% yield) of a light tan hydrobromide; m.p. 190–191°.⁷

The hydrochloride of V, prepared in the customary manner and recrystallized several times from alcohol, melted at 192–193°.⁸

Anal. Calcd. for C₁₃H₁₆N₂·HCl; C, 72.84; H, 5.78. Found: C, 72.62; H, 5.84.

Reaction between α -(Benzohydrilamino)-pyridine (V) and 2-Dimethylaminoethyl Chloride.—A mixture of V [prepared from 51.1 g. (0.15 mole) of the hydrobromide salt and 20% sodium hydroxide solution and extracted with benzene] and 6.6 g. (0.17 mole) of sodamide⁹ in 250 ml. of dry benzene was refluxed for forty-five minutes with the evolution of ammonia and the formation of a brown sodium salt of V. A volume of 100 ml. of benzene solution of 2-di-

(5) It is known from references 3 and 4 that gentle heating alone will convert benzohydril chloride to *sym*-tetraphenylethane.

(6) C and H analyses by Mr. Charles Beazley, Skokie, Illinois.

(7) Ssokow, *J. Gen. Chem. (U.S.S.R.)*, **10**, 1457 (1940); *Chem. Zentr.*, **112**, I, 2246 (1941), using a similar procedure, reported 195–196° but gave no yield.

(8) Ssokow reported 190–191°.

(9) Vaughn, Vogt and Nieuwland, *THIS JOURNAL*, **56**, 2121 (1934).

(1) Postdoctorate fellow, 1950–1951.

(2) Huttner, Djerassi, Beears, Mayer and Scholz, *THIS JOURNAL*, **68**, 1999 (1946).

(3) Huntress, "Organic Chlorine Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948, pp. 30–32.

(4) Anschütz, *Ann.*, **235**, 220 (1886).