| Halogen compound	Solvent	B. p., °C.	Catalyst	Product	Yield, %
2-Bromodibenzofuran	Triethylene glycol[a]	290	Cu–CuSO₄	Dibenzofuran	55
2,8-Dibromodibenzofuran	Triethylene glycol[a]	290	None	Dibenzofuran	50
2,8-Dibromodibenzothiophene	Triethylene glycol[a]	290	Cu–CuSO₄	Dibenzothiophene	54
2,8-Dibromodibenzofuran	Diethylene glycol[b]	244	None	Dibenzofuran and	22
				2-Bromodibenzofuran	10
2,8-Dibromodibenzofuran	Ethanol	78	None	Starting material	..

[a] Eastman Kodak Company. Technical grade.   [b] Eastman Kodak Company, Practical grade.

der our experimental conditions.[5] Omitting the copper–copper sulfate catalyst had little effect on the results. The results of these reactions are given in Table I.

It has been shown by Nef[6] and by Fry and co-workers[7] that alcohols and glycols react with alkali at elevated temperatures to yield hydrogen. While an explanation of the reductive debromination achieved in the present instance might be based on the direct action of the hydrogen produced, a more likely mechanism (reactions 2-5) would appear to be one similar to those recently proposed for the Meerwein–Ponndorf–Verley reduction[8,9,10] and the reduction of ketones by primary alcohols.[11] The authors consider reactions (3) and (4) to represent parts of a concerted process which occurs without the liberation of hydride ions as such. It is possible that an unidentified tarry residue, which was obtained whenever reductive debromination occurred, was formed by resinification of the aldehyde produced in accordance with reaction (5).

$$HOCH_2(CH_2OCH_2)_2CH_2OH + 2NaOH \longrightarrow$$
$$NaOCH_2(CH_2OCH_2)_2CH_2ONa + 2H_2O \quad (2)$$

$$NaOCH_2(CH_2OCH_2)_2CH_2ONa \longrightarrow$$
$$Na\overset{+}{O}CH(CH_2OCH_2)_2\overset{+}{C}HONa + 2H^- \quad (3)$$

$$+ 2H^- \longrightarrow$$

$$+ 2Br^- \quad (4)$$

$$2Br^- + NaO\overset{+}{C}H(CH_2OCH_2)_2\overset{+}{C}HONa \longrightarrow$$
$$2NaBr + CHO(CH_2OCH_2)_2CHO \quad (5)$$
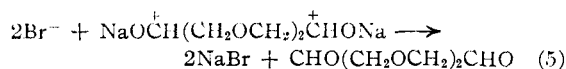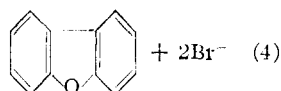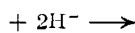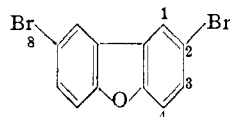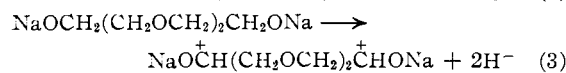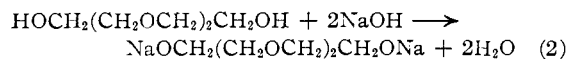
The ease with which the bromine atoms were replaced by hydrogen atoms suggests that the procedure described may be of use for the replacement of halogen by hydrogen in other aromatic compounds.

The authors are grateful to William Meikle for assistance.

Experimental

General Procedure.—In a typical reaction, 10 g. (0.0405 mole) of 2-bromodibenzofuran, 8.5 g. of sodium hydroxide,

3.0 g. of cupric sulfate, 10 g. of copper turnings, 1 g. of copper-bronze, and 75 ml. of triethylene glycol were placed in a 250-ml. two-necked flask equipped with air condenser and motor stirrer. The reaction mixture was slowly heated, with stirring, to reflux and maintained at this temperature for twelve hours. Vacuum distillation and addition of water to the distillate yielded 3.7 g. (55%) of product melting at 75-78°. Crystallization from dilute ethanol gave 3.1 g. (45%) of dibenzofuran; m. p. and mixed m. p. with an authentic sample was 83-84°.

In a further attempt to replace the halogen atom by an hydroxyl group, kerosene[12] was employed as the reaction medium, thus diminishing the probability of hydrogen formation. Only starting material was isolated.

(12) National Aniline and Chemical Company. British Patent 181,673. Dec. 14, 1921 [C. A., 16, 3762 (1922)].

DEPARTMENT OF CHEMISTRY
IOWA STATE COLLEGE
AMES, IOWA   RECEIVED FEBRUARY 20, 1950

The Use of Double Dilution for the Simultaneous Determination of Yield and Activity of Radioactive Compounds[1]

BY ROWLAND H. MAYOR[2] AND CLAIR J. COLLINS

Isotope dilution methods have been used extensively to determine yields in chemical and biological processes when the yield or purity is so low that it is impossible to isolate quantitatively the pure product.[3,4,5] When these methods are applied to the determination of the yield of a radioactive compound, an aliquot of the reaction mixture is diluted with a known amount of the inactive product, and a sample of the diluted compound is isolated and assayed for radioactivity. The measured specific activity, A_1, is related to the yield, X, in mg. by the equation

$$A_1(D_1 + X) = A_0X \quad (1)$$

In the usual case, where D_1 is very large with respect to X, the equation becomes

$$X = (A_1D_1)/A_0 \quad (2)$$

where A_0 is the specific activity of the undiluted compound, and D_1 is the weight of diluent added.

Using either equation (1) or (2) the amount of the product, X, may be calculated using the known D_1 and the determined A_1, if the specific activity, A_0, of the undiluted product is known either by an independent determination or by calculation from the known specific activity of the previous radioactive reactant.

When the quantity A_0 is not known and cannot

(5) Replacement of halogen by hydrogen in 1- and 2-haloanthra-quinones using an ethanol–sodium hydroxide solution was reported by Goldstein and Gardner, ibid., 56, 2130 (1934).

(6) Nef, Ann., 335, 310 (1904).

(7) (a) Fry, Schutze and Weitkamp, THIS JOURNAL, 46, 2268 (1924); (b) Fry and Schutze, ibid., 50, 1131 (1928).

(8) Jackman and Mills, Nature, 164, 789 (1949).

(9) Lutz and Gillespie, THIS JOURNAL, 72, 344 (1950).

(10) Doering and Young, ibid., 72, 631 (1950).

(11) Hargreaves and Owen, J. Chem. Soc., 750 (1947).

(1) This paper is based upon work performed for the Atomic Energy Commission at the Oak Ridge National Laboratory.

(2) Rhode Island State College, Kingston, Rhode Island.

(3) D. Rittenberg and G. L. Foster, J. Biol. Chem., 133, 737 (1940).

(4) A. S. Keston, S. Udenfriend and R. K. Cannan, THIS JOURNAL, 68, 1390 (1946); 71, 249 (1949).

(5) C. A. Ropp, ibid., 73, 4459 (1951).

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_1^{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_1^{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).

CHEMISTRY DIVISION
OAK RIDGE NATIONAL LAB.
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The Crystal Structure of Ferric Bromide

BY N. W. GREGORY

The crystal structure of ferric chloride has been studied by several investigators. According to Wooster[1] it may be assigned a rhombohedral unit cell of the DO_5 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, Geierberger[2] 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 Krose[4] 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

$d$obsd.	Estimated rel. intensity	Index	$d$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).