

The precipitated brick-orange dichloride (III) was removed by filtration and transferred quickly to a container for immediate storage in a refrigerator; the yield was 13–16 g (78–95%). At room temperature, spontaneous evolution of chlorine from the solid occurred. When a chloroform solution of the dichloride is allowed to sit exposed to the air at room temperature for a day, starting material can be recovered in good yield.

Attempted Hydrolysis of 1-(Dichloroiodo)apocamphane.—Approximately 1.2 g (3.7 mmoles) of 1-(dichloroiodo)apocamphane (III) was placed in a mortar at -5° , covered with 2 g of anhydrous sodium carbonate, and then ground with a pestle. With trituration there was added 0.5 ml of 5 M sodium hydroxide; a black paste resulted. When additional 2.5 ml of base was added, the color of the suspension changed to white. Water (20 ml) was added and grinding continued until all solid matter had gone into solution. Tests for iodide and chloride ions were positive; when the solution was extracted with ether and the ether evaporated, no residue of iodoso compound was obtained. The fate of the carbon skeleton was not pursued further.

9-Bromotriptycene.—Benzene, generated by the method of Friedman and Logullo²⁴ from 3.7 g (0.026 mole) of anthranilic acid and 3.5 g (0.030 mole) of isoamyl nitrite, was added to 6.2 g (0.024 mole) of 9-bromoanthracene in 80 ml of methylene chloride. A chromatographic separation yielded 3.5 g (44%) of crude, yellow product which was recrystallized from methylcyclohexane to give nearly white crystals: mp 250–254° (lit.²⁵ 246–248°); ν (CHCl₃) 3045, 2980, 1605, 1450 (doublet), 1285, 1155, 1035, 935, 840 (doublet) cm⁻¹.

Anal. Calcd for C₂₀H₁₃Br (333.0): C, 72.07; H, 3.94; Br, 23.99. Found: C, 72.30; H, 4.00; Br, 23.88.

Iodobenzene Dichloride and Triptycylithium.—A solution of 4.00 g (12 mmole) of 9-bromotriptycene in a mixture of 95 ml of benzene and 225 ml of ether was cooled to -50° . Over a period of 0.75 hr there was added with stirring under argon 9.5 ml (15.2 mmole) of 1.6 M *n*-butyllithium in hexane. The mixture was stirred for 0.5 hr at -50° , then for 1 hr at -70° and 3.25 g (11.8 mmole) of iodobenzene dichloride was added portionwise. The resulting mixture was stirred at -70° for 10 hr and then the reaction flask was allowed to stand in a refrigerator for 2 days. A suspended white solid (0.47 g) which was removed by filtration and washed with water proved to be 9-bromotriptycene, mp 253–255°. Addition of potassium iodide solution to the above aqueous filtrate precipitated 0.1 g of diphenyliodonium iodide, mp 178°, and nmr spectrum identical with that of an authentic sample. The ethereal residue which contained chlorobenzene and iodobenzene in roughly equal amounts on evaporation gave 2.1 g of a mixture of 9-bromotriptycene and 9-iodotriptycene. No unreacted iodobenzene dichloride could be isolated.

Registry No.—1-Iodoapocamphane, 933-27-7; 9-iodotriptycene, 15364-53-1; V, 15364-54-2; 9-bromotriptycene, 15364-55-3.

(24) L. Friedman and F. M. Logullo, *J. Amer. Chem. Soc.*, **85**, 1549 (1963).
(25) P. D. Bartlett, *et al.*, *ibid.*, **72**, 1003 (1950).

The Synthesis of Chlorobenzene-*d*₅ in a Radiofrequency Discharge

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Studies conducted in this laboratory dealing with the reactions of halobenzenes in an electrodeless radiofrequency (RF) discharge required the use of isotopically pure chlorobenzene-*d*₅. This material is not available commercially and a survey of the literature failed to uncover a method for its preparation. The synthesis of bromobenzene-*d*₅ has, however, been reported^{1,2} and this material is commercially available³

in 99.5% isotopic purity. Hence, a method for efficiently converting bromobenzene-*d*₅ into chlorobenzene-*d*₅ would be desirable.

Walling and Miller⁴ had converted bromobenzene into chlorobenzene by photolytic chlorination, and it seemed that this procedure might be suitable for the synthesis of chlorobenzene-*d*₅. However, the original procedure afforded low yields of chlorobenzene based on the amount of bromobenzene reacted. In an attempt to maximize the conversion of bromobenzene into chlorobenzene by this reaction, a wide range of chlorine to bromobenzene ratios were investigated in this laboratory. Repeated attempts to obtain chlorobenzene by this route afforded a maximum of 20% conversion based on the amount of bromobenzene used.

Work performed elsewhere,⁵ as well as in this laboratory, has demonstrated that aromatic carbon-halogen bonds can be broken with facility in an electrodeless RF discharge. Thus, it seemed reasonable that bromobenzene might be efficiently converted to chlorobenzene if it were passed through an RF discharge in the presence of chlorine. An attempt to effect this conversion by passing an equal mole ratio of chlorine gas and bromobenzene vapor through a 28-Mc electrodeless discharge afforded an approximately 1:1 mixture of chlorobenzene and bromobenzene together with trace amounts of benzene and higher boiling materials. The recovered products represented about 87% of the bromobenzene exposed to the discharge; the remainder undergoes complex competing reactions to give polymeric products and noncondensable gases. The over-all yield of chlorobenzene, based on the amount of bromobenzene reacted, is therefore approximately 45%.

The maximum conversion to chlorobenzene seems to occur with a 1:1 mole ratio of bromobenzene to chlorine. An investigation disclosed that higher chlorine-bromobenzene ratios resulted in the formation of a greater proportion of nonrecoverable products and a sharply increased percentage of benzene in the recovered material. For example, when a 7:1 ratio of chlorine to bromobenzene was used, only 43% of the reacted bromobenzene was converted to condensable materials; the remainder reacted to form polymeric materials and noncondensable gases. The condensable product was found to be a mixture of chlorobenzene and bromobenzene, together with a substantial amount of benzene. The over-all yield of chlorobenzene, based on the amount of bromobenzene reacted, was greatly reduced. These data are summarized in Table I.

Experiments in which bromobenzene-*d*₅ was used and the product mixture separated by preparative gas chromatography afforded chlorobenzene which was shown to be fully deuterated by mass spectrometry. Additionally, the recovered bromobenzene and benzene were also found to be fully deuterated.

The mechanism by which the presence of excess chlorine results in the formation of increased amounts

(1) R. I. Akawie, U. S. Atomic Commission NAA-SR-3043 (1958); see *Chem. Abstr.*, **53**, 11,295d (1959).

(2) B. Bak, J. N. Schoolery, and Y. A. Williams, *J. Mol. Spectr.*, **22**, 525 (1958).

(3) Stohler Isotope Chemicals, Rutherford, N. J. 07070.

(4) B. Miller and C. Walling, *J. Amer. Chem. Soc.*, **79**, 4187 (1957).

(5) J. K. Stille and C. E. Rix, *J. Org. Chem.*, **31**, 1591 (1966).

TABLE I
PRODUCTS FORMED FROM CHLORINE AND BROMOBENZENE
IN A RADIOFREQUENCY DISCHARGE

Mole ratio of Cl ₂ -C ₆ H ₅ Br	— % composition of material condensed at -78° ^a —			Higher boiling products
	C ₆ H ₅ Br	C ₆ H ₅ Cl	C ₆ H ₆	
1:1	50	49	1	0.5
7:1	44	33	23	Trace

^a Normalized to exclude polymeric deposits and noncondensable gases.

of benzene remains obscure at present. However, a free-radical process in which chlorine atoms abstract hydrogen from the aromatic ring to form HCl, which subsequently undergoes hydrogen abstraction by phenyl radicals to form benzene, seems likely. Further work is planned to investigate this possibility.

Experimental Section

A Heathkit Model TX-1 transmitter operating at a frequency of 28 Mc and an output of 100 w was used to supply power to the discharge tube. Power was coupled into the discharge tube, an 18-mm o.d. Pyrex tube, by an externally wound copper helix 2 cm in diameter and 11 cm long. The discharge tube wall temperature normally was approximately 30°.

In operation, the system was evacuated to <0.01 torr and then back filled with bromobenzene vapor and chlorine gas which were introduced through an inlet manifold-mixing chamber. The total pressure was adjusted to approximately 0.3 torr. Bromobenzene was bled through the discharge at a rate of 0.004 to 0.006 mole per hour and chlorine vapor was introduced at whatever rate was required to give the desired mole ratio.

Both analytical and preparative gas chromatography was conducted using SE-30 columns. The deuterium content of the discharge products was measured by mass spectrometry.

Bromobenzene-*d*₅ of 99.5% isotopic purity was obtained from Stohler Isotope Chemicals. Reagent grade chlorine was obtained from the Matheson Co.

Registry No.—Chlorobenzene-*d*₅, 3114-55-4.

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A Convenient Procedure for the Preparation of Low-Boiling Alcohols and Amines via Lithium Aluminum Hydride and Deuteride Reduction

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In order to facilitate the elucidation of the mechanisms of aprotic and protic diazotizations of aliphatic amines, it was necessary to prepare a series of deuterated amines and alcohols. The syntheses usually involved a LiAlH₄ or LiAlD₄ reduction of either a nitrile, acid, or ester. Since the products of these reductions were low boiling and water soluble, isola-

tion procedures usually recommended¹ were generally unsatisfactory. A procedure was developed which is efficient and convenient and is based on the use of high-boiling ether solvents as the reaction medium and high-boiling ether alcohols as product liberating reagents and isolation of product by distillation directly from the reaction mixture, a technique that heretofore has only been used in the preparation of labeled alcohols in a few isolated cases.²⁻⁶ The scope and limitations of this technique were examined in detail and are reported herein.

The technique was used successfully to prepare labeled and unlabeled amines and alcohols with boiling points up to 117° in yields (isolated) ranging from 50 to 90%. Larger scale reductions (1-2 moles of oxidant) generally gave better yields (80-90%), especially in the case of the low molecular weight amines.

The use of this technique for the preparation and isolation of amines has not been previously reported. It is more convenient and efficient than the classical methods of product work-up and isolation from complex hydride reductions.¹

All of the reductions listed in Table I were conducted in diethylene glycol diethyl ether. This solvent is usually satisfactory, however, some reductive cleavage⁷ occurs yielding ethanol, which can be an annoying product contaminant. This was first suspected in the reduction of 2,2,2-*d*₃-acetic acid, since the deuterium content of the ethyl alcohol obtained was approximately 6%-*d*₀, 2%-*d*₂, and 92%-*d*₃. This was verified when the reduction of propionic acid was conducted in diethylene glycol diethyl ether. The propanol obtained contained 4% ethanol. However, other solvents, such as diethylene glycol dibutyl ether or diglyme,⁸ can be used when necessary to avoid this problem.

Several limitations exist in the choice of the quenching alcohols. High boiling alcohols, such as octyl alcohol, are not satisfactory since insoluble soaps are formed which completely frustrate work-up. 1,2-Diols, *e.g.*, ethylene glycol, form insoluble gelatinous precipitates which effectively prevent complete hydride decomposition and product isolation. Monoalkyl ethers of ethylene and diethylene glycol, *e.g.*, *n*-butoxyethanol and diethylene glycol monoethyl ether, were found to be the most suitable.

Experimental Section

General Reaction Procedure.—The nitrile, ester, or acid (1 mol) was added dropwise (0.5-1 hr) at 5-70° (external cool-

(1) R. F. Nystrom and W. G. Brown, *J. Amer. Chem. Soc.*, **70**, 3738 (1948); *ibid.*, **69**, 1197 (1947).

(2) For example, reduction of carbon dioxide³ and acetic-1-C¹⁴ acid⁴ with LiAlH₄ was carried out in diethylene glycol diethyl ether and after addition of diethylene glycol monobutyl ether the alcohols (methanol and ethanol-1-C¹⁴) were distilled out from the reaction mixture. Similarly ethanol⁵ was prepared via LiAlH₄ reduction of acetic acid followed by quenching with β-phenoxyethanol and 1,1-*d*₂-propanol⁶ by reduction of phenyl propionate in triglyme (triethylene glycol dimethyl ether) followed by addition of benzyl alcohol.

(3) R. F. Nystrom, W. H. Yanko, and W. G. Brown, *J. Amer. Chem. Soc.*, **70**, 441 (1948).

(4) R. Ostwald, P. T. Adams, and B. M. Tolberts, *ibid.*, **74**, 2425 (1952).

(5) J. D. Cox and H. S. Turner, *J. Chem. Soc.*, 3176 (1950).

(6) R. L. Baird and A. A. Aboderin, *J. Amer. Chem. Soc.*, **86**, 252 (1964).

(7) Cleavage of ethers by LiAlH₄ has also been observed by others. *Cf.* ref 3 and 4 and J. D. Cox, H. S. Turner, and R. J. Warne, *J. Chem. Soc.*, 3167 (1950).

(8) These solvents are partially cleaved to butanol and methanol, respectively.