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

Mole ratio of Cl_2–C_6H_5Br	—% composition of material condensed at −78° [a]—			
	C_6H_5Br	C_6H_5Cl	C_6H_6	Higher boiling products
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

LESTER FRIEDMAN AND ANTHONY T. JUREWICZ

Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106

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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 $LiAlH_4$ or $LiAlD_4$ reduction of either a nitrile, acid, or ester. Since the products of these reductions were low boiling and water soluble, isolation procedures usually recommended[1] 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 cleavage[7] 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-

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(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 dioxide[3] and acetic-1-C^{14} acid[4] with $LiAlH_4$ was carried out in diethylene glycol diethyl ether and after addition of diethylene glycol monobutyl ether the alcohols (methanol and ethanol-1-C^{14}) were distilled out from the reaction mixture. Similarly ethanol[5] was prepared *via* $LiAlH_4$ reduction of acetic acid followed by quenching with β-phenoxyethanol and 1,1-d_2-propanol[6] 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).

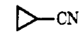
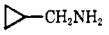
(6) R. L. Baird and A. A. Aboderin, *J. Amer. Chem. Soc.*, **86**, 252 (1964).

(7) Cleavage of ethers by $LiAlH_4$ 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.

TABLE I

ISOLATED YIELDS OF AMINES AND ALCOHOLS

Reactant	Moles	Reductant[a]	Product	% yield
CD_3CO_2D	1.0	$LiAlH_4$	CD_3CH_2OH	80–90[b]
$CH_3CH_2CO_2H$	0.1	$LiAlH_4$	$CH_3CH_2CH_2OH$	85[c]
$CH_3CD_2CO_2H$	0.26	$LiAlH_4$	$CH_3CD_2CH_2OH$	76
CH_3CD_2CN	0.11	$LiAlH_4$	$CH_3CD_2CH_2NH_2$	55
CD_3CH_2CN	0.64	$LiAlH_4$	$CD_3CH_2CH_2NH_2$	50
$(CH_3)_2CHCN$	0.12	$LiAlD_4$	$(CH_3)_2CHCD_2NH_2$	83
$(CH_3)_2CDCO_2CH_2CH_2OC_4H_9$	1.2	$LiAlH_4$	$(CH_3)_2CDCH_2OH$	78
$(CD_3)_2CDCN$	0.1	$LiAlH_4$	$(CD_3)_2CD—CH_2NH_2$	81
$CH_3CH_2CH_2CN$	0.24	$LiAlD_4$	$CH_3CH_2CH_2CD_2NH_2$	67
$CH_3CH_2CD_2CN$	0.11	$LiAlH_4$	$CH_3CH_2CD_2CH_2NH_2$	86
$CH_3CD_2CH_2CN$	0.09	$LiAlH_4$	$CH_3CD_2CH_2CH_2NH_2$	76
$CD_3CH_2CH_2CN$	0.13	$LiAlH_4$	$CD_3CH_2CH_2CH_2NH_2$	82
	1.0	$LiAlH_4$		75

[a] All reductions were effected in diethylene glycol diethyl ether and quenched with butoxyethanol or diethylene glycol monoethyl ether. [b] Contaminated with CH_3CH_2OH. [c] Contaminated with ~5% CH_3CH_2OH.

ing) to a stirred mixture of lithium aluminum hydride (or deuteride) (1 mole)[9] in diethylene glycol diethyl ether[10] (500 ml). The mixture was then heated for 1 hr at 100°. Hydrolysis with *n*-butoxyethanyl alcohol (360 g, 3 mol) was effected at 0–10°. A short distilling column was inserted and the product directly distilled.[11] The product was usually of sufficient purity for use in further chemical transformations. Further purification was accomplished by redistillation or in the case of amines, the amine hydrochloride was prepared.

Registry No.—Lithium aluminum hydride, 1302-30-3; lithium aluminum deuteride, 14128-54-2.

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(9) In all cases, reduction of nitriles, acids, or esters, 1 mole of complex hydride was used per mole of oxidant.

(10) The diethylene glycol diethyl ether was distilled over calcium hydride or preferably lithium aluminum hydride.

(11) This distillation requires elevated pot temperatures, probably as a result of hydrogen bonding of the product with the monoalkyl glycol ether or Lewis acid-base complexing with the complex metal alcoholate. It is recommended that a portion of material be collected above the boiling point of product (glpc check) and that this be redistilled in order to obtain the maximum yield.

Anomalies in the Acetylation of *o*- and *p*-Xylenes[1]

LESTER FRIEDMAN AND ROBERT KOCA

Department of Chemistry, Case Western Reserve University,
Cleveland, Ohio 44106

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In the course of another investigation it became necessary to prepare 3,4-dimethylacetophenone (**1**). The material prepared from the aluminum chloride-catalyzed reaction of acetic anhydride and *o*-xylene following the standard procedure[2,3] was unexpectedly found (*via* glpc analysis)[4] to be a two-component mixture of 3,4-dimethylacetophenone (**1**, 52%) and 2,4-dimethylacetophenone (**2**, 48%).

Acetyl chloride in various solvents has also been widely used to effect acetylation of aromatic hydrocarbons.[5] The general procedure[6] for acetylation using acetyl chloride is the addition of an equimolar mixture of acetyl chloride–aromatic hydrocarbon to a stirred mixture of 1 mol of aluminum chloride in carbon disulfide. Ferric chloride has also been used as the catalyst in this method.[7] In the acetic anhydride procedure,[2,3] the anhydride (1 mol) is added dropwise to a stirred mixture of the aromatic hydrocarbon (1.25 mol) and aluminum chloride (2.8 mol) in carbon disulfide. Another useful technique introduced by Baddeley[8] and later used extensively by Brown[9] for acetylation of the methylbenzenes involves the addition of a homogenous solution of a 1:1 molar complex of acetyl chloride–aluminum chloride in ethylene chloride to a solution of the aromatic hydrocarbon (1 mol) in ethylene chloride. Since 2,4-dimethylacetophenone (**2**) was a major product from the reaction of acetic anhydride with *o*-xylene, it was felt that this reaction should be investigated to determine its origin and that a general survey of acetylation procedures would be useful. The results of this investigation are presented in Table I.

The unexpected product **2** which occurs both from acetic anhydride acetylation (acetic anhydride addition) of *o*-xylene or *p*-xylene is not a result of isomerization of the acetophenones, but it does arise by prior isomerization of the *o*- or *p*-xylenes to *m*-xylene presumably through the more stable σ-complex of *m*-xylene.[10] This was demonstrated by running a series of reactions in which the acetic anhydride was present in catalytic amounts (Table II). Little or no 2,4-dimethylaceto-

(1) Financial support (Grant No. 1348-AL) from the Petroleum Research Fund is gratefully acknowledged.

(2) (a) C. R. Noller and R. Adams, *J. Amer. Chem. Soc.*, **46**, 1889 (1924); (b) R. Adams and C. R. Noller in "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1941, p 109.

(3) In fact 3,4-dimethylacetophenone was previously prepared by this method. *Cf.* W. P. Campbell and M. D. Soffer, *J. Amer. Chem. Soc.*, **64**, 417 (1942).

(4) The mixture could also be separated by fractional distillation. *Cf.* Experimental Section.

(5) P. H. Gore in "Friedel–Crafts and Related Reactions," Vol. III, Part 1, G. A. Olah, Ed., Interscience Publishers, Inc., New York, N. Y., 1964, Chapter XXXI.

(6) (a) C. F. H. Allen, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p 3. (b) A. Claus and R. Wollner, *Ber.*, **18**, 1856 (1885).

(7) (a) W. H. Perkin, Jr., and J. F. S. Stone, *J. Chem. Soc.*, **127**, 2275 (1925); (b) C. S. Marvel, J. H. Saunders, and C. G. Overberger, *J. Amer. Chem. Soc.*, **68**, 1085 (1946).

(8) G. Baddeley, *J. Chem. Soc., Suppl. 1*, S99 (1949).

(9) (a) H. C. Brown, G. Marino, and L. M. Stock, *J. Amer. Chem. Soc.*, **81**, 3310 (1959); (b) G. Marino and H. C. Brown, *ibid.*, **81**, 5929 (1959).

(10) (a) D. A. McCaulay, B. H. Shoemaker, and A. P. Lien, *Ind. Eng. Chem.*, **42**, 2103 (1950); (b) H. C. Brown and J. D. Brady, *J. Amer. Chem. Soc.*, **74**, 3570 (1952).