(4.81), 3.08 (4.15), and 322 (4.20); nmr (10% solution in F_3CCOOH) δ 8.2–7.4 (complex, aromatic H's), 4.35, 4.07, 3.68, 3.40 (estd 4 H, AB quartet with relatively intense inside peaks, aliphatic H's). The quartet arises from two equivalent pairs of methylene protons in which the protons of each pair have calculated δ 4.18 (1 H, d, $J_{gem} = 17$ Hz) and 3.57 ppm (1 H, d, $J_{gem} = 17$ Hz), respectively.

4,4-Dimethylhomophthalimide (1) with Phosphorus Oxychloride.—4,4-Dimethylhomophthalimide (1), mp 118–119°, was prepared from homophthalimide[5] by a method similar to one already described.[10] After crystallization from acetic acid–water (1:4), product was obtained in yields as high as 60%; ir (KBr) 3185, 3077, 1720, 1695, and 1605 cm^{-1}; uv max (6.0 × 10^{-5} M in 95% C_2H_5OH) 243 mμ (log ϵ 4.07), 282 (3.13), and 290 (3.17). A mixture of 5.0 g of the dimethyl compound 1 (0.027 mol) with 25 ml of phosphorus oxychloride was sealed in a glass tube and heated for 7.5 hr in an oil bath at 180 ±1°. Removal of excess reagent from the clear brown reaction mixture by distillation under reduced pressure left a residue, to which 40 ml of 95% ethanol was added. After cooling the mixture in an ice bath, the precipitate was collected, dried, and freed of acid by washing its benzene solution with several portions of dilute aqueous potassium hydroxide. When the product was brought out of benzene, 5.0 g (82%) of 1-chloro-3-chloromethyl-4-methylisoquinoline (2), mp 165–168°, was obtained. A sample for analysis, mp 169–170°, was prepared by further crystallization from the same solvent.

Anal. Calcd for $C_{11}H_9Cl_2N$: C, 58.43; H, 4.00. Found: C, 58.4; H, 4.0.

Dichloro compound 2 has been reported before with mp 165–166°,[1] 166°,[2] and 162–164°.[4]

When the reaction temperature was 170°, the yield of dichloro compound 2 was much lower, while at 210–220° only tar was obtained. With any given set of conditions, the yield of dichloro compound was lower when Merck and Co. "Reagent Grade" or Matheson Coleman and Bell phosphorus oxychloride (both colorless) was used than when J. T. Baker Chemical Co. "Analyzed Reagent" (slightly yellow) was used. Experiments with phosphorus oxychloride from a freshly opened bottle plus a few drops of concentrated hydrochloric acid showed no improvement in yield. Thus, we cannot support the suggestions that either hydrogen chloride or the partial hydrolysis products of phosphorus oxychloride are responsible.[11] Addition of a little lithium chloride to the reaction had very little effect.

The reported[12] high-yield conversion of homophthalimide to 1,3-dichloroisoquinoline by heating with benzenephosphonyl dichloride could be repeated without difficulty. However, experiments with 4,4-dimethylhomophthalimide (1) using 4–10 molar equiv of benzenephosphonyl dichloride at several temperatures ranging from 160–240° and for periods ranging from 1.5–96 hr gave no dichloro product 2.[13] Starting material was recovered at 160 and at 190°. One reaction at 240° gave small amounts of crystalline 3-chloromethyl-4-methylisocarbostyril, mp 251–254°.[4]

Registry No.—5, 6116-54-7; 6, 21371-76-6; 7, 2178-32-7; 13, 21347-41-1.

(10) S. Gabriel, *Chem. Ber.*, **19**, 2363 (1886); **20**, 1198 (1887).

(11) Jones[2] reported that old specimens of reagent gave better results and proposed that free acid accelerates the process. Others have noted that the effectiveness of phosphorus oxychloride in related processes depends on aging and exposure to air. *Cf.* H. E. Baumgarten, *J. Amer. Chem. Soc.*, **77**, 5109 (1955); A. Albert and W. Gledhill, *J. Soc. Chem. Ind.*, **64**, 169 (1945). H. R. Snyder and F. X. Werber [*J. Amer. Chem. Soc.*, **72**, 2962 (1950)] have suggested that polyphosphoric acid may be implicated in explaining the efficacy of "old" reagents. Marquardt and Nair[4] deliberately add some concentrated hydrochloric acid to their phosphorus oxychloride.

(12) M. M. Robison, *J. Amer. Chem. Soc.*, **80**, 5481 (1958).

(13) The experiments with benzenephosphonyl dichloride were performed by Gerald Katz.
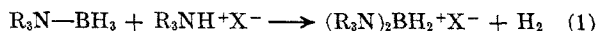
Heterocyclic Boronium Ions. The Reactions of Diamine Salts with Sodium Borohydride

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In recent years, several methods for synthesizing bis(amine)boronium ions, $(R_3N)_2BH_2^+$, have been reported.[1] One of the most versatile of these is the method of Miller and Muetterties involving the fusion of an amine–borane with an appropriate salt of a tertiary amine (eq 1). We now wish to report a

$$R_3N{-}BH_3 + R_3NH^+X^- \longrightarrow (R_3N)_2BH_2^+X^- + H_2 \quad (1)$$

modification of the Miller–Muetterties reaction which is particularly well suited for the preparation of heterocyclic boronium ions (2).

We have found that the fusion of equimolar amounts of the disalt of a 1,2- or 1,3-diamine (1) with sodium borohydride affords the corresponding five- or six-membered heterocyclic boronium ion (2) in reasonably good yields (eq 2). For example, the difluoroborate
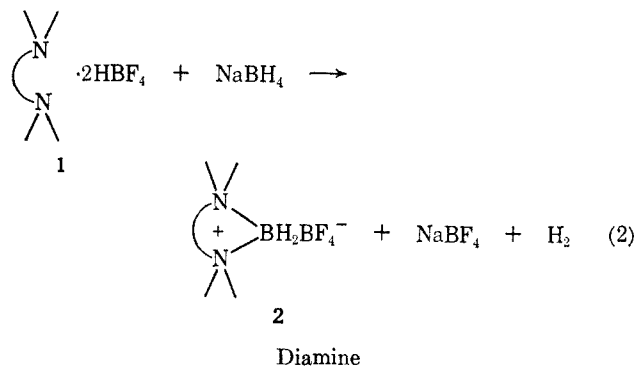
Diamine

a, N,N,N'N'-tetramethylethylenediamine	d, *trans*-N,N,N',N'-tetramethyl-1,2-diaminocyclohexane
b, N,N,N',N'-tetramethyl-1,2-propanediamine	e, N,N,N',N'-tetramethyl-*o*-phenylenediamine
c, N,N,N',N'-tetramethyl-1,3-propanediamine	f, N,N'-dimethylpiperazine

salt[2] of N,N,N',N'-tetramethylethylenediamine (1a) reacts with sodium borohydride[3] at 180–200° to yield 2a. The small amount (<5%) of diborane adduct of the diamine which is also formed can be readily separated from the other products by extraction with hot benzene. Experimentally it was found desirable to use a slight excess of borohydride to ensure that there is no unreacted disalt present in the product mixture, as it is not easily separated from the boronium salt. Separa-

(1) (a) J. E. Douglass, *J. Amer. Chem. Soc.*, **84**, 121 (1962); (b) H. Nöth, H. Beyer, and H. J. Vetter, *Ber.*, **97**, 110 (1964); (c) N. E. Miller and E. L. Muetterties, *J. Amer. Chem. Soc.*, **86**, 1033 (1964); (d) J. E. Douglass, *ibid.*, **86**, 5431 (1964); (e) G. E. Ryschkewitsch, *ibid.*, **89**, 3145 (1967); (f) J. E. Douglass, G. R. Roehrig, and O. H. Ma, *J. Organometal. Chem.*, **8**, 421 (1967); (g) K. C. Nainan and G. E. Ryschkewitsch, *J. Amer. Chem. Soc.*, **91**, 330 (1969).

(2) Fluoroborate salts were chosen because of their relatively low melting points and because the boronium fluoroborates are stable, easily crystallizable compounds.

(3) In general, lithium borohydride mixtures fuse at slightly lower temperatures and give slightly better yields; experimentally, however, it is more convenient to use the less sensitive sodium borohydride.

TABLE I

DIAMINE DIFLUOROBORATES (1) AND (DIAMINE)BORONIUM FLUOROBORATES (2)

Compound no.	Mp, °C	Molecular formula	Analyses, %							
			C Calcd	C Found	H Calcd	H Found	B Calcd	B Found	N Calcd	N Found
1a	180–181	$C_6H_{18}B_2F_8N_2$	24.69	24.96	6.22	6.33			9.60	9.96
1b	94–96	$C_7H_{20}B_2F_8N_2$	27.48	27.74	6.61	6.56			9.16	9.23
1c	176–178	$C_7H_{20}B_2F_8N_2$	27.48	27.60	6.61	6.69			9.16	9.27
1d	227–230	$C_{10}H_{24}B_2F_8N_2$	34.75	34.80	6.99	7.08			8.10	7.95
1e	230–232	$C_{10}H_{18}B_2F_8N_2$	35.34	35.67	5.34	5.44			8.24	8.17
1f	225–226	$C_6H_{16}B_2F_8N_2$	24.90	25.02	5.56	5.30			9.67	9.68
2a	260–262	$C_8H_{18}B_2F_4N_2$	33.40	33.20	8.40	8.34	10.03	10.17	12.99	13.03
2b	236–237	$C_7H_{20}B_2F_4N_2$	36.56	36.43	8.77	8.65	9.42	9.56	12.18	12.15
2c	284–285	$C_7H_{20}B_2F_4N_2$	36.56	36.48	8.77	8.67	9.42	9.62	12.18	12.22
2d	275–278	$C_{10}H_{24}B_2F_4N_2$	44.49	44.41	8.96	9.05	8.01	8.19	10.38	10.13
2e	210–212	$C_{10}H_{18}B_2F_4N_2$	45.51	45.39	6.87	7.01	8.19	8.37	10.61	10.57
2f	252–255	$C_8H_{16}B_2F_4N_2$	33.69	33.59	7.54	7.48	10.12	10.20	13.10	13.25

tion of 2 from sodium fluoroborate is readily accomplished by taking advantage of the greatly differing solubilities in cold water of the two reagents. Recrystallization of the crude product from hot water affords material of high purity in yields ranging from 42–78%.

Proof of structure rests upon elemental analyses (Table I) and infrared and proton magnetic resonance spectral data. Compounds **2a–f** show infrared absorption bands at *ca.* 2480 and 2350 cm⁻¹, characteristic of the BH_2 grouping. In their nmr spectra the N-methyl resonances fall 0.1–0.3 ppm upfield from their positions in the corresponding disalts, which is consistent with the assigned structures in which each nitrogen atom carries less than one net positive charge.

Experimental Section

Melting points were obtained on a calibrated Mel-Temp apparatus. Elemental analyses were performed by Galbraith Laboratories. Infrared spectra were obtained with a Perkin-Elmer Model 237 instrument and nmr spectra were determined with a Varian A-60A spectrometer. All of the diamines were commercially available with the exception of *trans*-N,N,N',N'-tetramethyl-1,2-diaminocyclohexane, which was prepared by the Eschweiler–Clark methylation of *trans*-1,2-diaminocyclohexane.[4] The latter was obtained by converting the commercial *cis–trans* mixture (Aldrich Chemical Co., *ca.* 40:60 according to gc analysis using a 0.125 in. × 6 ft column packed with 10% DC-710 on 60–80 mesh Chromosorb W precoated with 5% KOH) into the hexahydroquinoxaline derivative **3** by reaction with benzil, isolating the *trans* isomer by fractional crystallization, and then regenerating the diamine by hydrolysis with dilute hydrochloric acid.[5] Analysis by gc indicated a purity of >98%.

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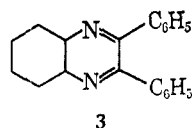
Fluoroborate Salts (1).—With the exception of **1e**, the difluoroborate salts were prepared using the following procedure. Aqueous 48% fluoroboric acid diluted with an equal volume of 95% alcohol was added slowly to a cooled solution of an equivalent amount of the diamine in five times its volume of ether. The precipitate which formed was filtered off, washed successively with alcohol and ether, and then recrystallized from ethanol–water. Salts **1b** and **1d** are somewhat hygroscopic and must be carefully dried before use in the fusion reaction.

The disalt of tetramethyl-*o*-phenylenediamine was prepared by adding the pure diamine to a 50% excess of 48% fluoroboric acid. The crystals which formed upon cooling were filtered off and

(4) F. Winternitz, M. Mousseron, and R. Dennilauler, *Bull. Soc. Chim. Fr.*, 382 (1956).

(5) A. I. Smith, U. S. Patent 3,163,675 (1964); *Chem. Abstr.*, **62**, 7656 (1964).

dried in a vacuum desiccator over sodium hydroxide. Every attempt at recrystallization led to the loss of 1 mol of acid to give the more stable monosalt.

See Table I for melting points and analytical data.

Fusion Experiments.—Powdered difluoroborate salt (20 mmol) and 21 mmol of sodium (or lithium) borohydride were placed in a 100-ml Fischer–Porter pressure tube, and after the tube was purged with dry nitrogen and sealed, the contents were thoroughly mixed. The tube was immersed in a sand bath and the temperature was gradually raised to 200° and held there for 4 hr. In the case of **1c**, the mixture had to be heated to 220° for 6 hr. After the mixture was allowed to cool to room temperature and solidify, the clump of material was pulverized with a glass rod and then triturated with two 20-ml portions of hot benzene to remove the small amount of diborane adduct formed. The residue was dissolved in 15 ml of hot water, and after a small amount of gray insoluble material was filtered off, the solution was cooled in an ice bath. The white crystals which formed were collected on a filter and washed successively with small portions of cold water, 95% ethanol, and ether. One recrystallization from hot water (or 50% aqueous ethanol) was usually sufficient to give material of high purity.

See Table I for melting points and analytical data.

Registry No.—Sodium borohydride, 1303-74-8; **1a,** 21330-41-6; **1b,** 21330-42-7; **1c,** 21330-43-8; **1d,** 21330-44-9; **1e,** 21330-45-0; **1f,** 21330-46-1; **2a,** 21330-47-2; **2b,** 21330-48-3; **2c,** 21330-49-4; **2d,** 21330-50-7; **2e,** 21330-51-8; **2f,** 21392-77-8.

A Method for Deoxygenation of Allylic and Benzylic Alcohols

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The replacement of an allylic or benzylic hydroxyl group by hydrogen using hydride displacement is sometimes complicated by difficulties in the conversion of the hydroxyl function into a suitable leaving group. The most commonly used activated derivatives, chlorides, bromides, and arylsulfonates, may be so reactive as to be hard to obtain in satisfactory purity or even unavailable. Such a situation was recently encoun-