TABLE I

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

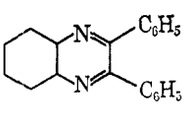
Compound no.	Mp, °C	Molecular formula	Analyses, % C Calcd	C Found	H Calcd	H Found	B Calcd	B Found	N Calcd	N Found
1a	180–181	$C_6H_{18}B_2F_8N_2$	24.69	24.96	6.22	6.33			9.60	9.96
1b	94–96	$C_7H_{20}B_2F_8N_2$	27.48	27.74	6.61	6.56			9.16	9.23
1c	176–178	$C_7H_{20}B_2F_8N_2$	27.48	27.60	6.61	6.69			9.16	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	$C_6H_{18}B_2F_4N_2$	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	$C_6H_{16}B_2F_4N_2$	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%.



3

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 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.

Acknowledgment.—Support of this work by the National Science Foundation (Grants GP-4487 and GP-7835) is gratefully acknowledged.

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A Method for Deoxygenation of Allylic and Benzylic Alcohols

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Received June 25, 1969

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-

TABLE I

$$ROH \xrightarrow{\text{reaction 1}} ROSO^-{}_3C_5H_5NH^+ \xrightarrow{\text{reaction 2}} RH \quad (1)$$
I II

Substrate I[a] (mmol)	Reaction 1: SO_3–py, mmol	Reaction 1: Time, hr[b]	Reaction 2: $LiAlH_4$, mmol	Reaction 2: THF, ml	Reaction 2: Time at 25°, hr[c]	Product II (yield, %)[d]
Geraniol (0.5)	0.75	3	3	5	3	*trans*-2-6-Dimethylocta-2,6-diene (98)
Farnesol (0.5)	0.75	3	3	5	3	*trans,trans*-2,6,10-Trimethyldodeca-2,6,10-triene (95)
Benzyl alcohol (1.0)	2.0	5	6	12	5	Toluene (75)
Indanol (0.5)	1.0	20	3	6	5	Indan (64) Indene (11)
Indanol (0.5)	1.0	20	3[e]	6	5	Indan (87) Indene (6)

[a] Concentration, 0.25 *M* in THF. [b] Temperature 0–3°. [c] After 1 hr at 0°. [d] Yield determined by vpc analysis using internal standard. [e] Also contained 1.0 mmol of $AlCl_3$.

tered in a total synthesis of the sesquiterpene sesquicarene.[1] For this case the problem was solved by using the pyridine–sulfur trioxide complex in tetrahydrofuran as the reagent for hydroxyl activation according to eq 1 and carrying out the reduction step without isolation of the intermediate sulfate monoester. In view of the effectiveness of the method in this case and its potential utility and convenience more generally, the application of the technique to other substrates has been investigated.

Four typical cases, geraniol, farnesol, benzyl alcohol, and 1-indanol, are reported here. In each case the alcohol was converted to the sulfate monoester in tetrahydrofuran at 0–3° with a moderate excess of pyridine–sulfur trioxide reagent, using thin layer chromatographic (tlc) analysis to determine the extent of reaction as a function of time. After complete esterification an excess of lithium aluminum hydride in tetrahydrofuran was added to effect reduction, leading to the experimental results which are summarized in Table I. It is noteworthy that in the cases of the allylic alcohols geraniol and farnesol, neither *cis–trans* isomerization nor allylic transposition was observed to a significant extent. In the case of 1-indanol a substantial amount of indene was obtained as a by-product. However, by the use of the reducing agent lithium aluminum hydride–aluminum chloride (3:1), the yield of this by-product was reduced to 6% and that of indan raised to 87%.

It is apparent that the method described here for the replacement of alcoholic OH by hydrogen is both efficient and convenient and that it is easily competitive even when conventional procedures[2] can be applied.

Experimental Section

General Method.—To a solution of the alcohol in tetrahydrofuran (THF) (freshly distilled from $LiAlH_4$) was added at 0° pyridine–sulfur trioxide complex (Aldrich), and the mixture was stirred at 0–3° for 3–20 hr until the reaction was complete. Then $LiAlH_4$ [or $LiAlH_4$–$AlCl_3$ (3:1)] in THF was added at 0°, and the mixture was stirred at 0° for 1 hr and then at 25° for 3–5 hr. After the excess of $LiAlH_4$ was destroyed with aqueous sodium hydroxide, ether and a measured amount of internal standard for vpc analysis were added. The precipitate was filtered, and the filtrate was used for vpc analysis. The products were identified by vpc and nmr comparison with known compounds.

Reduction of *trans,trans*-Farnesol.—To a solution of pure *trans,trans*-farnesol in 2 ml of THF was added at 0° 120 mg (0.75 mmol) of pyridine–sulfur trioxide complex, and the suspension was stirred at 0–3° for 3 hr. Analysis by tlc at this stage showed that the reaction was complete. A solution of 114 mg (3 mmol) of $LiAlH_4$ in 3 ml of THF was added at 0°, and then the mixture was stirred at 0° for 1 hr and at 25° for 3 hr. After 0.11 ml of water, 0.11 ml of 15% aqueous sodium hydroxide, and 0.33 ml of water were added at 0°, ether (20 ml) was added, and the precipitate was filtered and washed with ether. The filtrate and washings were concentrated at 60 mm, and the residue was purified by preparative tlc (silica gel, hexane, R_f 0.86) to give 98 mg (95%) of pure *trans,trans*-2,6,10-trimethyldodeca-2,6,10-triene, which was homogeneous by vpc analysis (10 ft, 10% Carbowax 20-M, 180°, 60 ml N_2, retention time 2.5 min). Bulb-to-bulb distillation [bp 160° (30 mm) (bath temp)] gave 90 mg (87.4%) of the triene as a colorless oil (spectra unchanged): molecular ion at *m/e* 206, main peak at *m/e* 69; nmr (CCl_4) δ 1.57 (s, 12 H, $CH_3C{=}C$), 1.63 (s, 3 H, $CH_3C{=}C$), 1.9–2.1 (multiplet, 8 H, $=CCH_2CH_2C=$), 4.8–5.2 (multiplet, 3 H, vinyl). An authentic sample was prepared by reaction of *trans,trans*-farnesyl bromide with lithium aluminum hydride.

Registry No.—Geraniol, 106-24-1; farnesol, 106-28-5; benzyl alcohol, 100-51-6; 1-indanol, 6351-10-6.

Acknowledgment.—This work was supported by the National Science Foundation.

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The Synthesis of 2-Amino-1-adamantanol

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Received April 11, 1969

The chemistry of adamantane has received considerable attention in recent years. Numerous 1-substituted and some 2-substituted derivatives have been prepared.[1] Herein we report the details of the first preparation of a simple 1,2-disubstituted adamantane. Since our preliminary communication[2] two other reports on this subject have appeared.[3,4]

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