tyldiphenylsilyl (*t*-BDPSi) ethers as exemplified in Table I (entry 8). Free hydroxyl groups likewise did not interfere with the overall transformation (entry 7).[17] Thus the chemoselectivity and predictable reactivity of dimethylboron bromide should make it a reagent of considerable value.

Finally, phosphine oxides and sulfones failed to react under the present reaction conditions.

In summary, dimethylboron bromide and 9-borabicyclo[3.3.1]nonyl bromide rapidly and smoothly deoxygenate dialkyl, aryl alkyl, and diaryl sulfoxides at low temperature under nonreducing and quasi-neutral conditions. As such and because of their well-established reactivity and chemoselectivity,[10] dimethylboron bromide, in particular, and 9-borabicyclo[3.3.1]nonyl bromide should be considered as reagents of choice for the reduction of sulfoxides. Boron tribromide, on the other hand, has certain limitations compared to the dialkylboron bromides in that it is significantly slower in the reduction of diaryl sulfoxides and it reacts with free alcohol groups. In many cases, however, it will serve as an excellent, inexpensive alternative for the reduction of sulfoxides to sulfides.

Experimental Section

General Methods. Crude products were purified by either bulb-to-bulb distillation using a Büchi GKR-50 distillation apparatus or by flash chromatography using 230–400-mesh silica gel (E. Merck). The purity of known compounds was ascertained by TLC using commercial silica gel plates (Analtech, Uniplate-Silica Gel GF) and by spectral means (IR, ^{1}H NMR).

Glassware and syringes were dried in an oven (120 °C) prior to use. Methylene chloride was distilled from CaH_2 and stored over 4-Å molecular sieves.

Dimethylboron bromide was purchased from the Alfa Division of the Ventron Corporation, or it was prepared as described previously.[10c] Care should be taken when manipulating neat dimethylboron bromide as it is *pyrophoric* when exposed to moist air. Solutions (1.0–1.5 M) of this reagent were prepared in dry CH_2Cl_2 and could be stored at −15 °C for several months without noticeable decomposition or handling problems. Solutions of 9-BBN-Br and BBr_3 in CH_2Cl_2 were purchased from the Aldrich Chemical Co.

a. Reduction of Sulfoxides by Me_2BBr. A typical example follows. A cold (−23 °C), stirred solution of diphenyl sulfoxide (2.0 mmol), in 7.1 mL of dry CH_2Cl_2, under argon, was saturated with propene for 5 min. A solution of dimethylboron bromide (1.72 M, 2.91 mL) in CH_2Cl_2 was then added dropwise. After $^1/_2$ h at −23 °C and 10 min at 0 °C the reaction mixture was quenched with 2 mL of saturated aqueous $NaHCO_3$ followed by 2 mL of 10% aqueous sodium thiosulfate. After 2 min, ether (50 mL) was added, the organic layer separated and washed with water (5 mL) and brine (5 mL), and dried over $MgSO_4$. Concentration and reconcentration from MeOH (5 mL) gave, after bulb-to-bulb distillation, pure diphenyl sulfide (94%).

b. Reduction of Sulfoxides by 9-BBN-Br. A typical example follows. A cold (−23 °C), stirred solution of di-*n*-butyl sulfoxide (2.0 mmol), in 5 mL of dry CH_2Cl_2, under argon, was saturated with propene for 5 min. A solution of 9-BBN-Br in CH_2Cl_2 (1.00 M, 5.0 mL) was then added dropwise and the reaction mixture was stirred at −23 °C for $^1/_2$ h and at 0 °C for 10 min. Quenching and workup as detailed above gave a pale yellow oil. Filtration through a short column of silica gel (10 g, elution solvent: hexane–ether, 98:2) gave after bulb-to-bulb distillation of the resultant oil, pure di-*n*-butyl sulfide (95%).

c. Reduction of Sulfoxides by BBr_3. A typical example follows. A cold (−23 °C), stirred solution of dibenzyl sulfoxide (2.0 mmol), in 8 mL of dry CH_2Cl_2, under argon, was saturated with propene for 5 min. A solution of boron tribromide in CH_2Cl_2 (1.00 M, 2.0 mL) was then added and the mixture was stirred at −23 °C for $^1/_2$ h and at 0 °C for 10 min. Quenching and workup as detailed above gave a pale yellow oil. Concentration and reconcentration from MeOH (5 mL) gave, after bulb-to-bulb distillation, pure dibenzyl sulfide (90%).

(17) For the preparation of this compound and the corresponding sulfide. See: Hamel, P. A.; Rokach, J. U.S. Patent 4 237 160.

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Registry No. $Bu_2S{=}O$, 2168-93-6; *sec*-$Bu_2S{=}O$, 13153-06-5; $PhCH_2S(O)Me$, 824-86-2; $(PhCH_2)_2S{=}O$, 621-08-9; $PhS(O)Me$, 1193-82-4; $Ph_2S{=}O$, 945-51-7; Bu_2S, 544-40-1; *sec*-Bu_2S, 626-26-6; $PhCH_2SMe$, 766-92-7; $(PhCH_2)_2S$, 538-74-9; PhSMe, 100-68-5; Ph_2S, 139-66-2; Me_2BBr, 5158-50-9; BBr, 10294-33-4; $HO(CH_2)_2SPh$, 699-12-7; 9-BBN-Br, 22086-45-9; 3-(bromomethyl)dibenzo[*b*,*f*]thiepin, 92055-55-5; 3-(hydroxymethyl)dibenzo[*b*,*f*]thiepin, 77167-91-0; 3-(hydroxymethyl)benzo[*b*,*f*]thiepin 5-oxide, 77167-92-1; 2-(phenylsulfinyl)ethyl 6-*O*-(*tert*-butyldiphenylsilyl)-2,3,4-tri-*O*-methyl-α-D-glucopyranoside (isomer 1), 92078-27-8; 2-(phenylsulfinyl)ethyl 6-*O*-(*tert*-butyldiphenylsilyl)-2,3,4-tri-*O*-methyl-α-D-glucopyranoside (isomer 2), 92078-28-9; 2-(phenylthio)ethyl 6-*O*-(*tert*-butyldiphenylsilyl)-2,3,4-tri-*O*-methyl-α-D-glucopyranoside, 92078-29-0; methyl 6-*O*-(*tert*-butyldiphenylsilyl)-2,3,4-tri-*O*-methyl-β-D-glucopyranside, 91928-35-7; 1-bromo-1-deoxy-6-*O*-(*tert*-butyldiphenylsilyl)-2,3,4-tri-*O*-methyl-D-glucopyranose, 91928-34-6.

Supplementary Material Available: Preparative details and full characterization data (IR, ^{1}H NMR, MS, chemical analyses, and melting points when applicable) for all new compounds (3 pages). Ordering information is given on any current masthead page.

Chiral Synthons from Arabinose. Preparation of 1,3-Diols and β-Benzyloxy Ketones

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Arabinose is readily available in both enantiomeric forms.[1] Accordingly, the development of arabinose derivatives for use as starting materials in enantiospecific synthesis is of special interest. Chiral 1,3-diol and β-hydroxy ketone units are present in many natural products of biological importance.[2] We now report the preparation of several enantiomerically pure compounds of this type, which have potential as chiral building blocks.

Benzyl 2,3-anhydro-β-D-ribopyranoside[3] (**1**) and the L-enantiomer (**2**) are easily prepared from D- and L-arabinose, respectively (Scheme I). Regiospecific, reductive opening of the oxirane ring was performed with sodium bis(2-methoxyethoxy)aluminum hydride (Red Al, Aldrich) to give benzyl 3-deoxy-β-D- and -L-*xylo*-pyranoside[4] (**3** and **4**). Viti[5] recently found that the use of tetrahydrofuran as solvent in Red Al reduction of epoxy alcohols gave a high 1,3:1,2 diol ratio (normally) > 100:1). However, only acyclic compounds were studied, where complexation of the aluminum hydride reagent with the

(1) Of the pentoses, D- and L-arabinose, D-ribose, and D-xylose are moderately priced.
(2) Masamune, S.; Choy, W. *Aldrichimica Acta* **1982**, *15*, 47.
(3) Garegg, P. *Acta Chem. Scand.* **1960**, *14*, 957.
(4) Methyl 3-deoxy-β-L-xylopyranoside has been prepared: Mukherjee, S.; Todd, A. R. *J. Chem. Soc.* **1947**, 969. *Note added in proof.* Methyl 3,6-dideoxy-α-D-*xylo*- and -α-L-*lyxo*-hexopyranoside were recently reported: Baer, H. H.; Astles, D. J. *Carbohydr. Res.* **1984**, *126*, 343.
(5) Viti, S. M. *Tetrahedron Lett.* **1982**, *23*, 4541.

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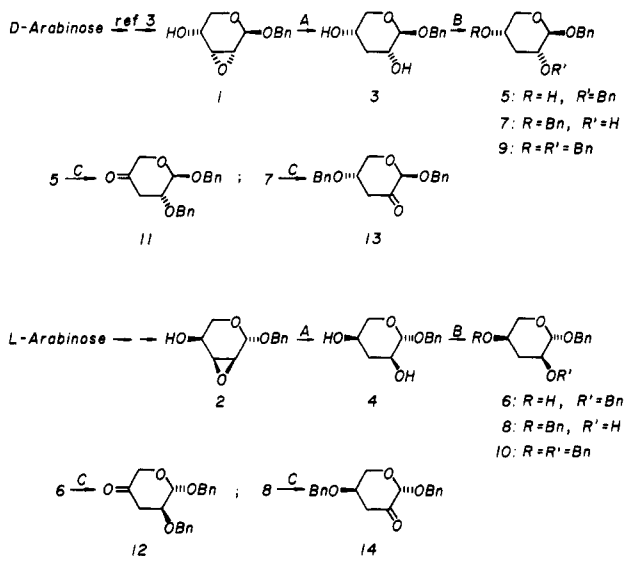
Table I. Yields and Physical Data for Compounds 1–14

product[a]	method	yield,[b] %	$[\alpha]^{20c}_D$, deg	mp, °C	R_f[d]	^{1}H NMR[e]	^{13}C NMR[f]
1	ref 3	58[g]	−63 (c 1.4)	76.5–78.0	0.27	5.04 (s)	93.5, 62.1, 61.6, 51.8
2		55[g]	+65 (c 1.1)	75.0–78.0	0.27	5.04 (s)	93.5, 62.1, 61.6, 51.8
3	A	68, 17[h]	−146 (c 1.9)	92.5–93.5	0.11	4.77 (s)	98.9, 66.9, 65.5, 64.7, 30.8
4	A	80, 16[h]	+144 (c 1.0)	92.5–94.0	0.11	4.77 (s)	98.9, 66.9, 65.5, 64.7, 30.8
5	B	33	−109 (c) 0.8)	oil	0.34	4.91 (d, J = 1.3 Hz)	96.0, 73.8, 65.1, 65.0, 28.6
6	B	38	+104 (c 1.2)	oil	0.34	4.91 (d, J = 1.3 Hz)	96.0, 73.8, 65.1, 65.0, 28.6
7	B	22	−119 (c 0.8)	49.0–50.0	0.54	4.78 (d, J = 2.2 Hz)	99.5, 72.2, 66.7, 60.8, 28.9
8	B	26	+118 (c 0.5)	48.0–50.0	0.54	4.72 (d, J = 2.2 Hz)	99.5, 72.2, 66.7, 60.8, 28.9
9	B	19	−35 (c 0.7)	36.0–37.0	0.70	4.54 (s)	103.1, 74.5, 71.6, 66.4, 33.9
10	B	16	+25 (c 0.9)	36.0–37.0	0.70	4.54 (s)	103.1, 74.5, 71.6, 66.4, 33.9
11[i]	C	82	−110 (c 0.8)	oil	0.63	5.01 (d, J = 2.5 Hz)	206.3, 97.1, 75.2, 67.6, 40.5
12	C	81	+116 (c 0.6)	oil	0.63	5.01 (d, J = 2.5 Hz)	206.3, 97.1, 75.2, 67.6, 40.5
13	C	60	−138 (c 1.0)	78.5–79.5	0.61	4.79 (s)	200.2, 98.6, 75.3, 60.8, 40.8
14[i]	C	79	+142 (c 0.6)	78.5–79.5	0.61	4.79 (s)	200.2, 98.6, 75.3, 60.8, 40.8

[a] Satisfactory analytical data were reported for all new crystalline compounds listed in the table. [b] Isolated yield. [c] In chloroform. [d] SiO_2, ethyl acetate:hexane, 1:1. [e] $CDCl_3$, Me_4Si, ppm, anomeric proton signal. [f] $CDCl_3$, Me_4Si, ppm, sugar ring carbon signals. [g] Overall yield from D- and L-arabinose, respectively. [h] Starting material recovered in reaction B. [i] IR (cm^{-1}) 11, 1740; 14, 1750.

Scheme I[a]



[a] A, Red Al/THF; B, $NaH/PhCH_2Cl/DMF$; C, $(COCl)_2/Me_2SO/(i\text{-}Pr)_2NEt/CH_2Cl_2$.

hydroxyl group could influence the stereoselective delivery of hydride.

Benzylation of **3** and **4** with 1 equiv of benzyl chloride gave **5**, **7**, **9**, and **6**, **8**, **10**, respectively. These compounds were easily separated by column chromatography (see R_f values in Table I). Oxidation[6] of **5**, **6**, **7**, and **8** gave the ketones **11**, **12**, **13**, and **14**, respectively, which are suitable starting materials for the synthesis of enantiomerically pure compounds. This aspect is currently under investigation in our laboratory.

Experimental Section

Method A. The epoxy alcohol **2** (11.1 g; 50.0 mmol) was dissolved in tetrahydrofuran (300 mL) and the solution was cooled (0 °C). Sodium bis(2-methoxyethoxy)aluminum hydride (Red Al, 79% in toluene, 45 mL, 150 mmol) was added dropwise under nitrogen and the mixture was stirred overnight. Water (30 mL) was added dropwise with cooling. Extraction with ether, drying (Na_2SO_4), and concentration gave **4** (11.2 g, 100%). Recrystallization from ethyl acetate:hexane gave pure **4** (8.97 g, 80%).

Method B. Sodium hydride (1.88 g, 37.5 mmol) was dissolved in dimethylformamide (175 mL) and the diol **4** (8.40 g, 37.5 mmol) was added. After 3 h, benzyl chloride (4.76 g, 37.5 mmol) was added dropwise (50–60 °C) and the mixture was stirred overnight and finally partitioned between dichloromethane and water. The organic phase was dried ($MgSO_4$), co-distilled with toluene, and subjected to chromatography (SiO_2, ethyl acetate:hexane, gradient 1:10 → 1:5 → 1:2 → ethyl acetate) to give **6**, **8**, **10**, and recovered **4** (see Table I).

Method C. Dimethyl sulfoxide (1.40 g, 17.9 mmol) in dichloromethane (10 mL) was added to a cooled (−60 °C) solution of oxalyl chloride (1.14 g, 8.98 mmol) in dichloromethane (15 mL). After 10 min, alcohol **8** (2.36 g, 7.52 mmol) in dichloromethane (10 mL) was added, followed by diisopropylethylamine (3.50 g, 37.6 mmol) after further 15 min. When the mixture had reached room temperature, water (20 mL) was added and the organic phase was washed with water, dried ($MgSO_4$), and concentrated to give crystalline **14** (in analogous preparations, **11** and **12** were isolated by column chromatography: SiO_2, ethyl acetate:hexane, 1:10).

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Registry No. 1, 67412-71-9; 2, 65359-87-7; 3, 56809-43-9; 4, 91632-08-5; 5, 91632-09-6; 6, 91632-10-9; 7, 91632-11-0; 8, 91632-12-1; 9, 91632-13-2; 10, 91632-14-3; 11, 91632-15-4; 12, 91632-16-5; 13, 91632-17-6; 14, 91632-18-7.

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Perfluoroalkyl Isocyanates: General Synthesis by the Pyrolysis of Disilyl Esters of Hydroxamic Acids†

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Trifluoromethyl isocyanate and other perfluoroalkyl isocyanates are usually prepared by the classical Curtius Rearrangement,[1] since routes based on the phosgenation of the unstable α-fluoroamines are not possible. However, the acyl azide precursors needed are capriciously explosive, and at least two investigators have been injured while trying to prepared trifluoromethyl isocyanate by this method. Recent work by us has demonstrated that 2-(trifluoromethyl)-1,3,4-dioxazol-2-one is another efficient intermediate to trifluoromethyl isocyanate, but this intermediate is also capriciously explosive.[2]

We now report a general, high yield method for preparing perfluoroalkyl isocyanates that is both safe and convenient. A modification of the Lossen rearrangement,[3]

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