benzo[*b*]thiophene[11]] in ether–benzene (50:50 ml) with cooling to maintain the temperature below 25°. The mixture was stirred in an atmosphere of nitrogen and heated under reflux for 4 hr and then poured onto cold aqueous NH_4Cl. The oily amine (1.7 g) was isolated, but since its hydrochloride could not be crystallized, the product was characterized as its hydrogen oxalate. The latter was prepared in ethanol and recrystallized from methanol to furnish 1.1 g (4%) of colorless needles, mp 179–181° dec.

Anal. Calcd for $C_{12}H_{15}NS \cdot C_2H_2O_4$: C, 56.9; H, 5.8; N, 4.7. Found: C, 57.1; H, 5.8; N, 4.9.

N,N-Dimethyl-2-(2-benzo[*b*]thienyl)ethylamine Hydrochloride.—A dry solution of 2-dimethylaminoethyl-1-chloroethane (0.2 mole) in toluene (100 ml) was added to 2-benzo[*b*]thienyllithium[12] [prepared from 13.7 g (0.1 mole) of benzo[*b*]thiophene and 0.2 mole of butyllithium] in ether (140 ml) at 10°. The mixture was stirred in an atmosphere of nitrogen and heated under reflux for 6 hr and then poured onto crushed ice. The amine (8.0 g of oil) was isolated and converted into its hydrochloride. Crystallization of the latter from 2-propanol yielded 4.9 g (20%) of colorless needles, mp 227–229°.

Anal. Calcd for $C_{12}H_{16}ClNS$: C, 59.6; H, 6.7; N, 5.8. Found: C, 59.5; H, 6.9; N, 5.7.

A pure sample of the **amine**, obtained by neutralization of the hydrochloride, was crystallized from pentane as colorless needles, mp 39–41°.

Anal. Calcd for $C_{12}H_{15}NS$: C, 70.2; H, 7.4; N, 6.8. Found: C, 70.3; H, 7.5; N, 6.6.

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D-Arabinose and 2-Deoxy-D-ribose Derivatives

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In a program directed toward nucleoside synthesis a number of derivatives of D-arabinose and 2-deoxy-D-ribose were synthesized. A few of these were new compounds which seemed worth recording in the chemical literature. These compounds were ethyl 2,3,5-tri-*O*-benzyl-D-thioarabinoside (I), 2,3,5-tri-*O*-benzyl-D-arabinose diethyl mercaptal (II), 2,3,5-tri-*O*-benzyl-4-*O*-acetyl-D-arabinose diethyl mercaptal (III), 5-*O*-trityl-2,3,4-tri-*O*-benzoyl-D-arabinose (IV), and 5-*O*-trityl-2-deoxy-D-ribose ethylene mercaptal (V).

Treatment of 2,3,5-tri-*O*-benzyl-β-D-arabinose with ethyl mercaptan and aqueous HCl[1] gave I. More vigorous conditions formed II. Oxidation[2] of 5-*O*-trityl-2,3,4-tri-*O*-benzoyl-D-arabinose diethyl mercaptal[3] with HgO–$HgCl_2$ gave IV. 2-Deoxy-D-ribose ethylene mercaptal[4] was converted to V by reaction with trityl chloride in pyridine.[2]

Experimental Section[5]

Ethyl 2,3,5-Tri-*O*-benzyl-D-thioarabinoside (I).—2,3,5-Tri-*O*-benzyl-β-D-arabinofuranose (4.2 g, 0.01 mole), 1.24 g (0.02 mole) of ethyl mercaptan, and 1 ml of concentrated HCl were mixed and macerated with a glass rod until a homogeneous paste was achieved. The mixture was refrigerated overnight. About 2.5 ml of water was added, and the mixture was extracted with 5 ml of $CHCl_3$. The $CHCl_3$ extract was dried ($MgSO_4$), filtered, and evaporated to dryness under reduced pressure, yield 3.45 g. The product was chromatographed on 100 g of Woelm neutral alumina (3% water) packed in benzene. The column was eluted with C_6H_6–$CHCl_3$ (8:2) collecting fifty 10-ml fractions. Fractions 9–30 were combined and evaporated to dryness under reduced pressure. The product was a clear oil (2.5 g, 54%). Thin layer chromatography [silica gel; C_6H_6–CH_3OH (95:5)] gave a single spot with R_f 0.49. The infrared spectrum (neat) had bands at 3000, 2820, 1490, 1445, 1355, 1250, 1195, 1105, 1035, 975, 905, 734, and 695 cm^{-1}.

Anal. Calcd for $C_{28}H_{32}SO_4$: C, 72.39; H, 6.94; S, 6.90. Found: C, 72.05; H, 6.87; S, 6.64.

2,3,5-Tri-*O*-benzyl-D-arabinose Diethyl Mercaptal (II).—A mixture of 4.2 g (0.01 mole) of 2,3,5-tri-*O*-benzyl-β-D-arabinofuranose, 1 ml of concentrated H_2SO_4, and 50 ml of ethyl mercaptan was stirred vigorously under anhydrous conditions overnight. Chloroform (50 ml) and 50 ml of water were added to the reaction mixture. The $CHCl_3$ layer was removed and extracted successively with 50 ml of 2.0 *N* NaOH solution, 50 ml of saturated $NaHCO_3$ solution, and 50 ml of water. The $CHCl_3$ solution was filtered, and the filtrate was evaporated to dryness under reduced pressure to give an oil (5.19 g). The product was chromatographed on the same system as in the previous experiment but using 200 g of alumina. Elution was done with 200 ml of C_6H_6–$CHCl_3$ (9:1), 250 ml of C_6H_6–$CHCl_3$ (8:2), and C_6H_6–$CHCl_3$–CH_3OH (78:20:2), collecting one hundred 10-ml fractions. Fractions 68–78 were combined and concentrated under reduced pressure to give 1.15 g of a pale yellow oil. The R_f value [silica gel; C_6H_6–CH_3OH (99:1)] was 0.43. The infrared spectrum had bands at 3495, 2810, 1475, 1440, 1385, 1335, 1250, 1200, 1085, 1025, 905, 734, and 697 cm^{-1}.

Anal. Calcd for $C_{30}H_{38}S_2O_4$: C, 68.40; H, 7.27; S, 12.17; O, 12.15. Found: C, 68.12; H, 7.45; S, 12.11; O, 12.11.

2,3,5-Tri-*O*-benzyl-4-*O*-acetyl-D-arabinose Diethyl Mercaptal (III).—A solution of 6.5 g (0.012 mole) of 2,3,5-tri-*O*-benzyl-D-arabinose diethyl mercaptal and 12 ml of acetic anhydride in 90 ml of anhydrous pyridine was allowed to stand at room temperature overnight. The solution was poured into a vigorously stirred mixture of 200 g of ice and 200 ml of $CHCl_3$. The resulting mixture was allowed to stand until the ice had melted. The $CHCl_3$ layer was removed and extracted with three 100-ml portions of ice-cold 3 *M* $NaHSO_4$ solution, two 150-ml portions of saturated $NaHCO_3$ solution, and 150 ml of water. The $CHCl_3$ solution was filtered through paper, and the solvent was removed from the filtrate by evaporation under reduced pressure. The residue was a pale amber oil (6.9 g, 99%). Thin layer chromatography [silica gel; C_6H_6–C_6H_{12}–CH_3OH (50:47:3)] showed a single spot with R_f 0.62. The infrared spectrum (neat) had no absorption in the hydroxyl region but had a strong band at 1730 cm^{-1} (ester). Other infrared bands were at 2980, 2900, 2820, 1460, 1440, 1362, 1230, 1090, 1085, 1025, 965, 907, 750, 733, and 695 cm^{-1}.

Anal. Calcd for $C_{32}H_{40}S_2O_5$: C, 67.57; H, 7.09; S, 11.27; O, 14.08. Found: C, 67.17; H, 7.17; S, 10.90; O, 14.06.

5-*O*-Trityl-2,3,4-tri-*O*-benzoyl-D-arabinose (IV).—A mixture of 29.95 g (0.037 mole) of 5-*O*-trityl-2,3,4-tri-*O*-benzoyl-D-arabinose diethyl mercaptal, 35 g of yellow HgO, 40 g of $HgCl_2$, 25 ml of water, and 375 ml of acetone was stirred at room temperature overnight. The mixture was filtered, and the filter cake was washed thoroughly with acetone. The combined filtrate and washings were evaporated to dryness under reduced pressure. The residue was partitioned between 200 ml of water and 200 ml of $CHCl_3$. The phases were separated, and the aqueous phase was extracted with 50 ml of $CHCl_3$ which was combined with the previous $CHCl_3$ phase. The $CHCl_3$ solution was washed with three 100-ml portions of water, filtered, and evaporated to dryness under reduced pressure to give 23.4 g of residue. A portion (11.6 g) of the residue was crystallized from C_6H_6, and a second fraction was obtained by dilution of the mother liquor with Skellysolve B. The total yield of recrystallized material was 8.6 g. The crystalline material was combined with 2.5 g from another experiment and recrystallized from 50 ml of C_6H_6: 7.17 g, mp 92–93°, $[\alpha]^{25}D$ +46° (*c* 2, $CHCl_3$). The ultraviolet spectrum (C_2H_5OH) had maxima at 229 mμ (ε 36,800), 254 (2950), 260 (2450), 266 (2300), 270 (2300), 273 (2300), and 281 (1850). The infrared spectrum (Nujol mull) had bands at 1725, 1600, 1580, 1490, 1245, 1100, 1090, 1065, 1020, 710, and 700 cm^{-1}. The nmr spectrum in $CDCl_3$ had a multiplet centered at δ 3.57 (2 H on C-5), a multiplet centered at 5.88 (2 H on C-3 and C-4), a doublet of doublets centered at 6.73 (H on C-2), multiple peaks at 7.0–8.28 (aromatic), and a singlet at 9.78 (aldehyde H).

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Anal. Calcd for $C_{45}H_{36}O_8 \cdot C_6H_6$: C, 78.24; H, 5.73; benzene, 9.96. Found: C, 78.75; H, 5.73; benzene 7.08.

5-*O*-Trityl-2-deoxy-D-ribose Ethylene Mercaptal (V).—A solution of 8.8 g (0.042 mole) of 2-deoxy-D-ribose ethylene mercaptal[4] and 12.3 g (0.043 mole) of trityl chloride in 70 ml of anhydrous pyridine was allowed to stand at room temperature for 3 days. The reaction mixture was poured into a mixture of 350 g of ice and 270 ml of $CHCl_3$ with stirring. After the ice had melted, the $CHCl_3$ layer was removed. The aqueous layer was extracted with 80 ml of $CHCl_3$. The combined $CHCl_3$ solutions were washed as in the previously described acylation but using 120-ml portions. The $CHCl_3$ solution was dried ($MgSO_4$), filtered, and evaporated to dryness under reduced pressure. The residue (23.6 g) was chromatographed on 600 g of alumina as previously described but packing and eluting with C_6H_6–$CHCl_3$–CH_3OH (78:20:2) and collecting one hundred 10-ml fractions. Fractions 14–40 were combined and evaporated to dryness under reduced pressure. The residue (19.8 g) was crystallized from 150 ml of C_6H_6–C_6H_{12} (1:2) to give 6.9 g (36%) of crystalline solid, mp 125–128°.

A portion of the product was recrystallized twice from the same solvent system; mp 130–132°, $[\alpha]^{25}D$ −8.8° (*c* 4, $CHCl_3$). The ultraviolet spectrum (C_2H_5OH) had maxima at 230 mμ (ε 8150), 253 (896), and 258 (874) with shoulders at 264 and 269 mμ. The infrared spectrum had bands at 3500, 3470, 1590, 1580, 1485, 1065, 775, 760, 740, 705, 700, 690, and 630 cm^{-1}. The nmr spectrum (in $CDCl_3$) had a doublet of doublets centered at δ 1.86 (2 H), a triplet centered at 2.66 (2 H), a singlet at 3.13 (4 H), multiple peaks centered at 3.37 (2 H), multiple peaks centered at 3.89 (2 H), a triplet centered at 4.66 (1 H), and multiple peaks at 7.22–7.58 (15 H).

Anal. Calcd for $C_{28}H_{28}S_2O_3$: C, 68.99; H, 6.23; S, 14.17; O, 10.61. Found: C, 69.17; H, 6.25; S, 14.22; O, 11.08.

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Carboranes. II. An Analog of 1,4-(Dimethanesulfonoxy)butane[1,2]

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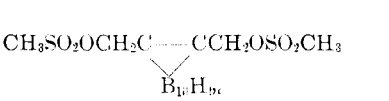
The preparation of a boron-containing bismethanesulfonate was undertaken for possible application in neutron-capture therapy.[3] An *o*-carborane analog of the alkylating agent, bis(methanesulfonoxy)butane (Myleran),[4] was synthesized from 1,4-bismethanesulfonoxybutyne for evaluation in tumor-bearing animals.



Experimental Section[5]

1,4-Bismethanesulfonoxybutyne.—An experimental preparative procedure and the physical characteristics of this compound have not been described, though pharmacological studies are reported.[6] A similar procedure to that described for the sulfonation of dihydroxyalkynes[7] was used.

A solution of 8.6 g (0.1 mole) of 1,4-butynediol in 15.8 g (0.2 mole) of pyridine was added to 100 ml of a 1:1 mixture of THF and ethyl ether. To this stirred anhydrous solution, 22.9 g (0.2 mole) of ethanesulfonyl chloride was added dropwise, maintaining the temperature of the reaction mixture below 5°. Upon completion of the addition, the mixture was stirred for 4 hr at the same temperature. The solution was then concentrated under reduced pressure to one-third of its volume. The pyridine hydrochloride was discarded and the filtrate was treated with an equal volume of water. The mixture became warm and two layers separated. The upper, organic phase was removed and concentrated to an oil which solidified on treatment with ethanol. This product, 5.1 g (21%), was recrystallized from 2 vol of ethanol and yielded white crystals, mp 85.5–86.5°.

Anal. Calcd for $C_6H_{10}O_6S_2$: C, 29.74; H, 4.16; S, 26.47. Found: C, 29.88; H, 4.15; S, 26.23.

1,2-Bis(methanesulfonoxymethyl)carborane.—A solution of 4.84 g (0.02 mole) of 1,4-bis(methanesulfonoxybutyne) and 2.44 g (0.02 mole) of sublimed decaborane ($B_{10}H_{14}$) in 50 ml of dry acetonitrile was refluxed for 28 hr. The solvent was then removed under reduced pressure and the residue was refluxed in 40 ml of methanol for 4 hr. Removal of the alcohol on a rotatory evaporator left an oil from which 3.4 g (47%) of a crude solid was obtained by use of an ethanol–water mixture. Recrystallization from ethanol yielded 1.5 g of the pure carborane, mp 93–94°.

Anal. Calcd for $C_5H_{20}B_{10}O_6S_2$: C, 19.98; H, 5.59; B, 30.01; S, 17.79. Found: C, 20.23; H, 5.56; B, 29.81; S, 17.54.

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Some Hydrazine Derivatives of (4-Biphenylyl)glyoxal

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4-Biphenylglyoxal and its derivatives have been shown by Cavallini and his co-workers[1] to have both *in vitro* and *in vivo* activity against several viruses. The data presented by these workers indicated that a high degree of antiviral activity was associated with the condensation products of biphenylylglyoxals and *p*-aminobenzoic acid, and that these derivatives were better absorbed than the parent glyoxal. In the antibacterial nitrofurans, condensation with a substituted hydrazine confers activity on the weakly active aldehyde.[2] It was of interest therefore to prepare similar derivatives of (4-biphenylyl)glyoxal to compare their activity with that of the parent compound. This communication describes the synthesis of the derivatives listed in Table I.

These compounds, unlike the parent biphenylylglyoxal, did not possess *in vivo* activity against herpes simplex or the influenza PR8 virus.[3]

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