Boron Compounds. 40.[1] O-Ethylboranediyl Derivatives of Dulcitol

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1,6-Bis-*O*-diethylboryl-2,3:4,5-bis-*O*-ethylboranediyldulcitol (**2**) and 1,6:2,3:4,5-tris-*O*-ethylboranediyldulcitol (**3**) are prepared from dulcitol and ethylboron compounds. 2,3:4,5-Bis-*O*-ethylboranediyldulcitol (**4**) is prepared by selective deborylation of **2** and **3** using methanol. The regioselective O-derivatization of **4** is investigated with benzoyl chloride, acetic anhydride, and tosyl chloride. One obtains the boron-containing **5a** and the boron-free dulcitol derivatives **6a–c** and **7**.

Much interest has been centered on the use of the phenylboranediyl protective group for the selective O-derivatization of polyalcohols and carbohydrates.[2] The fact that the reaction of phenylboronic acid with glycerol yields a mixture of phenylboranediyl derivatives of glycerol with five- and six-membered *O*-phenylboranediyl rings[3] prompted us to investigate new routes which allow the selective introduction of *O*-ethylboranediyl groups into polyhydroxy systems. The availability of triethylborane,[4] coupled with the fact that the *O*-ethylboranediyl derivatives of polyalcohols have not been described, motivated our present investigations[5–9] into the possible structures and some specific reactions of the *O*-ethylboranediyl derivatives of polyhydroxy compounds.

Conflicting structural assignments have been made for the *O*-phenylboranediyldulcitol derivative,[10–12] and also an extremely low yield was obtained in the derivatization of "1,3:4,6-bis-*O*-phenylboranediyldulcitol" to 1,3,4,6-tetra-*O*-acetyl-2,5-di-*O*-benzoyldulcitol.[11] The use of alcohols and water for washing[2,11] *O*-phenylboranediyl derivatives is a questionable practice as the selective deborylation of *O*-ethylboranediyl groups with methanol has been observed.[8,9]

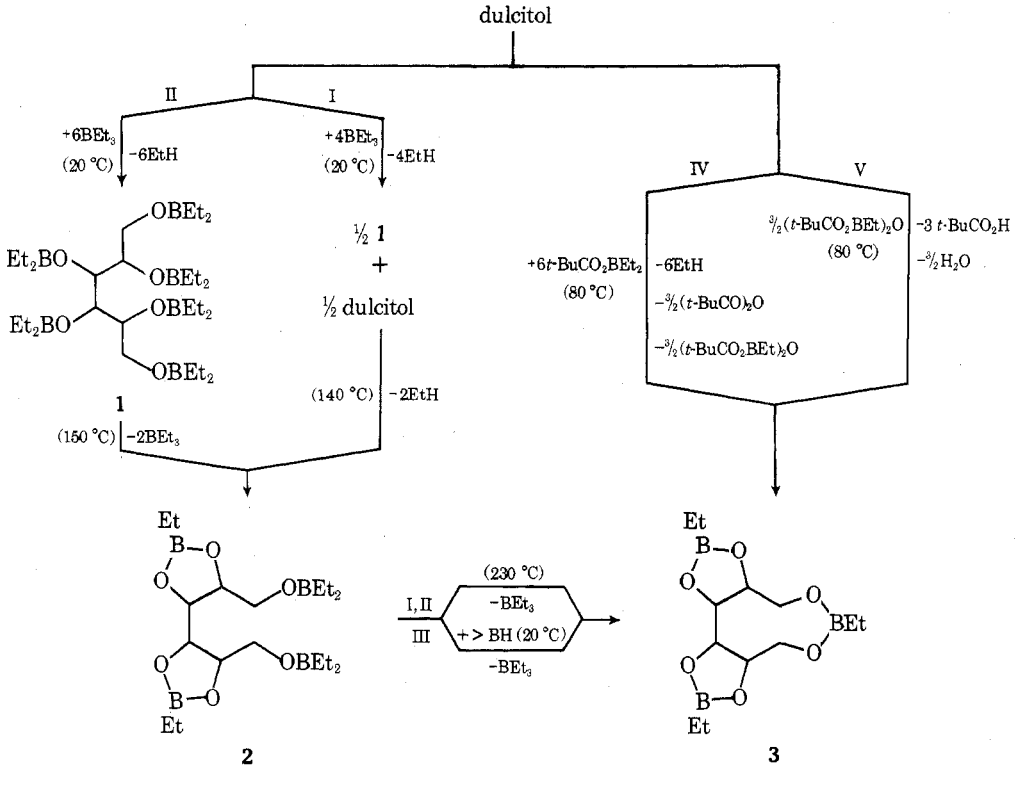
Results and Discussion

A. O-Diethylborylation and O-Ethylboranediylation of Dulcitol. 1,6-Bis-*O*-diethylboryl-2,3:4,5-bis-*O*-ethylboranediyldulcitol (**2**) can be prepared in two ways (Scheme I). The first method involves two stages. Firstly 1,2,3,4,5,6-hexakis-*O*-diethylboryldulcitol (**1**) is prepared analogously to the previously described perdiethylborylation of polyols,[5] by reaction of dulcitol with activated triethylborane[13] in an exothermic reaction at room temperature. Two moles of triethylborane is then eliminated from **1** by heating to 150 °C and **2** is obtained in 96% yield. **2** can also be prepared, without isolating **1**, by reaction of dulcitol with 4 mol of triethylborane. In the first part of this reaction dulcitol is added to activated triethylborane[13] at room temperature and 4 mol of ethane are evolved. The resultant mixture of dulcitol and **1** is subsequently heated to 140 °C causing a further 2 mol of ethane to be liberated, generating **2** in 93% yield.

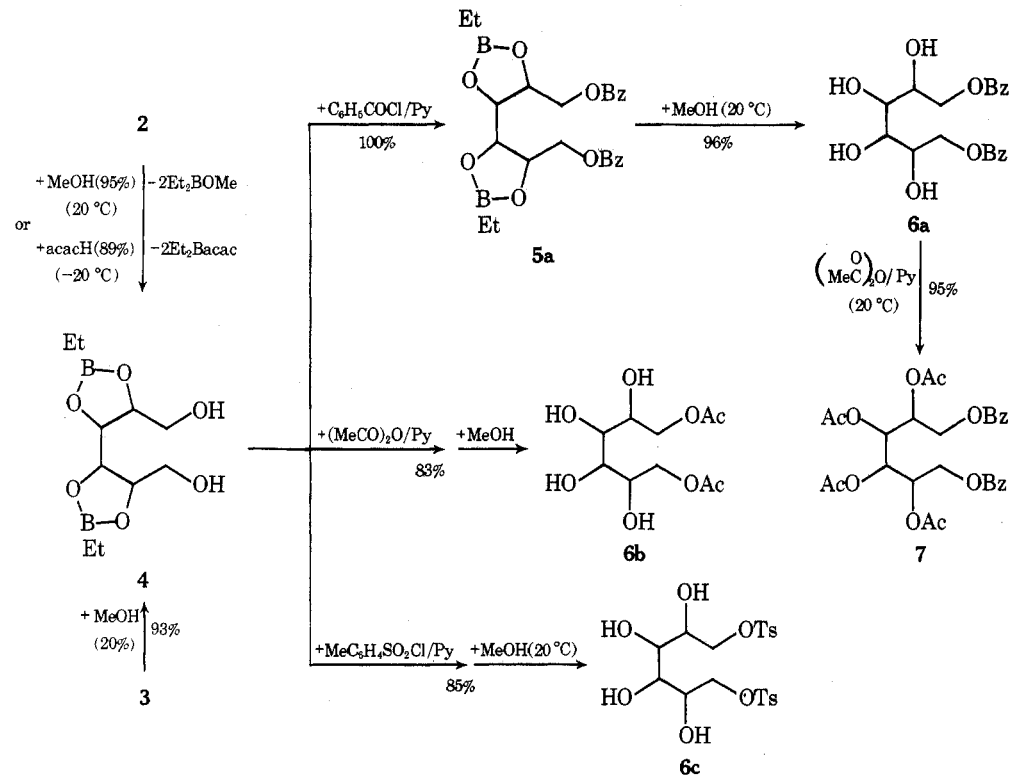
1,6:2,3:4,5-Tris-*O*-ethylboranediyldulcitol (**3**) can be prepared using the five routes I–V (see Scheme I).

3 can be obtained by pyrolysis of **1** (route I) or **2** (route II). The thermal elimination of 2 mol of triethylborane from **1** to yield **2** occurs at 150 °C, whereas 230 °C is required in order to eliminate the third mole. This temperature lies in the range for intermolecular elimination of triethylborane[6] from two *O*-diethylboryl groups. Intramolecular ring formation occurs exclusively in the pyrolyses of **1** and **2**. The addition of catalytic amounts of >BH[14] to **2** at room temperature also leads to the formation of **3** (route III) in 98% yield.

Scheme I



Scheme II



Bz = C_6H_5CO-; Ac = CH_3CO-; Ts = p-$CH_3C_6H_4SO_2$-

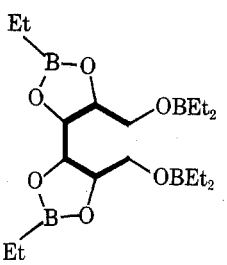
Reaction between dulcitol and diethylboryl pivalate[13] gives directly **3** at 80 °C, accompanied by evolution of 6 mol of ethane and formation of 1.5 mol of bis(ethylpivaloyloxy)-diboroxane[7] and 1.5 mol of pivalic acid anhydride (route IV). The relatively low yield (66%) of **3** is due to the difficulty encountered in the separation of this compound from the bis(ethylpivaloyloxy)diboroxane.[15] **3** can, however, be prepared in 87% yield by reaction of the latter with dulcitol at 80 °C (route V); pivalic acid (3 mol) and water (1.5 mol) in this case are formed as side products.

B. Regioselective O-Derivatization of Dulcitol. The diethylboryl groups of **2** can be selectively removed by addition of methanol at room temperature.[9] The solid 2,3:4,5-bis-*O*-ethylboranediyldulcitol (**4**) is obtained in 95% yield (see Scheme II). Selective deborylation of **3** may also be effected using methanol at room temperature; the nine-membered ethylboranediyl ring is opened, and **4** is obtained in 93% yield.

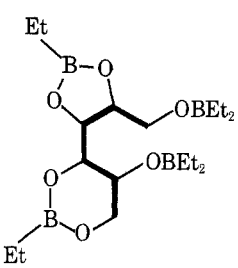
By the normal procedure benzoylation of **4** gives 1,6-di-*O*-benzoyl-2,3:4,5-bis-*O*-ethylboranediyldulcitol (**5a**); this can be deborylated with methanol to give the known 1,6-di-*O*-benzoyldulcitol[16] (**6a**). Analogously **6b**[17] is formed in 95% yield by deborylation of the di-*O*-acetyl derivative of **4**.

The selective deborylation of **2** with acetylacetone to give pure **4** can only be achieved below 0 °C; at room temperature a mixture of compounds is obtained. A study of the temperature dependence of this reaction shows that the yield of **4** decreases with increasing temperature, whereas the yield of **3** increases and rises to ca. 50% at 100 °C. At this temperature an, as yet, unidentified solid containing four hydroxyl groups and one *O*-ethylboranediyl group is obtained. This compound is also formed when pure **4** is heated to 100 °C in the presence of acetylacetone. However, **4** remains unchanged after 1 h at 120 °C in the absence of acetylacetone.

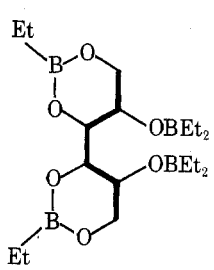
C. Structure Determination of 2, 3, and 4. The fact that the pyrolysis of **1** between 140 and 180 °C causes the elimination of only 2 mol of triethylborane, rather than 3 as in the case of mannitol[9] and sorbitol,[18] indicates that two five- or six-membered ethylboranediyl rings are formed in this reaction, and hence the three structures **2, 2a,** and **2b** are possible. The symmetry of **2** is reflected in its ^1H NMR spectrum (see Experimental Section). The ^{11}B NMR spectrum of a neohexane (2,2-dimethylbutane) solution of **2** verifies the presence of two *O*-diethylboryl groups and two *O*-ethylboranediyl groups.[5] The position of the symmetrical signal for the *O*-ethylboranediyl boron atoms at δ 34 ppm indicated the presence of the structure **2** with two five-membered 1,3,2-dioxaborolane rings.[6] Higher membered OBO rings have signals at δ 30 ppm.[6-8]



2



2a



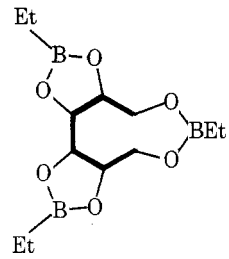
2b

Further proof for this structural assignment is given by the fact that the high-yield selective deborylation of **2** to **4** is possible. The two hydroxyl groups appear as a triplet at τ 5.07 ppm with J = 5.5 Hz in the ^1H NMR spectrum of a dimethyl

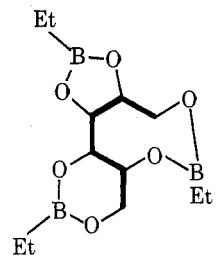
sulfoxide solution of 4. This triplet indicates that the two hydroxy groups are primary.[19]

Benzoylation and deborylation of 4 can be effected in 96% yield to give the known 1,6-di-*O*-benzoyldulcitol,[10] thus giving final proof of the structure of **2.**

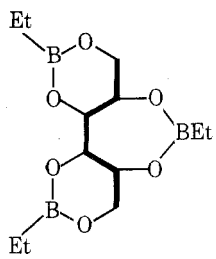
An extremely high temperature (230 °C) is required for the formation of the third *O*-ethylboranediyl ring. This is the temperature required for intermolecular elimination of triethylborane;[6] it is reasonable, therefore, to assume that a seven-, eight-, or nine-membered ring is formed under these reaction conditions. No intermolecular products are formed; thus structures **3, 3a,** and **3b** are possible.



3



3a



3b

The ^{11}B NMR spectrum of 3 in neohexane shows the presence of five-membered rings; however, the breadth of the signal observed does not allow an unequivocal interpretation. The nine-membered ring would be expected to have a signal at ca. δ 30 ppm, this being the range for six- and higher membered rings.

Proof of the structure of 3 is furnished by its facile selective deborylation to 4 (see Scheme II), which involves opening of the nine-membered ethylboranediyl ring.

Comparison of *O*-Ethyl- with *O*-Phenylboranediyl Derivatives of Dulcitol. The first *O*-phenylboranediyl derivative of dulcitol was prepared in 1958. However, no structural assignment was attempted.[10] In the latter paper it is mentioned that the ratio of dulcitol to phenylboroxine is unimportant, and tris-*O*-phenylboranediyldulcitol is always obtained. Later, the preparation and derivatization of 1,3:4,6-bis-*O*-phenylboranediyldulcitol in poor yield (10%) is described.[11] It is interesting to note that the preparation involves the use of hot water and methanol. We suggest that the use of such solvents leads to either the selective deborylation of one *O*-phenylboranediyl ring or an intermolecular linkage. This is comparable with the selective deborylation of **2** to **4.**

The reaction of dulcitol with triphenylborane in toluene (see Experimental Section) gives a tris-*O*-phenylboranediyldulcitol in a yield of 93% which has mp 162 °C; this is identical with the derivative prepared from phenylboronic acid and dulcitol in acetone.[10] Treatment of this derivative with warm water leads to the selective cleavage of one of the *O*-phenylboranediyl rings.

It was recently proposed, on the basis of fragmentation in the mass spectrometer, that the *O*-phenylboranediyl derivative of dulcitol is 1,3:2,4:5,6-tris-*O*-phenylboranediyldulcitol without giving the means of preparation of this derivative.[12]

Summary. The use of the protective *O*-ethylboranediyl group offers distinct advantages over the *O*-phenylboranediyl group. A choice of five routes (I–V) is available for introducing the *O*-ethylboranediyl groups into polyalcohols. The products can be distilled in vacuo, and in several cases[6–9] the analyses by GLC methods are possible. A useful tool in the determination of the structure of *O*-ethylboranediyl derivatives is ^{11}B NMR spectroscopy, where characteristic high-field chemical shifts (δ 34.5 ppm) are obtained specifically for five-membered rings.

Many of the dulcitol derivatives can be selectively deborylated with methanol at room temperature. The number of hydroxy groups in the products can be quickly and accurately determined with the help of activated triethylborane.[5,26] The selectively deborylated products can be O-derivatized with benzoyl chloride, acetic anhydride, or tosyl chloride in good yield.

Experimental Section

General. All experiments were carried out in dry, deoxygenated solvents under an atmosphere of argon.

Analyses. Ethane was measured with a mass spectrometer CEC 103. The purity of 3 was determined gas chromatographically[20] with a M + F 720 (3-m steel column filled with SF 96 on Embacel). The ^1H NMR,[21] ir,[22] and mass spectra[23] were obtained using the instruments Varian A-60 or HA-100, Perkin-Elmer 125, and Varian MAT CH5, respectively. ^{11}B NMR[24] spectra were recorded at 32.1 MHz with $Et_2O{\cdot}BF_3$ as an external standard (deshielding $\delta > 0$). Boron was determined by flame photometry of methanol solutions with a M4QIII from Carl Zeiss. C, H analyses were carried out by Dornis and Kolbe, Mülheim-Ruhr. The B_C values were obtained by the described quantitative analysis using anhydrous trimethylamine *N*-oxide in boiling benzene.[25a] The BC_2 values were obtained by oxidation with anhydrous trimethylamine *N*-oxide in boiling pentane.[25b] The hydroxy groups were determined using activated triethylborane.[5,26]

Reagents. Dulcitol was obtained from Baker Chemical Co. Triethylborane,[4] tetraethyldiborane,[27] diethylboryl pivalate,[13] and bis(ethylpivaloyloxy)diboroxane[14] have been synthesized in our pilot plant and laboratory, respectively.

Preparation. A. 1,2,3,4,5,6-Hexakis-*O*-diethylboryldulcitol (1). Triethylborane (84 g, 0.857 mol), which was activated by 0.2 ml of diethylboryl pivalate, was added dropwise (2 h) to a stirred suspension of dulcitol (23.2 g, 127 mmol) in heptane (120 ml) and ethane (17.74 nl, MS) was evolved. The temperature rose to 45 °C. After the removal of the excess of triethylborane and heptane in vacuo colorless 1 (73.5 g, 98%) was obtained as residue: MS (70 eV) no M^+; found *m/e* 561 (B_6, rel intensity 5), 462 (B_5, 22), 407 (B_4, 66), 309 (B_4, 89), 99 (B_1, 100); ^1H NMR (CCl_4, 60 MHz) τ 5.48 (m, 4 H), 5.92 (m, 4 H), 9.13 (s, 60 H).

Anal. Calcd for $C_{30}H_{68}B_6O_6$ (589.7): B, 11.00; B_C, 7.33. Found: B, 11.15; B_C, 7.13.[25a]

B. 1,6-Bis-*O*-diethylboryl-2,3:4,5-bis-*O*-ethylboranediyldulcitol (2). Route I (Pyrolysis of 1). 1 (56 g, 95 mmol) was heated to 150 °C and pure (GLC) triethylborane (18.5 g, 189 mmol) distilled over. Distillation of the residue in vacuo yielded colorless **2** (35.8 g, 95%), bp 120 °C (10^{-3} Torr).

Route II (Dulcitol and BEt_3 in the Ratio 1:4). Dulcitol (20 g, 110 mmol) was added in portions over 4 h to triethylborane (43 g, 439 mmol) containing 0.2 ml of diethylboryl pivalate. The temperature rose to a maximum of 50 °C and ethane (9.59 nl, 97.5%, MS) was liberated. The mixture was then heated to 130 °C (bath) and a further 5.25 nl (107%) of ethane (MS) was evolved. Distillation yielded **2** (40.3 g, 93%): bp 130 °C (10^{-3} Torr); MS (70 eV) no M^+; found *m/e* 365 (B_4, rel intensity 19), 197 (B_2, 13), 125 (B_1, 20), 111 (B_1, 47), 99 (B_1, 100), 98 (B_1, 44), 57 (B_1, 27); ^1H NMR (100 MHz, CCl_4) τ 5.65 (m, 2 H) [5.86 (m), 6.00 (d, J = 4 Hz), 4 H], 6.17 (dd, J = 11.5, 3 Hz, 2 H), 9.12 (m, 30 H); ^{11}B NMR (neohexane) δ 55 (1 B, half-width = 600 Hz) and 35 ppm (1 B, half-width ~ 600 Hz).

Anal. Calcd for $C_{18}H_{38}B_4O_6$ (393.8): B, 10.98; B_C, 5.49; B_{C_2}, 1.83. Found: B, 10.89; B_C, 5.34;[25a] B_{C_2}, 1.91.[25b]

Tris-1,6:2,3:4,5-*O*-ethylboranediyldulcitol (3). Route IV (Dulcitol and Diethylboryl Pivalate). Dulcitol (10.4 g, 57.1 mmol) was added in portions in 2 h to diethylboryl pivalate (61.7 g, 363 mmol) at 80 °C and ethane (MS) (7.85 nl, 102%) evolved. Fractionation yielded excess diethylboryl pivalate (3.4 g) (^1H NMR), bp 68 °C (12 Torr), 97% (GC) pivalic acid anhydride (15 g), bp 84 °C (12 Torr), 28 g of a mixture of 80% bis(ethylpivaloyloxy)diboroxane, and 20% **3** (^1H NMR), bp 108 °C (0.2 Torr), and **3** (11.2 g, 66%), bp 114 °C (5×10^{-3} Torr).

Dulcitol and Bis(ethylpivaloyloxy)diboroxane. Route V. A mixture of dulcitol (3.2 g, 17.6 mmol) and bis(ethylpivaloyloxy)diboroxane (16.4 g, 55 mmol) was heated to 80 °C for 30 min. Distillation in vacuo yielded **3** (4.5 g, 87%), bp 100 °C (10^{-3} Torr).

From 1 and 2 with Ethyldiborane (Route III). A mixture of **1** (51.6 g, 87.5 mmol) and ethyldiborane (882.3 mg, 15.05‰ H^-, 13.6 mmol BH) was stirred for 4 days at room temperature. The >BH was then destroyed by bubbling in ethylene for 0.5 h and the triethylborane (21.4 g) was distilled in vacuo. Further distillation yielded **2** (16 g, 62%), bp 99 °C (10^{-3} Torr), and **3** (13.2 g, 38%), bp 131 °C (10^{-3} Torr).

From 2 with >BH (Route III). A mixture of **2** (11.6 g, 29.5 mmol) and 0.2 ml of ethyldiborane (with 15.1‰ H^-) was stirred for 6 h at room temperature. Triethylborane (2 g) was removed in vacuo and **3** (8.5 g, 98%), bp 99 °C (10^{-3} Torr), was obtained.

3 by Pyrolysis of 2 (Route I). **2** (7.8 g, 19.8 mmol) was heated to 230 °C for 5 h during which time triethylborane (1.6 g) distilled over. Pure (GLC) **3** (5.4 g, 92%) was obtained by distillation of the residue: MS (70 eV) no M^+; found *m/e* 197 (B_2, rel intensity 18), 111 (B_1, 44), 99 (B_1, 100), 57 (B_1, 22); ^1H NMR (CCl_4, 100 MHz) τ 5.60 (m, 2 H), 5.80 (m, 3 H), 6.04 (d, J = 2 Hz, 2 H), 6.16 (br s, 1 H), 9.14 (m, 15 H); ^{11}B NMR (neohexane) δ 34 ppm with shoulder (30 ppm) (half-width = 600 Hz).

Anal. Calcd for $C_{12}H_{23}B_3O_6$ (295.8): B, 10.97; B_C, 3.66. Found: B, 10.84; B_C, 3.63.[25a]

C. 2,3:4,5-Bis-O-ethylboranediyldulcitol (4). 4 from 2 with Methanol. Methanol (10 ml) was added to **2** (6.4 g, 16.3 mmol). The mixture was stirred for 30 min at room temperature. After removal of the methanol and diethylmethoxyborane mixture (8.6 g with 4.09% B), **4** (4 g, 95%) remained as a colorless powder, mp 97 °C.

4 from 3 with Methanol. Methanol (10 ml) was added to **3** (11 g, 37.2 mmol). The mixture was stirred for 15 min at room temperature. After removal of the methanol and ethyldimethoxyborane mixture (15.8 g with 2.34% B) in vacuo (15 Torr), **4** (8.9 g, 93%) was obtained as residue: mp 97–98 °C; MS (70 eV) no M^+, found *m/e* 227 (B_2, rel intensity 2), 197 (B_2, 13), 129 (B_1, 18), 111 (B_1, 44), 99 (B_1, 100), 98 (45), 31 (B_0, 6); ir (Nujol) 3285 (OH), 1355 cm^{-1} (BO); ^1H NMR (Me_2SO-d_6, 60 MHz) τ 5.07 (t, J = 5.5 Hz, 2 H), 5.5–6.2 (m, 4 H), 6.5 (m, 4 H), 9.16 (m, 10 H); ^{11}B NMR (Me_2SO) δ 33 ppm (half-width ~ 1300 Hz).

Anal. Calcd for $C_{10}H_{20}B_2O_6$ (257.9): B, 8.38; B_C, 2.79; H^+, 0.782. Found: B, 8.36; B_C, 2.72;[25a] H^+, 0.774.

4 from 2 with Acetylacetone. Acetylacetone (10 ml) was added dropwise to a stirred solution of **2** (5 g, 12.7 mmol) in hexane (20 ml) at −20 °C. After 1 h, **4** was filtered off, washed with hexane, and vacuum dried. The yield of **4** was 2.9 g (89%), mp 97 °C.

4 with Acetylacetone at 100 °C. A mixture of **4** (1.4 g, 5.4 mmol) and acetylacetone (5 ml) was heated to 100 °C for 1 h. After cooling to room temperature hexane (10 ml) was added, and the solid was filtered off, washed with hexane, and dried in vacuo giving mono-O-ethylboranediyldulcitol (0.5 g, 84%), mp ~156 °C. On concentrating the filtrate **3** (0.8 g, ~100%) (^1H NMR) was obtained: MS (70 eV) no M^+; found *m/e* 129 (B_1, rel intensity 24), 111 (B_1, 41), 99 (B_3, 100); ^1H NMR (Me_2SO-d_6; 60 MHz) τ 5.65 (m, 6 H), 6.60 (m, 6 H), 9.18 (m, 5 H).

Anal. Calcd for $C_8H_{17}BO_6$ (220.0): B, 4.92; B_C, 1.64; H^+, 1.83. Found: B, 4.93; B_C, 1.54;[25a] H^+, 1.83.

Pyrolysis of 4. **4** (1.8 g) remained unchanged (melting point) after being heated to 120 °C for 1 h.

D. O-Derivatization of 4. 1,6-Di-O-benzoyl-2,3:4,5-bis-O-ethylboranediyldulcitol (5a). From 4 with Benzoyl Chloride. Benzoyl chloride (3.63 g, 25.8 mmol) was added dropwise in 30 min to a stirred solution of **4** (3.3 g, 12.8 mmol) in pyridine (20 ml) at 0 °C. The mixture was then stirred for 8 h at room temperature before filtering off the pyridine hydrochloride. Concentration of the filtrate in vacuo yielded **5a** (6.0 g, 100%): mp 121 °C; MS (70 eV) no M^+; found *m/e* 331 (B_2, rel intensity 12), 270 (B_1, 12), 233 (B_1, 12), 111 (B_1, 82), 105 (B_0, 100), 77 (B_0, 28); ^1H NMR (CD_3CN, 60 MHz) τ 1.98 (m, 4 H), 2.43 (m, 6 H), 5.39 (m, 2 H), 5.56 (m, 6 H), 9.16 (m, 10 H).

Anal. Calcd for $C_{24}H_{28}B_2O_8$ (466.1): B, 4.64; B_C, 1.55. Found: B, 4.71; B_C, 1.79.[25a]

1,6-Di-O-benzoyldulcitol (6a). 6a from 5a with Methanol. 5a (5.5 g, 11.8 mmol) and methanol (40 ml) yielded **6a** (4.4 g, 96%): mp 206 °C; MS (70 eV) no M^+; found *m/e* 237 (rel intensity 38), 207 (19), 196 (74), 178 (23), 165 (69), 123 (95), 105 (100), 77 (22).

Anal. Calcd for $C_{20}H_{22}O_8$ (390.4): C, 61.53; H, 5.86; H^+, 1.033. Found: C, 61.56; H, 5.66;[25a] H^+, 1.056.

1,6-Di-O-benzoyl-2,3,4,5-tetra-O-acetyldulcitol (7). From 6a with Acetic Anhydride. Acetic anhydride (10 ml) was added dropwise to a solution of **6a** (2.1 g, 5.4 mmol) in pyridine (10 ml). After stirring for 3 h at room temperature the solution was concentrated in vacuo to yield crude **7** (2.85 g, 95%): mp 224 °C (recrystallized once from glacial acetic acid); MS (70 eV) found *m/e* 436 (rel intensity 3), 423 (8), 351 (34), 279 (54), 207 (54), 105 (100), 43 (57).

Anal. Calcd for $C_{28}H_{30}O_{12}$ (558.5): C, 60.21; H, 5.41. Found: C, 60.19; H, 5.30.

1,6-Di-O-acetyldulcitol (6b). From 4 with Acetic Anhydride. Acetic anhydride (10 ml) was added to **4** (0.7 g, 2.7 mmol) in pyridine (10 ml). The mixture was stirred for 1 h at room temperature. Pyridine and acetic anhydride were removed in vacuo (10^{-2} Torr). Two 15-ml portions of methanol were added to the residue and the solution was concentrated in vacuo (15 Torr). **6b** (0.6 g, 83%), mp 168 °C, was obtained: ^1H NMR (Me_2SO-d_6, 60 MHz) τ 5.55 (m, 2 H), 6.0 (br s, 6 H), [6.57 (m), 6.67 (s), 5 H)], 7.99 (s, 5 H).

Anal. Calcd for $C_{10}H_{18}O_8$ (266.3): C, 45.11; H, 6.81; H^+, 1.51. Found: C, 45.14; H, 6.80; H^+, 1.51.

1,6-Di-O-p-tosyldulcitol (6c). From 4 with Tosyl Chloride. *p*-Tosyl chloride (2.7 g, 14.2 mmol) was added in portions to a stirred solution of **4** (1.8 g, 7 mmol) in pyridine (15 ml). The temperature rose to a maximum of 29 °C. After stirring for 10 h at room temperature, water (40 ml) was added dropwise causing the pyridine hydrochloride to go into solution and **6c** to precipitate out. After filtration, washing with water, and drying in vacuo **6c** (2.9 g, 85%), mp 128–130 °C (mp 134 °C from THF), was obtained: MS (70 eV) no M^+; found *m/e* 275 (rel intensity 3), 172 (30), 155 (22), 103 (51), 91 (100), 73 (76).

Anal. Calcd for $C_{20}H_{26}S_2O_{10}$ (490.6): C, 48.97; H, 5.34; S, 13.07; H^+, 0.822. Found: C, 49.05; H, 5.08; S, 13.05; H^+, 0.79.

Dulcitol and Triphenylborane. Dulcitol (5.5 g, 30.2 mmol) was added to triphenylborane (55.4 g, 0.23 mmol) in toluene (75 ml) at room temperature and the mixture was then heated under reflux for 3 h. After removal of solvent (GC: 19.19% benzene and 80.7% toluene) the solid residue (41.4 g) was heated to 180 °C at 10^{-3} Torr to remove the excess triphenylborane (28 g) and crude tris-O-phenylboranediyldulcitol (12.4 g, 93%) was obtained: mp 162 °C[10] (from diethyl ether); MS (70 eV) M^+ *m/e* 440 (B_3, rel intensity 41), 159 (B_1, 51), 147 (B_1, 100), 91 (B_0, 30); ^1H NMR (Me_2SO-d_6, 60 MHz) τ 2–2.8 (m, 15 H), 4.9–5.9 (m, 8 H).

Anal. Calcd for $C_{24}H_{23}B_3O_6$ (440.0): B, 7.37; B_C, 2.46. Found: B, 7.27 B_C, 2.50.

Bis-O-phenylboranediyldulcitol. A mixture of tris-O-phenylboranediyldulcitol (0.4 g, 0.9 mmol) and water (20 ml) was heated to 60 °C for 2 h. The insoluble material product was filtered off and dried in vacuo to give bis-O-phenylboranediyldulcitol hydrate (0.3 g, 89%): mp 137 °C[11]; ^1H NMR (Me_2SO-d_6, 60 MHz) τ 2–2.7 (m, 9 H), 5–6.5 (m, 11 H).

Anal. Calcd for $C_{18}H_{20}B_2O_6 \cdot H_2O$ (372.2): H^+, 1.08. Found: H^+, 1.17.

Registry No.—**1**, 58881-46-2; **2**, 58881-47-3; **3**, 58881-48-4; **4**, 58881-49-5; **5a**, 58881-50-8; **6a**, 20847-03-4; **6b**, 58917-44-5; **6c**, 20847-02-3; **7**, 58881-51-9; triethylborane, 97-94-9; dulcitol, 608-66-2; diethylboryl pivalate, 34574-27-1; bis(ethylpivaloyloxy)diboroxane, 52164-70-2; ethyldiborane, 16924-34-8; mono-O-ethylboranediyldulcitol, 58881-52-0; benzoyl chloride, 98-88-4; acetic anhydride, 108-24-7; *p*-tosyl chloride, 98-59-9; triphenylborane, 960-71-4; tris-O-phenylboranediyldulcitol, 58881-53-1; bis-O-phenylboranediyldulcitol, 4248-37-7.

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Electron Adducts of Acrylic Acid and Homologues. Spectra, Kinetics, and Protonation Reactions. A Pulse-Radiolytic Study

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Pulse radiolysis–kinetic absorption spectrophotometry has been employed to study the addition of electrons to acrylic acid and to several of its homologues in aqueous solution as well as spectral properties and subsequent chemical transformations of the electron adducts. Specific rates of reaction of e_{aq}^- with the acid anions at room temperature in units of 10^{10} M^{-1} s^{-1} are acrylate, 0.53 ± 0.05; methacrylate, 0.45 ± 0.4; *trans*-crotonate, 0.13 ± 0.01; β,β-dimethylacrylate, 0.059 ± 0.002; *trans,trans*-sorbate, 0.58 ± 0.03; *trans*-cinnamate, 1.4 ± 0.1. The specific rates of reaction of e_{aq}^- with the corresponding un-ionized carboxylic acids are all in the range (1.5–2.9) × 10^{10} M^{-1} s^{-1}. Spectra of reversibly diprotonated (i.e., uncharged) and monoprotonated (mononegative) electron adducts were characterized for all six acids. The main features of the spectra of the diprotonated adducts are an intense band, λ_{max} ~250–350 nm, ϵ_{max} ~(1–4) × 10^4 M^{-1} cm^{-1}, and a weaker band, λ_{max} ~350–490 nm, ϵ_{max} ~10^3 M^{-1} cm^{-1}. Spectra of the monoprotonated adducts are red shifted ~10–40 nm relative to corresponding diprotonated adducts. The spectrum of the unprotonated (dinegative) adduct could be determined only for cinnamate; it is additionally red shifted ~25 nm. Values of pK_a (radical) for the process $RCO_2H_2\cdot \rightleftarrows RCO_2H\cdot^- + H^+$ fall in the range 5–8 for the six acids; pK_a (radical) for the second dissociation of the electron adduct of cinnamic acid is 11.6. An anomalous spectral change was observed with acrylic acid around pH 5. Decay of the diprotonated electron adducts of all the acids except β,β-dimethylacrylic is second order, $2k$ ~ (1–7) × 10^9 M^{-1} s^{-1}. Decay of the monoprotonated electron adducts of all the acids in the absence of catalytic species is first order, k_{H_2O} ~ (0.1–2) × 10^5 s^{-1}. α-Carbon radicals, $RR'CH\dot{C}HCO_2^-$, were identified spectrally as the products of irreversible decay of the monoprotonated electron adducts of acrylic, methacrylic, β,β-dimethylacrylic, and crotonic acids; catalysis of the decay process by OH^- was observed for all the adducts except that of cinnamic acid. More detailed investigation of the decay of CH_2-$CHCO_2H\cdot^-$ established general acid (Bronsted $\alpha = 0.43 \pm 0.04$) and general base catalysis as well. Electron transfer from the monoprotonated electron adducts of acrylic and crotonic acids to a number of acceptors was studied as a function of $E^{0\prime}$ of acceptor and pH. Spectra of α-carbon radicals generated by addition of H atoms to each of the acids (except cinnamic) at pH ~1 have λ_{max} ~290–300 nm, ϵ_{max} ~450–1800 M^{-1} cm^{-1}, and $2k_{decay}$ ~ (1–2) × 10^9 M^{-1} s^{-1}. Results of these studies are compared with those of a similar investigation involving acrylamide and its homologues.

In a recent communication,[2a] we described two types of protonation reactions of the electron adduct of acrylic acid in aqueous solution. We now report a detailed study of the reactions of electron adducts of several substituted acrylic acids by the technique of pulse radiolysis–kinetic spectrometry.

Pulse radiolytic studies of α,β-unsaturated acids have been reported for acrylic acid,[2,3] benzoic acid,[4] and maleic and fumaric acids.[5] A number of related studies by ESR technique have also been reported. In the reaction of e_{aq}^- with acrylic acid at pH 12,[6] only the C-protonated electron adduct, $CH_3\dot{C}HCO_2^-$, was observed. The electron adducts of a large number of α,β-unsaturated acids produced by the reaction of ammoniated electrons have also been characterized by means of the ESR technique.[7]

An ESR spectrum observed when neat acrylic acid was irradiated with ^{60}Co γ rays at 77 K was attributed to the electron adduct.[8] Exposure of neat acrylic acid to externally generated H atoms under the same conditions gave a product which was identified as the H atom adduct to the β carbon.[9] ^{60}Co γ ray irradiation of acrylic acid at 77 K in frozen solutions in several aprotic solvents, e.g., triethylamine, methyltetrahydrofuran, or 3-methylhexane, gave stable electron adducts, while the species observed in frozen protic solutions was the same as that resulting from addition of H to β carbon.[10] An optical absorption spectrum attributed to the electron adduct of cinnamic acid has also been measured in solution at 77 K in 2-methyltetrahydrofuran.[11]

Experimental Section

Radiolysis of water produces e_{aq}^- along with other species, eq 1.

$$H_2O \longrightarrow e_{aq}^-,\ OH,\ H,\ H_2O_2,\ H_2,\ \text{and}\ H_3O^+ \qquad (1)$$

Hydroxyl radicals were scavenged by the addition of *tert*-butyl alcohol to the solutions, eq 2.

$$OH + (CH_3)_3COH \rightarrow \dot{C}H_2C(CH_3)_2OH + H_2O \qquad (2)$$

$$k_2 = 5.2 \times 10^8\ M^{-1}\ s^{-1}\ (\text{ref } 12)$$

The alcohol radicals formed in reaction 2 are generally unreactive and do not have significant absorption in the wavelength region involved in this work.[13] The contribution of transient species formed from the reaction of H atoms (yield ~20% that of e_{aq}^-) to the net observed spectra and kinetics is considered to be relatively small (see below).

Single pulses of 30-ns duration from a Febetron 705 machine were employed to produce the short-lived electron adducts. The technique employed has been described in detail.[13,14]

Materials. The following chemicals were used as received: Ma-