Hydrated Oxocarbons, I[1]

Preparation and Reactions of
Tetrakis[organoboranediylbis(oxy)]cyclobutanes

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Octahydroxycyclobutane (**1**) reacts with various monoorganoboranes to give in high yields the tetrakis[organoboranediylbis(oxy)] derivatives **2a – d**. These react with tertiary amines to yield either 1 : 2 or 1 : 4 adducts. Depending on the organo substituents at the boron atoms, alcoholyses of **2a – d** result in either partial or complete deborylation giving e. g. tetraalkoxybis[phenylboranediylbis(oxy)] derivatives of the cyclobutane ring (**7b, c**), or, with ring-opening, dimethyl dihydroxyfumarate (**5**).

Hydratisierte Oxokohlenwasserstoffe, I[1]

Herstellung und Reaktionen von Tetrakis[organoborandiylbis(oxy)]cyclobutanen

Aus Octahydroxycyclobutan (**1**) erhält man mit verschiedenen Monoorganoboranen in hohen Ausbeuten die Tetrakis[organoborandiylbis(oxy)]-Derivate **2a – d**, die mit tertiären Aminen 1 : 2- sowie 1 : 4-Additionsverbindungen bilden. Bei der Alkoholyse lassen sich **2a – d** in Abhängigkeit von den Organo-Substituenten an den Bor-Atomen partiell und vollständig entborylieren. Man erhält z. B. Tetraalkoxybis[phenylborandiylbis(oxy)]-Derivate des Cyclobutan-Rings (**7b, c**) oder, infolge Ringöffnung, Dihydroxyfumarsäure-dimethylester (**5**).

The cyclic polyols triquinol $[C(OH)_2]_6$ and leuconic acid $[C(OH)_2]_5$ have been known since the previous century[2,3]. A third compound of this class, octahydroxycyclobutane $[C(OH)_2]_4$, was first synthesized nearly two decades ago[4]. Except for a few reports concerning their structures, ring cleavage[5], and some condensation reactions with amines[6], the chemistry of these interesting and unique polyketohydrates has generally been neglected. They were, however, quickly recognized as ready precursors for the syntheses of the, as yet elusive, neutral cyclic oxocarbons[7].

Utilizing the well known high reactivity of certain organoboron reagents towards hydroxyl groups[8], we hoped, through a sequence of borylation – deoxyborylation, to facilitate the dehydration of these ketohydrates. In this report we describe the reaction of one of these, octahydroxycyclobutane (**1**), with various organoboron reagents. Compound **1** was expected to have special properties because of its strained four-membered ring and the sterically rigid hydroxyl groups.

Formation of Tetrakis[organoboranediylbis(oxy)]cyclobutanes 2

A suspension of **1** in mesitylene reacted with triethylborane (activated with diethyl-boryl pivalate[8]) in the expected fashion to release eight equivalents of ethane. A mass spectroscopic analysis of the major product component revealed the presence of a compound with a molecular ion of m/e 336 and a fragmentation pattern in conformity with structure **2a**. The same compound could easily be isolated when **1** was reacted with an excess of triethylboroxine in refluxing toluene.

Compound **2a** as well as the *n*- and isopropyl (**2b, c**) and the phenyl analogues (**2d**) could also be obtained in nearly quantitative yields by reacting **1** with the corresponding alkyl- or phenyldichloroboranes.

2a - d
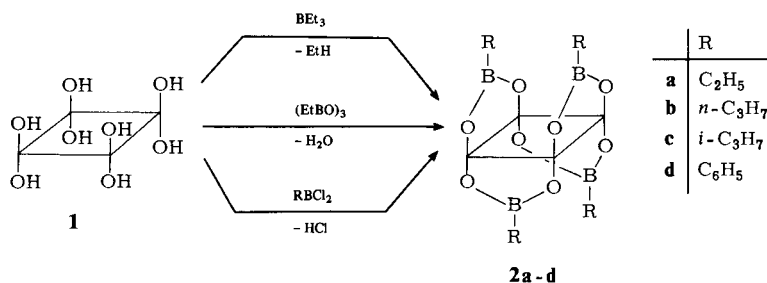
The ^{1}H NMR spectrum of **2a** showed a multiplet at 0.9 ppm resulting from B − Et groups and the ^{13}C NMR spectrum had a singlet at 109.14 ppm, a quartet at 6.82 ppm and a broad triplet at 3.0 ppm. The ^{11}B NMR spectrum showed a single peak at 37.1 ppm in agreement with $EtBO_2$ groupings in strained five-membered rings[9]. The gas chromatograms of **2a − c** showed only one peak indicating the formation of one of the two possible isomers. In all four derivatives the mass spectroscopic fragmentation patterns were essentially the same, albeit with different peak intensities. The absence of an $M^+/2$ peak indicates the exclusive formation of the less symmetrical isomer, as veri-fied by X-ray analysis, vide infra.

Chemical Reactivity of 2

The compounds **2a − d** are stable in an atmosphere of dry oxygen, survive flash pyrolysis at 550°C, and remain intact when irradiated in an argon atmosphere with a medium pressure Hg-lamp. In contrast to 1,3,2-dioxaborolane rings derived from simple 1,2-diols[10], the boranediylbis(oxy) groups in **2** are a part of a poly-acetal moiety and hence show different reactivities towards various reagents.

Reactions of 2 with Tertiary Amines

The addition of pyridine to ethereal solutions of **2a − d** causes the immediate preci-pitation of the pyridine addition complexes. Depending on the amount of pyridine added, adducts with up to four pyridine molecules per molecule of **2** could be isolated. However, the most stable species obtained were the 1:2 adducts. These could even be sublimed in vacuum and recrystallized from organic solvents. The room temperature

^{11}B NMR as well as the 80 MHz ^{1}H NMR spectra of the 1:2 adduct of 2a in $CDCl_3$ showed only one [11]B signal at 29.1 ppm and only two ^{1}H signals at 0.76 ppm (triplet) and 0.60 ppm (quartet) for all four B − Et groups, respectively. The upfield shift of the boron signal from δ = 37.1 to 29.1 in the adduct and the separation and shifting of the signal for the B − CH_2 group to higher field in the ^{1}H NMR spectrum are indicative of at least a partial sp^3 hybridization of the boron atoms.

At first it was thought that in these 1:2 adducts one pyridine molecule would be in a state of fast exchange between two B-atoms at the apices of the molecule, resulting in the unique polycyclic system 3. An X-ray structural analysis[11], however, revealed that contrary to this assumption the two pyridine molecules are bonded to two of the boron atoms from the *exo* side, forming sp^3 boron atoms and leaving the two remaining B-atoms in the sp^2 configuration as in 4. This finding, however, does not exclude the existence of a species similar to 3 in solution.

3   4
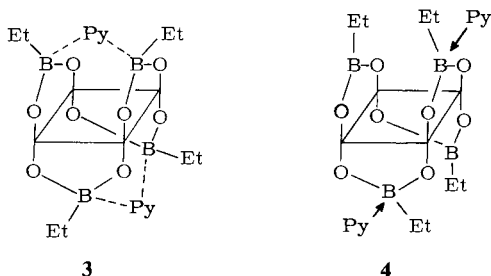
Reactions of stronger bases such as trimethylamine or quinuclidine with 2a or d depending on the amount of the amine used, or the reaction time, resulted in either the formation of a 1:2 amine adduct of 2, or the breakdown of 2 with the formation of a trimethylamine adduct of triethyl- or triphenylboroxine and a carbonyl-containing substance, the structure of which is still under investigation.

The ease of adduct formation in 2 seems to be a unique feature resulting from the presence of the acetal groupings of high electronegativity in the rings which consequently makes the boron atoms more electrophilic than in the comparable 1,3,2-dioxaborolanes in carbohydrates[12] or in tetrahydroxycyclobutanes. The latter show no significant chemical shift in their ^{11}B NMR spectra when obtained in pyridine as solvent[12,13].

Alcoholyses of 2

Organoboranediylbis(oxy) groups are generally easily solvolyzed when treated in protic solvents such as water or alcohols releasing the corresponding 1,2-diols[14].

In a similar reaction the compounds 2a − c were easily deborylated with methanol at room temperature and ring-opened to give dimethyl dihydroxyfumarate (5) in 90% yields. The latter was O-acetylated to give mixtures of the E/Z isomers 6 (g.l.c. ratio 61:39). The structures of 5 and 6 were proven by comparison with authentic materials.

5   6
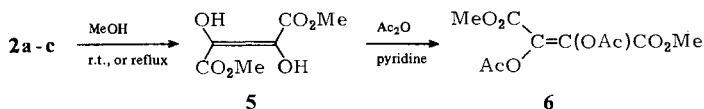
The reactions of **2a** with [D$_4$]methanol and of **2d** with methanol, both at room temperature, removed only two of the boron groups giving the tetrakis(deuteriomethoxy) and the tetramethoxy compounds **7a** and **7b**, respectively, in high yields. Refluxing **2a** in [D$_4$]methanol for 18 hours produced the deuterated analogue of **5** in 18% yield. The main products were the two isomers of the diester **10a**. Similarly, the continued refluxing of **2d** in methanol for 64 hours converted the initially formed **7b** into compounds **10b** and **8, 9, 11**. The distillation fraction containing compounds **10b** and **11** could be further deborylated to **5** on refluxing with methanol containing some small amounts of water. Compound **5** was also obtained from **7b** in one step by refluxing in methanol in the presence of a little water. The reaction of **2d** in refluxing [D$_4$]methanol afforded the diester **10a** after 72 h in 93% yield (by g.l.c.).

Attempted deborylation of **2d** with ethanol gave intractable mixtures, however, addition of catalytic amounts of boron trifluoride etherate resulted in the formation of the ethyl analogue **7c** in 82% yield. These reactions are summarized in Scheme 1.

Scheme 1
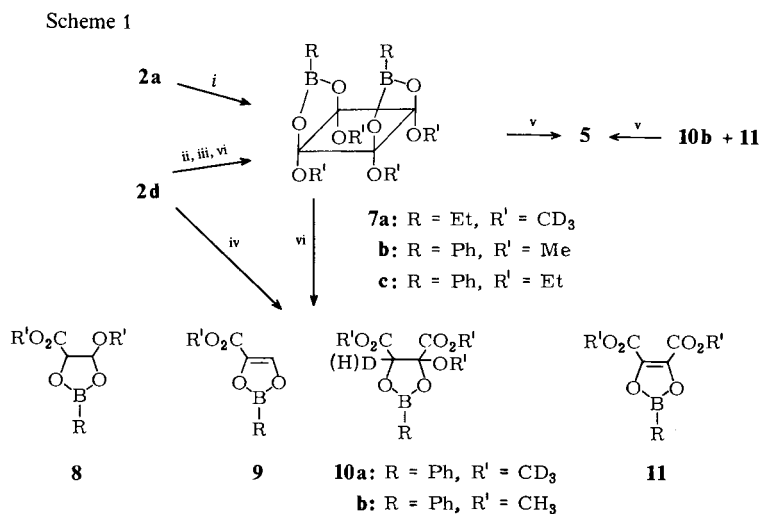
i = CD$_3$OD, r.t.; ii = MeOH, r.t.; iii = EtOH, BF$_3$, r.t.;
iv = CD$_3$OD, reflux; v = MeOH, H$_2$O, reflux; vi = MeOH, reflux.

The structural assignments for **7b** are based on analytical data, ^{1}H NMR, the appearance of a single peak for the cyclobutane carbon atoms at $\delta = 107.45$ in its ^{13}C NMR spectrum, and on the mass spectroscopic fragmentation giving the base peak at m/e 206, corresponding to the M$^+$/2 ion. Similarly, compound **7a** did not produce a molecular ion instead the first fragment ion observed at m/e 266 corresponded to M$^+$ − CD$_3$OC=O and the base peak at m/e 164 to M$^+$/2. The relative stereochemistry of the two dioxaborolane rings in **7** although not determined should, precluding rearrangements of the RBO groups during the formation of **7**, be as shown the *cis* configuration.

Compounds **10a** + **b** like **7a** + **b** did not show a molecular ion in their conventional mass spectra (E. I.). The first fragment ion at m/e 235 for compound **10b** corresponds to the loss of CO_2Me. However, chemical ionization using ammonia gas, produced a molecular ion at m/e 312 corresponding to $M^+ + NH_4^+$. **10b** showed a strong ester carbonyl absorption at 1750 cm^{-1} and its ^1H and ^{13}C NMR spectra (cf, experimental section) are in agreement with structure **10**. The structures for compounds **8**, **9**, and **11** are based on their ^1H NMR and mass spectra.

Any discussion of the mechanism for these reactions with alcohols, due to the complexity of the poly-equi-functionality of compound **2** can at present be only speculative. However, note should be taken that in contrast to the generally accepted mode of action of alcohols in deborylation reactions, where the prime position of nucleophilic attack is assumed to be the boron atom, in this special case, where strained acetalic positions are available as well, the C – O rather than B – O bond formation and cleavage appear to initiate the formation of **7**. Furthermore, as 2,3-dihydroxybutene-dicarboxylic acid derivatives are frequently formed in many reactions of octahydroxy-cyclobutane and its derivatives[13] the mechanistic Scheme 2 for the formation of compound **10** and **5**, described in this report, can serve to rationalize the mode of this general ring-opening reaction.

Scheme 2
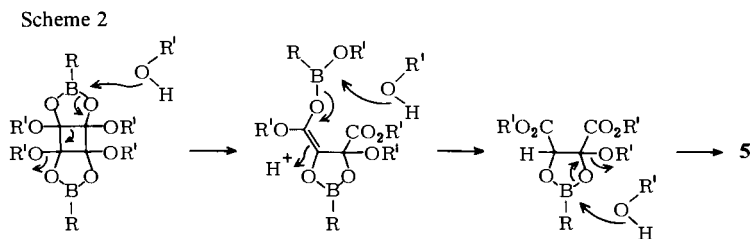
The reduced reactivity of the intermediates **7b** and **10b** in methanol and of **7a** and **10a** in deuterated methanol can be attributed to decrease of Lewis acidity of boron, due to electronic overlap from the aromatic ring to the empty p_z orbital of boron in the former and the decreased activity of deuterated methanol in the latter case.

Experimental Part

Melting points were determined in sealed capillary tubes with a Büchi melting point apparatus and are uncorrected. – ^1H NMR spectra: Varian EM 360 or Bruker WP 80. ^{11}B NMR spectra: Varian A 60 or XL 100. ^{13}C NMR spectra: XL 100. The internal standards were tetramethylsilane for ^1H and ^{13}C and boron trifluoride etherate for ^{11}B measurements. – Mass spectra: Varian CH 5.

Reaction of **1** *with triethylborane:* To a suspension of 2.0 g (10.9 mmol) of **1** in 25 ml of mesitylene were added 10.0 g (102 mmol) of activated triethylborane[8] slowly at room temperature. When the gas evolution slowed down the mixture was heated to reflux. A total of 2100 ml (87 mmol) of ethane evolved, resulting in a clear yellow solution. The solvent, excess reagent and

the volatiles were removed at room temperature in high vacuum. To the residue, a yellow slurry, pentane was added and the small amount of white solid removed. The filtrate was distilled (b.p. $70 - 80\,°C/10^{-3}$ Torr) to yield 2.8 g of a yellow liquid. This was shown by g.l.c. to be a complex mixture. The mass spectrum of the main component showed a molecular ion at $m/e = 336\,(M^+,$ B_4, 3%); 307 (B_4, 10); 280 (10); 279 (B_4, 45); 252 (B_3, 10); 223 (B_3, 90); 196 (B_2, 100); 140 (B_1, 20).

1,2:2,3:3,4:4,1-Tetrakis[ethylboranediylbis(oxy)]cyclobutane (**2a**) *from* **1** *and triethylboroxine:* A suspension of 2.3 g (12.3 mmol) of **1** in a solution of 6.3 g (33 mmol) of triethylboroxine in 70 ml of toluene was refluxed until dissolution was complete (about 1 h). Most of the solvent, water and the ethylboronic acid formed were distilled off at atmospheric pressure, followed by removal of all volatiles in vacuum. Chloroform was added to the light brown residue and filtered. The filtrate on evaporation of the solvent was distilled at high vacuum (b.p. $77\,°C/10^{-3}$ Torr) to give 3.7 g (90% yield) of a colourless liquid **2a** which solidified on cooling; m.p. $49 - 50\,°C$. $-$ ^{1}H NMR (60 MHz, $CDCl_3$): $\delta = 0.90$ (br). $-$ ^{13}C NMR ($CDCl_3$): $\delta = 109.14$ (s); 6.82 (q); 3.0 (tbr.). $-$ ^{11}B NMR (neohexane): $\delta = 37.1$. $-$ MS: $m/e = 336\,(M^+)$.

$C_{12}H_{20}B_4O_8$ (335.6)   Calcd. C 42.96 H 6.01 B 12.89   Found C 42.94 H 5.92 B 12.94

Bispyridine adduct **4** *of* **2a**: To a solution of 3.0 g (8.9 mmol) of **2a** in 35 ml of ether was added dropwise during 1 1/2 h a solution of 1.4 g (17.7 mmol) of pyridine in 15 ml of ether. The white solid that separated was filtered and washed thoroughly with ether and dried at high vacuum. Recrystallized from acetone/pentane as prisms, m.p. $154\,°C$ (dec.). $-$ ^{1}H NMR (80 MHz, $CDCl_3$): $\delta = 8.86$ (d of m, 4H); 8.01 (m, 2H); 7.62 (d of d, 4H); 0.76 (t, 12H); 0.60 (q, 8H). $-$ ^{11}B NMR ($CHCl_3$): $\delta = 29.1$.

$C_{22}H_{30}B_4N_2O_8$ (493.8)   Calcd. C 53.52 H 6.12 B 8.76 N 5.67
                                 Found C 53.54 H 6.16 B 8.68 N 5.81

1,2:2,3:3,4:4,1-Tetrakis[propylboranediylbis(oxy)]cyclobutane (**2b**): To a stirred suspension of 6.0 g (32.6 mmol) of **1** in 70 ml of benzene at $60\,°C$ was added dropwise 17.1 g (137.0 mmol) of dichloropropylborane (a mixture of approximately 83% *n*-$PrCl_2$ and 17% *i*-$PrCl_2$). After 2 h the solid had dissolved and a yellow solution resulted. The stirring was continued for 5 h until the evolution of HCl gas ceased. A small amount of solid had formed which was filtered off. The filtrate was evaporated in vacuum and the reside distilled at high vacuum (b.p. $115 - 116\,°C/10^{-3}$ Torr) to give 10.1 g (79% yield) of a colourless liquid, g.l.c. showed two components in 85 and 13% corresponding to **2b** and the isomer with three *n*-propyl and one isopropyl groups. $-$ ^{1}H NMR (60 MHz, $CDCl_3$): $\delta = 1.5$ (m, 8H); 1.0 (m, 20H). $-$ ^{11}B NMR ($CHCl_3$): $\delta = 38.3$. $-$ ^{13}C NMR ($CDCl_3$): $\delta = 109.21$ (s); 16.65 (t + q); 13.0 (br.). $-$ MS: $m/e = 392\,(M^+, B_4, 2\%)$; 349 ($B_4$, 15); 322 (17); 321 ($B_4$, 40); 294 ($B_3$, 8); 251 ($B_3$, 28); 224 ($B_2$, 100); 154 ($B_1$, 20).

$C_{16}H_{28}B_4O_8$ (391.7)   Calcd. C 49.08 H 7.21 B 11.04   Found C 49.03 H 7.12 B 10.96

1,2:2,3:3,4:4,1-Tetrakis[isopropylboranediylbis(oxy)]cyclobutane (**2c**): A suspension of 1.0 g (5.4 mmol) of **1** in 30 ml of benzene was reacted as in above experiment with 3.95 g (31.7 mmol) of dichloroisopropylborane. The liquid product **2c** was vacuum distilled (b.p. $87\,°C/10^{-3}$ Torr). $-$ ^{1}H NMR (80 MHz, $CDCl_3$): $\delta = 1.30$ (m, 4H); 1.04 (d, 24 H). $-$ ^{11}B NMR ($CDCl_3$): $\delta = 38.0$. $-$ MS: $m/e = 392\,(M^+, B_4, 2\%)$; 349 ($B_4$, 30); 322 (20); 321 ($B_4$, 40); 294 ($B_3$, 5); 251 ($B_3$, 100); 224 (15).

$C_{16}H_{28}B_4O_8$ (391.7)   Calcd. C 49.08 H 7.21   Found C 49.23 H 7.11

1,2:2,3:3,4:4,1-Tetrakis[phenylboranediylbis(oxy)]cyclobutane (**2d**): A suspension of 2.0 g (10.9 mmol) of **1** in a solution of 6.9 g (43.5 mmol) of dichlorophenylborane in 40 ml of benzene was heated to $60\,°C$ for 3 h. The gas evolution ceased and solution was complete. Pentane (100

ml) was added and allowed to crystallize to give 5.3 g (93% yield) of white prisms **2d**; m.p. 204 – 205 °C. – ^{11}B NMR: δ = 30.0. – MS: m/e = 528 (M$^+$, B$_4$, 10%); 500 (B$_4$, 18); 429 (16); 423 (B$_4$, 18); 396 (B$_3$, 40); 292 (B$_2$, 84); 188 (B$_1$, 30); 104 (B$_1$, 100).

$C_{28}H_{20}B_4O_8$ (527.8)   Calcd. C 63.73 H 3.82 B 8.19   Found C 63.69 H 3.89 B 7.82

Methanolysis of **2b**. *Formation of dimethyl dihydroxyfumarate* (**5**): A solution of 2.0 g of **2b** was refluxed for 1 h in 16 ml of methanol. On cooling 0.8 g (90%) of white needles separated, m.p. 159 – 160 °C. – ^{1}H NMR (60 MHz, [D$_6$]DMSO): δ = 7.5 (br., 2H); 3.7 (s, 6H). – ^{13}C NMR ([D$_6$]DMSO): δ = 164.8 (s); 132.3 (s); 51.7 (q). – MS: m/e = 176 (M$^+$, 40%); 148 (4); 120 (6); 117 (35); 92 (38); 88 (40); 60 (100); 45 (60); 33 (95).

$C_6H_8O_6$ (176.1)   Calcd. C 40.92 H 4.58   Found C 41.07 H 4.86

Methanolysis of **2a**: From a solution of 1.0 g of **2a** in 5 ml of methanol after standing at room temperature overnight separated 0.3 g of **5** in form of white needles, m.p. 159 – 160 °C (Lit.: 175 – 184 °C[15]; 165 – 173 °C[16]).

Dimethyl diacetoxyfumarate (**6**): The diol **5** (0.11 g, 0.63 mmol) was dissolved in 3 ml of a 1:2 mixture of acetic anhydride/pyridine and left overnight. The volatiles were evaporated in vacuum and the residue sublimed at 100 °C and 10^{-3} Torr to give 0.15 g (88%) of a white solid, m.p. 102 – 105 °C (Lit.[16] 105 – 108 °C). – ^{1}H NMR (60 MHz, CDCl$_3$): δ = 3.8 (s, 6H); 2.2 (s, H); 2.18 (s, H). – ^{13}C NMR (CDCl$_3$): δ = 168.0 (s); 166.9 (s); 161.4 (s); 160.6 (s); 137.7 (s); 135.5 (s); 52.99 (q); 20.3 (q); 20.1 (q). – MS: m/e = 260 (M$^+$, 1%); 218 (3); 187 (4); 176 (25); 43 (100).

$C_{10}H_{12}O_8$ (260.2)   Calcd. C 46.16 H 4.65   Found C 46.19 H 4.65

Reaction of **2a** *with [D$_4$]methanol at room temperature. Formation of 1,2,3,4-tetrakis(deuteriomethoxy)-1,2:3,4-bis[ethylboranediylbis(oxy)]cyclobutane* (**7a**): A solution of 0.9 g (2.7 mmol) of **2a** in 3.5 ml of [D$_4$]methanol was stirred at room temperature for 36 h. The volatiles were removed at reduced pressure and the residue sublimed in high vacuum at 50 °C to give 0.7 g (79% yield) of colourless prisms, m.p. 57 – 58 °C. – MS: m/e = 266 (M$^+$ – CD$_3$OC=O, 10%), 164 (M$^+$/2, 100).

Reaction of **2a** *with refluxing [D$_4$]methanol. Formation of* [D$_8$]-**5**: A solution of 1.1 g of **2a** in 4 ml of [D$_4$]methanol was refluxed for 18 h. The crystalline solid that separated was filtered to give 0.11 g (18% yield) of [D$_8$]-**5**, m.p. 167 – 170 °C. – IR (nujol film): 2370 (O – D), 2240, 2080 (CD$_3$), 1650 cm^{-1} (C=O). – MS: m/e = 184 (M$^+$).

Methanolysis of **2d**: A suspension of 0.2 g (0.4 mmol) of **2d** in 2 ml of methanol was stirred at room temperature overnight. The white crystals formed were collected to give 0.14 g (89% yield) of **7b**, m.p. 210 °C. – ^{1}H NMR (60 MHz, [D$_6$]acetone): δ = 7.9 (m, 4H); 7.5 (m, 6H); 3.55 (s, 12H). – ^{13}C NMR ([D$_6$]acetone): δ = 135.27 (d); 132.32 (d); 127.92 (d); 107.45 (s); 53.80 (q). – MS: m/e = 353 (M$^+$ – 59, 7%); 335 (2); 307 (2); 262 (2); 249 (4); 231 (4); 206 (M$^+$/2, 100); 203 (10); 191 (65); 119 (80); 59 (38).

$C_{20}H_{22}B_2O_8$ (412.0)   Calcd. C 58.30 H 5.38 B 5.25   Found C 58.09 H 5.36 B 4.93

Reaction of **2d** *in refluxing methanol:* A suspension of 6.9 g (11.2 mmol) of **2d** in 100 ml of methanol was refluxed. The solid dissolved and after about 1 h heavy suspension of a white solid was formed which on further reflux dissolved after about 24 h. The heating was continued for a total of 64 h, cooled and the small amount of white solid formed filtered to give 0.2 g (10% yield) of **5**. The filtrate was evaporated to dryness and distilled at high vacuum. Two fractions distilled over.

Fraction A, about 0.2 g, b.p. 67 °C/10^{-3} Torr, showed two carbonyl bands at 1760 and 1740 cm^{-1}. G.l.c. (20 m dexil capillary column) showed mainly two components (22 and 61%). – ^{1}H

NMR (CDCl$_3$, 80 MHz): δ = 8.24 m (2H), 7.99 m (3H), 6.62 s (1H), 3.75 s (3H) (minor component compound 9) and 7.88 m (2H), 7.42 m (3H), 5.60 d (1H, J = 6 Hz), 4.96 d (1H, J = 6 Hz), 3.84 s (3H), 3.48 s (3H) (compound 8 *cis*); 7.88 m (2H), 7.42 m (3H), 5.46 d (1H, J = 3 Hz), 4.71 d (1H, J = 3 Hz), 3.76 s (3H), 3.51 s (3H) (compound 8 *trans*). – MS: Two components: m/e = 204 (M$^+$, 9) and m/e = 236 (M$^+$, 8).

Fraction B, 2.2 g, b.p. 114°C/10^{-3} Torr, a viscous liquid, showed a carbonyl absorption at 1750 br cm^{-1}, g.l.c. (20 m dexil capillary column) showed mainly two components (77 and 18%).

Component A: ^{1}H NMR (CDCl$_3$, 80 MHz): δ = 7.92 m (2H), 7.40 m (3H), 5.11 s (1H), 3.83 s (3H), 3.75 s (3H), 3.47 s (3H) (compound 10b *cis*); 7.92 m (2H), 7.40 m (3H), 4.91 s (1H), 3.90 s (3H), 3.72 s (3H), 3.49 s (3H) (compound 10b *trans*). – ^{13}C NMR (CDCl$_3$, 25.16 MHz): δ = 167.8, 167.4, 166.8, 166.7 (ester C=O); 135.2 d, 132.3 d, 127.8 d, 124 br (aromatic C); 106.3 s (C-2, *trans*), 104.2 s (C-2, *cis*), 84.1 d (C-3, *cis*), 82.0 d (C-3, *trans*); 53.1, 52.9, 52.8, 52.6, 52.5, 52.4 (O–Me).

Component B (11): ^{13}C NMR: δ = 166.4 (ester C=O); 158.5 (C=C), 134.8 d, 132.6 d, 128.1 d (aromatic C); 52.2 (O–Me).

MS: Two components: major component, m/e = 294 (M$^+$, observed from C.I. spectrum using NH$_3$ gas), 235 (M$^+$ – CO$_2$Me, 50%), 176 (30), 119 (100); minor component, m/e = 262 (M$^+$).

Reaction of 2d with refluxing [D$_4$]methanol: A suspension of 0.19 g (0.36 mmol) of 2d in 1.5 ml of [D$_4$]methanol was refluxed. After 1 d a white solid was formed which on further heating dissolved. After 72 h the volatiles were removed at reduced pressure. To the residue 1 ml of ether was added and the ether phase separated from the white solid residue. This solid was identical (infrared spectrum) to triphenylboroxine. The ether solubles analyzed by g.l.c. on a 20 m dexil capillary column showed one component (10a, 93%) with an identical retention time as the major component of fraction B (cf. above experiment). – MS: Three components: major component, m/e = 304 (M$^+$, observed from C.I. spectrum using NH$_3$ gas), 268 (M$^+$ – CD$_3$OD, 5%), 242 (M$^+$ – CO$_2$CD$_3$, 50), 180 (30), 122 (100); minor component A, m/e = 156 (M$^+$, C$_6$H$_5$B(OCD$_3$)$_2$); minor component B, m/e = 312 (M$^+$, (PhBO)$_3$).

Hydrolysis of fraction B. Formation of 5: The distillation fraction B, 0.79 g, was dissolved in 4 ml of methanol, 5 drops of water added and refluxed for 6 h. The white solid that separated on cooling was filtered to give 0.32 g (70% yield) of 5.

Reaction of 7b with methanol/water. Formation of 5: A suspension of 0.5 g (1.2 mmol) of 7b was stirred in a refluxing solution of 10 ml of methanol and 0.5 ml of water. After 3 h a new white solid had formed. The solution was cooled and filtered to give 0.17 g (80% yield) of 5.

Ethanolysis of 2d: A suspension of 0.7 g (1.3 mmol) of 2d in 5 ml of ethanol and 0.2 ml of boron trifluoride etherate was stirred at room temperature for 2 h. At reduced pressure the solution was evaporated to about 1/2 the original volume, a white crystalline solid 7c, 0.5 g (82%) separated, m.p. 116–117°C. – ^{1}H NMR (60 MHz, CDCl$_3$): δ = 7.95 (m, 4H); 7.45 (m, 6H); 3.90 (q, 8H); 1.25 (t, 12H). – ^{11}B NMR (CDCl$_3$): δ = 30.0. – ^{13}C NMR (CDCl$_3$): δ = 135.1 (d); 132.1 (d); 127.9 (d); 107.5 (s); 62.4 (t); 15.5 (q). – MS: m/e = 395 (M$^+$ – 73, 5%); 322 (2); 293 (4); 234 (M$^+$/2, 70); 217 (7); 205 (20); 189 (10); 177 (63); 105 (100).

C$_{24}$H$_{30}$B$_2$O$_8$ (468.1)   Calcd. C 61.58 H 6.46 B 4.62   Found C 61.43 H 6.05 B 4.96

[1] This publication is at the same time part LVI of the series "Boron Compounds". For part LV see *K. M. Taba* and *W. V. Dahlhoff,* Synthesis **1982**, 652.

[2] *I. U. Lerch,* Liebigs Ann. Chem. **124**, 20 (1862).

[3] *H. Will,* Liebigs Ann. Chem. **118**, 177 (1858).

[4] *R. West, H. Y. Nin,* and *M. Ito,* J. Am. Chem. Soc. **85**, 2584 (1963).

[5] *W. Städeli, R. Hollenstein,* and *W. von Philipsborn,* Helv. Chim. Acta **60**, 948 (1977); *S. Skujins, I. Delderfield,* and *G. H. Webb,* Tetrahedron **24**, 4805 (1968).

[6] For these reactions and other background information see the review on the chemistry of the "Oxocarbons", in "The Chemistry of the Carbonyl Group", Vol. II, *J. Zawicky,* Ed., Wiley New York, N. Y. 1970; *M. B. Rubin,* Chem. Rev. **75**, 177 (1975); and *R. West,* "Oxocarbons", Academic Press, New York, N. Y. 1980.

[7] *R. Nietzki* and *T. Benckiser,* Ber. Dtsch. Chem. Ges. **18**, 499, 1833 (1885); **19**, 293 (1886); *F. Henle,* Liebigs Ann. Chem. **350**, 330 (1906); *F. Bergel,* Ber. Dtsch. Chem. Ges. **62 B**, 490 (1929).

[8] *R. Köster, W. Fenzl,* and *G. Seidel,* Liebigs Ann. Chem. **1975**, 352.

[9] *H. Nöth* and *B. Wrackmeyer,* NMR Basic Principles and Progress **14**, Nuclear Magnetic Resonance Spectroscopy of Boron Compounds, p. 141, Springer Verlag, Berlin 1978.

[10] *W. V. Dahlhoff* and *R. Köster,* Liebigs Ann. Chem. **1975**, 1625.

[11] *C. Krüger* and *Y. H. Tsay,* unpublished results.

[12] *W. V. Dahlhoff,* private communication.

[13] *M. Yalpani,* unpublished results.

[14] *W. V. Dahlhoff* and *R. Köster,* Heterocycles **18**, 421 (1982).

[15] *E. F. Hartree,* J. Am. Chem. Soc. **75**, 6244 (1953).

[16] *S. Goodwin* and *B. Witkop,* J. Am. Chem. Soc. **76**, 5599 (1954).

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