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Hydrated Oxocarbons, II[1a,b]

Preparation of a New Class of Thermochromic Boron Heterocycles from Octahydroxycyclobutane or Dihydroxybutenedioic Acid

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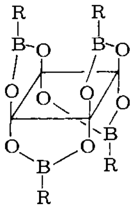
The reaction of octahydroxycyclobutane (**2**) with activated triethylborane gives a low yield of the thermochromic 2,6-diethyl-1,3,5,7-tetraoxa-2,6-dibora-4,8-octalindione (**5b**) by ring cleavage of **2**. Additional examples of this novel class of compounds have also been prepared directly by reacting dihydroxyfumaric acid (**6**) with various alkyl- or arylboranes. With the exception of the *tert*-butyl- (**5f**) and the aryl derivatives **5l, m**, the new compounds **5** undergo a temperature dependent colour change (yellow/colourless) in the solid state. The thermochromic transition temperature T_{th} depends on the substituents and lies between – 5 and 150 °C.

Hydratisierte Oxokohlenwasserstoffe, II[1a,b]

Darstellung einer neuen Klasse von thermochromen Bor-Heterocyclen aus Octahydroxycyclobutan oder Dihydroxybutendisäure

Die Reaktion von Octahydroxycyclobutan (**2**) mit aktiviertem Triethylboran ergibt in geringer Ausbeute unter Ringaufspaltung von **2** das thermochrome 2,6-Diethyl-1,3,5,7-tetraoxa-2,6-dibora-4,8-octalindion (**5b**). **5b** sowie andere Derivate dieser neuen Verbindungsklasse lassen sich aber in hohen Ausbeuten direkt aus Dihydroxyfumarsäure (**6**) mit verschiedenen Alkyl- oder Arylboranen herstellen. Mit Ausnahme der *tert*-Butyl- (**5f**) und der Aryl-Derivate **5l, m** verändern sämtliche Verbindungen **5**, abhängig vom Substituenten, zwischen – 5 und 150 °C im Festkörper ihre Farbe reversibel von gelb nach farblos.

We have previously reported that octahydroxycyclobutane (**2**) reacts with trialkylboranes, dichloroorganylboranes, and trialkylboroxines to give the pentacyclic compounds **1**[1)].



1

As a by-product of the reaction of trialkylboranes activated by diethyl(pivaloyloxy)borane as catalyst[2)] we consistently observed the formation of a small quantity (≈5%)

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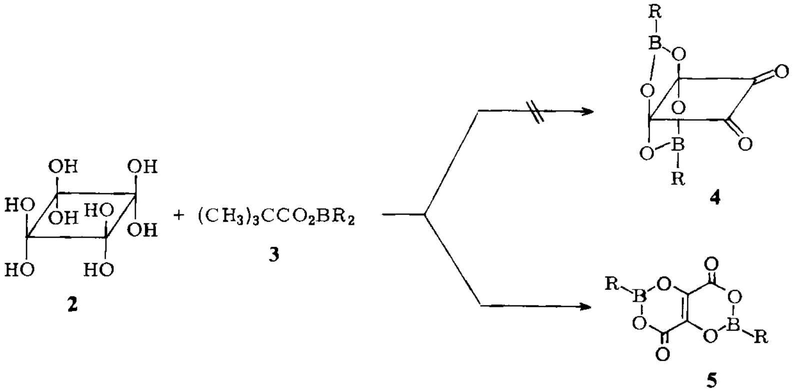
of a microcrystalline, high melting, and in non-protic solvents very insoluble compound which showed pronounced thermochromic behaviour. By altering the borylating agent to pure diethyl(pivaloyloxy)borane **3** (R = Et)[3], the reagent for ethylboranediylation[4], the yield of the thermochromic compounds **5** could be increased to about 50%. The temperature dependent colour changes observed were very sensitive to the substituents attached to the borylating agent. Thus the product obtained from (pivaloyloxy)dipropylborane with **2** is bright yellow at room temperature, but when heated to 70°C changes colour to silvery white without any observable change in the crystal shape. A similar change of colour was observed for the ethyl derivative, obtained from **3** (R = Et) and **2**, which is colourless at room temperature and bright yellow below −5°C. These effects are fully reversible.

The colourless form exhibits two strong carbonyl bands of nearly equal intensities at 1780 and 1733 cm^{-1} for the *B*-ethyl and at 1780 and 1733 cm^{-1} for the *B*-propyl derivative. On cooling below the thermochromic temperature these bands decrease in intensities considerably in the ethyl and disappear completely in the case of the propyl derivative. The decrease of the carbonyl band intensities, among other changes in the infrared spectrum, is accompanied by the formation of two new strong bands at about 1635 and 1545 cm^{-1}.

The ethyl derivative **5b** showed a molecular ion at *m/e* = 224 and analysed for $C_8H_{10}B_2O_6$. The ^1H NMR spectrum in deuterated dimethylsulfoxide showed only signals for the *B*-ethyl protons. A signal at $\delta = 7.6$ in the ^{11}B NMR spektrum is attributed to a RBO_2 group which is further coordinated to a strong donor, e.g., the solvent used. In the ^{13}C NMR spectrum, besides the signals for the *B*-ethyl carbons two singlets were observed at $\delta = 161.3$ and 135.0. These data and the successive losses of CO's from the molecular ion observed in the mass-spectrographic fragmentation pattern of these compounds are compatible with structure **4**.



R: See Table 1

The X-ray structure analysis[5] of the high temperature ("hot") form, however, revealed that these compounds have structure **5**, i.e., are organylborane derivatives of dihydroxybutenedioic acid (**6**). As a result of this structure determination, derivatives of **5** were subsequently prepared in yields up to 90% from the direct reaction of **6** with the corresponding triorganylboroxines or dimethoxy- and dihaloorganylboranes in refluxing benzene or toluene.

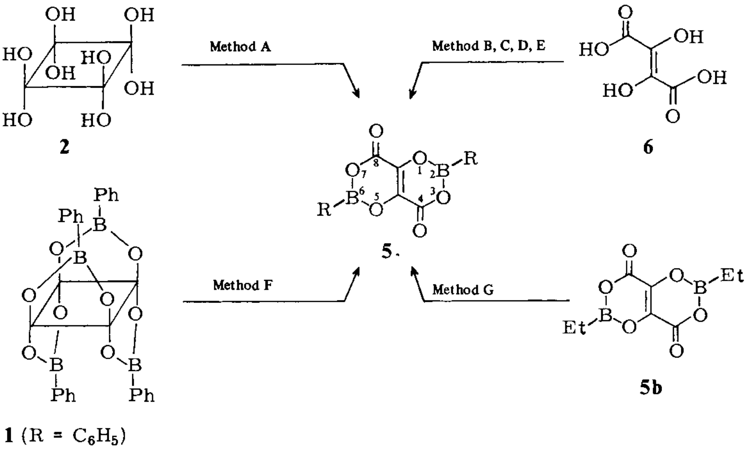
In some cases compounds **5** could also be prepared in high yield by thermal substituent exchange reactions. Thus the *p*-tolyl derivative **5m** was formed in 80% yield by the reaction of **5b** with tri-*p*-tolylboroxine in refluxing benzene.

This exchange reaction, however, was less successful in the substitution of aryl by alkyl groups and one alkyl by another. Even after repeated treatment of, for example, **5b** with excess tricyclohexylboroxine, the product **5h** was a mixture with mixed substituents.

A further method for obtaining **5** was through the reaction of **1** with diethyl(pivaloyloxy)borane **3** (R = Et). In this way the phenyl derivative **5l** was formed in over 90% yield from **1** (R = Ph) and **3** (R = Et). These reactions are outlined in Scheme 1.

The mechanism of this conversion (**1** to **5**) and the related ring opening reaction of **2** to **5** is not clear. But it appears that the per-oxygenated cyclobutane ring is strained and in reactions with boron as well as several other reagents, as a result of an internal redox reaction, opens to form dihydroxyfumaric and maleic acid derivatives[1,6].

Scheme 1



	R
5a	Me
b	Et
c	*n*-Pr
d	*i*-Pr
e	*i*-Bu
f	*t*-Bu
g	*n*-C_6H_{13}
h	*c*-C_6H_{11}
i	*n*-C_8H_{17}
j	*n*-$C_{16}H_{33}$
k	$C_6H_5CH_2$
l	C_6H_5
m	*p*-$CH_3C_6H_4$

Method A: +R_2BOPv, R = Et, *n*-Pr
B: +R_2BOPv, R = Et, *i*-Pr, *c*-C_6H_{11}, *n*-C_6H_{13}, $C_6H_5CH_2$
C: +$(RBO)_3$, R = Et, *t*-Bu, C_6H_5
D: +CH_3BBr_2
E: +$RB(OCH_3)_2$, R = *i*-Bu, *n*-C_8H_{17}, *n*-$C_{16}H_{33}$
F: +Et_2BOPv
G: +(*p*-$CH_3C_6H_4BO)_3$

Pv = Pivaloyl = $(CH_3)_3CCO$

Compounds **5** showed pronounced substituent effects. Amongst the various derivatives prepared, the methyl and the ethyl derivatives **5a, b** were colourless at room temperature but turned yellow below −5 and +5 °C, respectively. With the exception of the aryl and the *tert*-butyl substituted compounds **5**, all others were yellow at room temperature and changed to colourless between +72 and +150 °C (cf Table 1). The

Table 1. Preparation of compounds **5** and their analytical and physical data

5	R	Me- thod	Yield (%)	IR (KBr) ν(C=O) cm^{-1} cold	hot	Dec.[a]	T_{th}[b]	Colour[c]	MS M$^+$ and characteristic fragments (rel. abundance)	Calcd. Found.	Analyses C	H	B
a	Me	D	80		1775, 1742	300	−5	pale yellow	196 (M$^+$, 20), 126 (10), 68 (100)	$C_6H_6B_2O_6$ (195.7)	36.81 36.74	3.09 3.18	11.05 11.02
b	Et	B/C	70/95	1630, 1545	1780, 1733	300	5	yellow	224 (M$^+$, 90), 140 (80), 68 (100)	$C_8H_{10}B_2O_6$ (223.8)	42.94 43.00	4.50 4.56	9.66 9.62
c	*n*-Pr	A	30	1635, 1540	1780, 1733	300	75	yellow	252 (M$^+$, 60), 224 (100), 68 (70)	$C_{10}H_{14}B_2O_6$ (251.8)	47.69 47.66	5.60 5.18	
d	*i*-Pr	B	50	1635, 1545	1780, 1733	200	150	yellow	252 (M$^+$, 100), 68 (60), 43 (75)	$C_{10}H_{14}B_2O_6$ (251.8)	47.69 48.05	5.60 5.42	
e	*i*-Bu	E	53	1630, 1545	1780, 1740	210	72	yellow	280 (M$^+$, 15), 238 (60), 43 (100)	$C_{12}H_{18}B_2O_6$ (279.9)	51.19 51.63	6.49 6.26	7.73 7.96
f	*t*-Bu	C	48		1775			white	280 (M$^+$, 30), 265 (45), 56 (100)	$C_{12}H_{18}B_2O_6$ (279.9)	51.49 51.66	6.49 5.98	7.73 7.52
g	*n*-Hex	B	37	1640, 1550	1780, 1740	300	95	yellow	336 (M$^+$, 100), 279 (18), 225 (25)	$C_{16}H_{26}B_2O_6$ (336.0)	57.19 56.80	7.81 7.43	
h	*c*-Hex	B	41	1645, 1550	1780, 1735	140	88	yellow	332 (M$^+$, 40), 304 (38), 222 (100)	$C_{16}H_{22}B_2O_6$ (332.0)	57.89 57.52	6.68 6.93	6.51 6.15
i	*n*-Oct	E	38	1640, 1545	1785, 1738	190	75	yellow	392 (M$^+$, 100), 253 (20), 43 (80)	$C_{20}H_{34}B_2O_6$ (392.1)	61.26 60.92	8.74 8.95	
j	*n*-$C_{16}H_{33}$	E	66	1645, 1550	1780, 1738	155	115	yellow	616 (M$^+$, 95), 71 (30), 42 (100)	[d]			
k	Benzyl	B	35	1630, 1545	1780, 1740	230	87/98	yellow/ orange	348 (M$^+$, 100), 202 (25), 118 (75)	$C_{18}H_{14}B_2O_6$ (347.9)	62.14 62.20	4.06 3.86	6.21 6.58
l	Phenyl	C/F	90/90		1770, 1740	300		white	320 (M$^+$, 45), 204 (15), 104 (100)	$C_{16}H_{10}B_2O_6$ (319.9)	60.08 60.19	3.15 3.03	
m	*p*-Tol	G	80		1770, 1750	296		white	348 (M$^+$, 90), 118 (100), 91 (38)	$C_{18}H_{14}B_2O_6$ (347.9)	62.14 61.90	4.06 4.30	

[a] Most of these compounds began to decompose slightly below the temperature indicated as evident by colouration of the initially white crystals to brown. The temperature shown is that at which extensive decomposition occured. – [b] The thermochromic temperature T_{th} is the temperature at which the colour of the crystalline **5** changes on cooling or warming from room temperature. – [c] Colour of the cold modification. – [d] **5j** could not be obtained analytically pure since it decomposed during sublimation or recrystallisation from toluene.

aryl derivatives **5l**, **m** are colourless solids and were found to remain unchanged even when cooled to −269 °C in liquid helium. Both showed the same characteristic carbonyl bands at about 1770 and 1740 cm^{-1} in their infra-red spectra, as those derivatives which were thermochromic. However in the case of these aryl derivatives the infra-red spectra showed no temperature sensitivity and remained unchanged even when cooled to −100 °C. Another surprising substituent effect ist the temperature stability of the white *tert*-butyl derivative **5f**. In contrast to all other examples, this compound showed only a single carbonyl band at 1775 cm^{-1} in its infra-red spectrum.

While thermochromic compounds are well known and include, among others, such varied structures as certain transition metal salts and complexes7), bianthrones8), spiropyrans9), and Schiff's bases of salicylaldehydes10), this effect, as compared in some cases in our laboratories, is particularly marked in this new series. In all the above cases the thermochromic property is postulated to be the result of *intra*-molecular structural rearrangements. In this new series of thermochromic compounds the reaction causing the colour change is, as will be discussed in conjunction with the results of the X-ray structural analysis presented in the accompanying paper5), an *inter*-molecular reaction involving the boron atoms of one and the carbonyl oxygens of the neighbouring molecules.

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Experimental Part

Melting points and thermochromic transition temperatures: Sealed capilary tubes, Büchi melting point apparatus, uncorrected. – NMR spectra: ^1H Varian EM 360 or Bruker WP 80, ^{11}B and ^{13}C Varian XL 100, internal standards TMS for ^1H and ^{13}C and $(C_2H_5)_2O-BF_3$ for ^{11}B. – Mass spectra: Varian MAT CH5.

General procedures for the preparation of 2,6-diorgano-1,3,5,7-tetraoxa-2,6-dibora-4,8-octalindiones **5**

Method A: 2,6-Dipropyl-1,3,5,7-tetraoxa-2,6-dibora-4,8-octalindione (**5c**) *from octahydroxycyclobutane* (**2**) *and (pivaloyloxy)dipropylborane* (**3**, R = *n*-Pr): **3** (R = *n*-Pr) (17.6 g, 88.8 mmol) was added dropwise during 20 min to a refluxing suspension of 2.0 g (10.9 mmol) of **2** in 25 ml of benzene. Gas evolution commenced and continued for 1 h. The solid dissolved giving initially an orange solution. At the end of the reaction 2.05 l of propane gas had evolved (calcd. 1.95 l) and white shiny crystals had separated which on cooling turned yellow. These were filtered and washed with pentane to give 0.90 g (33%), m.p. 300 °C (dec.).

Method B: 2,6-Diethyl-1,3,5,7-tetraoxa-2,6-dibora-4,8-octalindione (**5b**) *from dihydroxybutenedioic acid* (**6**) *and diethyl(pivaloyloxy)borane* (**3**, R = Et): A suspension of 2.05 g (13.8 mmol) of **6** and 17 g (100 mmol) of **3** (R = Et) was slowly heated to about 70 °C. On completion of gas evolution (1.3 l, calcd. 1.32 l) the mixture was cooled, hexane added and the crystalline **5b** filtered and washed with hexane. Yield 2.3 g (77%), m.p. 300 °C (dec.).

Method C: 2,6-Diphenyl-1,3,5,7-tetraoxa-2,6-dibora-4,8-octalindione (**5l**) *from* **6** *and triphenylboroxine:* From a suspension of about 0.60 g (4.0 mmol) of **6** and 0.80 g (7.9 mmol) of triphenylboroxine in about 500 ml of benzene about 250 ml of the benzene was removed by azeotropic distillation. The remaining suspension was cooled, filtered and the crystalline **5l** washed with hexane. Yield 1.2 g (94%), m.p. 300 °C (dec.).

Method D: 2,6-Dimethyl-1,3,5,7-tetraoxa-2,6-dibora-4,8-octalindione (**5a**) *from* **6** *and dibromomethylborane:* To 1.0 g (6.8 mmol) of **6** in 20 ml of benzene cooled to 0 °C was added 14 mmol of dibromomethylborane. On warming to room temperature gas evolution started and continued for about 15 min. The mixture was then slowly heated under reflux for about 1/2 h, then cooled, filtered, and the crystalline **5a** washed thoroughly with hexane. Yield 1.15 g (87%), m.p. 300 °C (dec.).

Method E: 2,6-Diisobutyl-1,3,5,7-tetraoxa-2,6-dibora-4,8-octalindione (**5e**) *from* **6** *and isobutyldimethoxyborane:* From a suspension of 3.4 g (23.0 mmol) of **6** and 6.0 g (46.1 mmol) of isobutyldimethoxyborane in 100 ml of toluene about 50 ml of the toluene was removed by azeotropic distillation. The remaining suspension was cooled, filtered, and the yellow crystalline **5e** washed with hexane. Yield 3.8 g (60%), m.p. 210 °C (dec.).

Method F: **5l** *from* **1** (R = Ph) *and diethyl(pivaloyloxy)borane* (**3**, R = Et): **1** (R = Ph) (0.60 g, 1.1 mmol) and **3** (R = Et) (0.80 g, 4.7 mmol) were stirred and heated at 80 °C for 6 h. After cooling 10 ml of pentane was added and filtered. The colourless solid was washed thoroughly with 5 ml portions of pentane. It was sublimed in vacuo at 150 – 170 °C to give 0.32 g (≈90%) of a white solid; m.p. 300 – 310 °C (dec.).

Method G: 2,6-Bis(4-methylphenyl)-1,3,5,7-tetraoxa-2,6-dibora-4,8-octalindione (**5m**) *from* **5b** *and tris(4-methylphenyl)boroxine:* A mixture of 60 mg (0.27 mmol) of **5b** and 0.50 g (1.41 mmol) of tris(4-methylphenyl)boroxine in 10 ml of benzene were refluxed for 2 h. During the reaction, the starting materials dissolved and the product precipitated as a crystalline solid. After cooling it was filtered and washed with benzene and pentane. Sublimation at 150 °C and high vacuum gave 70 mg (80%) of a colourless solid; m.p. 296 °C (dec.).

In all cases the products formed were essentially pure. Further purification to give an analytically pure sample was achieved either by high vacuum sublimation at ca. 130 – 150 °C or by crystallisation from a large volume of toluene. The yields shown in Table 1 are those of purified products.

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1) 1a) Part I: *M. Yalpani, R. Köster,* and *G. Wilke,* Chem. Ber. **116**, 1336 (1983). – 1b) This publication is also part LVII of the series "Boron Compounds"; for part LVI see ref.1a).

2) *R. Köster, H. Bellut,* and *W. Fenzl,* Liebigs Ann. Chem. **1974**, 54.

3) *W. V. Dahlhoff, W. Schüssler,* and *R. Köster,* Liebigs Ann. Chem. **1976**, 387.

4) *W. V. Dahlhoff* and *R. Köster,* J. Org. Chem. **41**, 2316 (1976).

5) *M. Yalpani, R. Boese,* and *D. Bläser,* Chem. Ber. **116**, 3338 (1983), accompanying paper.

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8) *P. Nata* and *D. H. Evans,* J. Am. Chem. Soc. **103**, 7041 (1981).

9) *J. H. Day,* Chem. Rev. **62**, 65 (1962).

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[33/83]