130. Propellanes

Part LXXXI[1])

Why are Tetrakis[organoboranediylbis(oxy)]cyclobutanes Formed without a Trace of the Isomeric Tetrakis-dioxabora[3.3.2]propellanes?

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Dedicated to Prof. Dr. *Rolf Huisgen* on the occasion of his 65th birthday

(9.V.85)

MNDO and STO-3G calculations rationalize the relative instability of the title propellanes vis-à-vis the title products that are formed exclusively.

Introduction. – The chemical understanding of molecules and the wise behavior stemming therefrom are so well-known that an additional example scarcely requires description. Nevertheless, we wished to gain some insight into the factors dictating exclusive production of the non-propellanic products **1b–e** in preference to the isomeric propellanes **2b–e** upon treatment of octahydroxycyclobutane by various ring-forming boron derivatives such as $RBCl_2$, *etc.* [2]. Such behavior could not be relegated merely to *chutzpah*[2]) on the part of the reactants.

We have, therefore, conducted MO calculations for a series of molecules **1a–8a**, using both semi-empirical and *ab initio* methods.

Results. – The geometries of **1a–8a** were fully optimized using the MNDO method [4a]. Single-point STO-3G calculations (a modified version of the *Gaussian 80* series was

Table. *Heats of Formation, Total Energies, and Relative Energies of* **1a–8a**

Molecule	ΔH_f° [kcal·mol^{-1}][a])	Rel. energies [kcal·mol^{-1}][a])	Total energies [hartrees][b])	Rel. energies [kcal·mol^{-1}][b])
1a	−464.7	0	−840.73001	0
2a	−440.2	24.5	−840.70051	18.5
3a	−413.4	14.0	−792.81972	8.1
4a	−423.9	3.5	−792.83019	1.5
5a	−427.4	0	−792.83260	0
6a	−425.9	1.5	−792.83110	0.9
7a	−431.9	11.9	−816.76460	9.1
8a	−443.8	0	−816.77912	0

[a]) MNDO. [b]) Single-point STO-3G calculations at the MNDO-optimized geometries.

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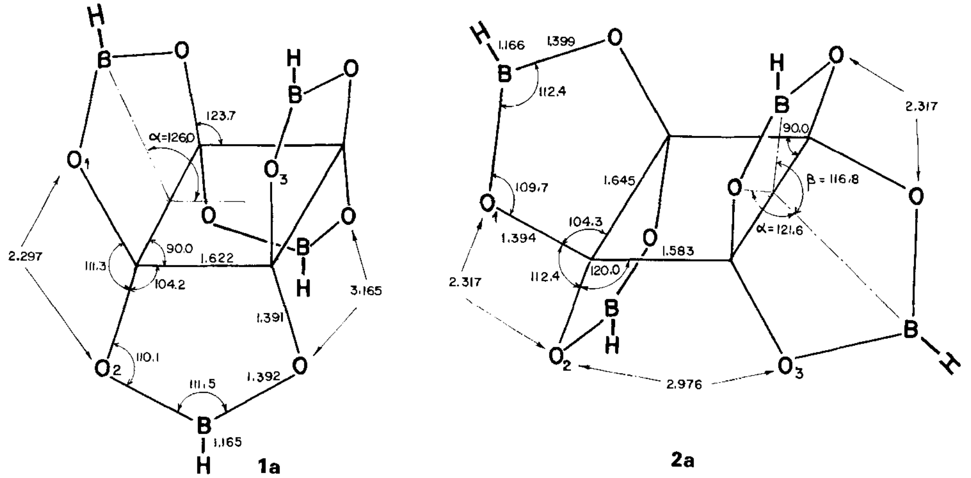
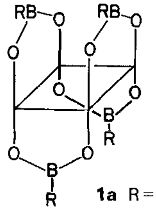
[1]) Part LXXX: [1].

[2]) See [3]. We dare not use the space required for the definition but any reader who cannot get this ref. may write to *D. G.*



1a **2a**

Fig. *MNDO-optimized geometries of* **1a** *and* **2a**. Bond lengths are given in Å and bond lengths in degrees. α is the dihedral angle between the dioxaborolane and the cyclobutane planes. β is the dihedral angle in **2** between two geminal dioxaborolane rings.



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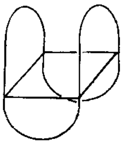
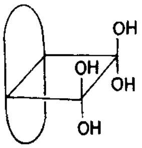
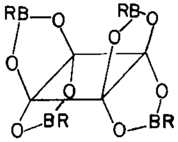




1a R = H
b R = Et
c R = Pr
d R = i-Pr
e R = Ph

1

3a



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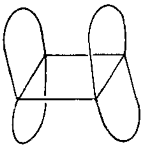
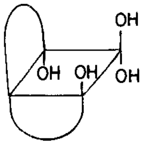
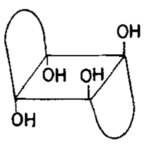




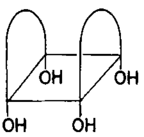
2a R = H
b R = Et
c R = Pr
d R = i-Pr
e R = Ph

2

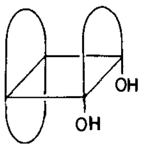
4a



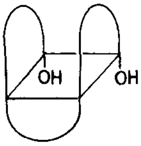
5a



6a



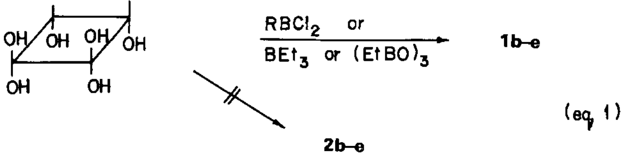
7a



8a

used: [4b]) at the MNDO-optimized geometries were then carried out. The calculated MNDO geometries of **1a** and **2a** are given in the Fig. and the energies of **1a**–**8a** appear in the *Table*.

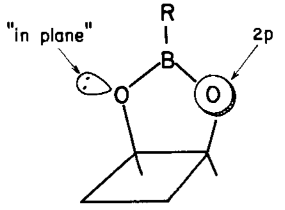
Discussion. – Exclusive formation of **1b–e** rather than the isomeric propellanes **2b–e** according to *Scheme 1* may reflect either thermodynamic or kinetic factors.



Scheme 1

The ^{18}O-exchange experiments recently reported [5] show that the boron-containing rings are formed stepwise *via* reversible reactions. It, therefore, appears that formation of **1b–e** is thermodynamically controlled, leading to the most stable product. Our calculations fully support this conclusion. Both MNDO and STO-3G find that their model **1a** is substantially more stable than **2a** which simulates the corresponding propellanes **2b–e**. According to MNDO, **1a** is more stable than **2a** by 24.5 kcal · mol^{-1}, albeit at STO-3G this energy difference decreases to 18.5 kcal · mol^{-1}. In general, these relatively simple methods are not expected to reproduce accurately the energy difference between **1a** and **2a**[3]). However, the calculated energy difference between **1a** and **2a** is so large that it may be reliably stated that **1a** *is substantially more stable*; we guess by $>$ 15 kcal · mol^{-1}. The same conclusion ought to hold for other compounds of type **1** vis-à-vis those of the propellanes **2**.

We now address the question as to why **2** is so strongly disfavored as compared to its isomeric **1**. We propose that this is primarily due to stronger repulsion between the oxygen lone-pairs in **2** relatively to those in **1**. Before turning to a detailed analysis of these interactions, we note that the two lone-pairs on each of the O-atoms are not equivalent. One is perpendicular to the boron-containing ring and has predominant 2p character, whilst the other lies in the plane of that ring and may be described as being roughly sp^2-hybridized (see **9**). Conjugation between the 2p lone-pairs and the empty 2p



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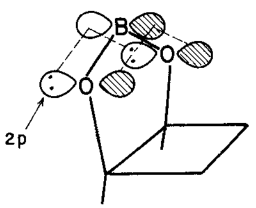

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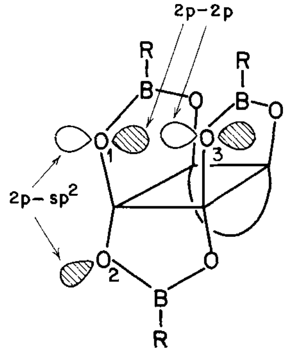
[3]) Note, however, that the composition of **1a** and **2a** is isodesmic (*i.e.* both have the same number and types of bonds). Isodesmic comparisons are generally much more reliable than non-isodesmic ones (in particular when relatively simple levels of theory are used), even when isomers are considered (*cf.* the non-isodesmic comparison of propene and cyclopropane [6]).

orbital of the B-atom dictates planarity of the dioxaborolane ring (see **10**). Note that the π-system of each dioxaboron moiety is isoelectronic with that in the allyl anion.

It is important to note that the 'in-plane' lone-pair lies considerably lower in energy than the 2p lone-pair [7a][4]. The destabilization resulting from the 4-electron interaction of two lone-pairs increases with the average energy of the interacting orbitals [8], implying that the destabilization resulting from interaction of two 2p lone-pairs is significantly larger than that between two sp^2 lone-pairs or between one 2p lone-pair and one sp^2 lone-pair[5].

Let us analyze the interactions between oxygen lone-pairs in **1** and **2** as shown schematically in **11** and in **12**, respectively.



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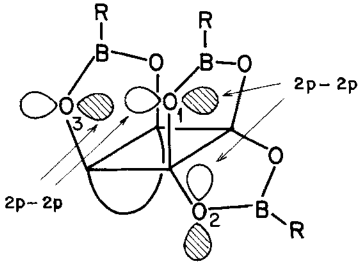

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In **2** (see **12**), each of the 2p lone-pairs interacts with two other 2p lone-pairs, one at a geminal O-atom, (*e.g.* O_1–O_2), and the other at an O-atom which lies across the cyclobutane ring (*e.g.* O_1–O_3). The situation in **1** (see **11**) is different. Each 2p lone-pair orbital interacts only with one 2p lone-pair orbital which lies across the cyclobutane ring (*e.g.* O_1–O_3). The geminal 2p lone-pairs (*e.g.* at O_1–O_2) are pointing away from each other, in roughly perpendicular directions so that their interaction is small. In **1** (see **11**), significant interactions between geminal O-atoms occur only between the 2p lone-pairs and the sp^2 lone-pairs. These orbitals are properly alligned for effective spatial overlap, but as noted above this interaction is much less destabilizing than a geminal 2p-2p interaction. We attribute most of the energy difference between **1** and **2** to the presence of *four* geminal 2p-2p interactions in **2** (see **12**) which are strongly destabilizing. In **1**, these interactions are substituted by the much less destabilizing 2p-sp^2 interactions.

The importance of the geminal 2p-2p interactions is also apparent when comparing the mono-propellane **3a** with the isomeric **4a**, **5a**, and **6a**. The former is less stable than the following three by 7–8 kcal·mol^{-1} at STO-3G. Our estimate that the 2p-2p interactions occurring across the cyclobutane ring are smaller, is reflected in the small energy difference between **5a** and **6a** (see *Table*). The geminal interactions being stronger than those

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[4] In H_2O, the energy difference between the two is 2.1 eV [7b].

[5] The same conclusion applies if one assumes that the destabilizing interaction between two filled orbitals increases as their energy separation decreases (see discussion in [8c]).

across the ring is a direct consequence of the geometry. In both **1a** and in **2a**, the O_1–O_2 distances (*e.g.* 2.32 Å in **2a**) are much shorter than the O_1–O_3 distances (*e.g.* 2.98 Å in **2a**). These differences are also found in the *Mulliken* population analysis: in **2a** the O_1–O_3 overlap population is practically zero whilst the O_1–O_2 overlap population is strongly repulsive (–0.014).

Another factor which disfavors **2** relatively to **1** is the higher geometrical rigidity of the propellane structure. In **1**, the 2p-2p interactions across the ring (*i.e.* between O_1 and O_3) can be reduced by increasing the angle α between the planes of the cyclobutane and the dioxaborolane rings (see the *Fig.* for definitions of α and of β). This deformation increases the O_1–O_3 separation and reduces the repulsive overlap between the two lone-pairs. In contradistinction for **2**, increase in α which reduces the O_1–O_3 interactions inexorably leads to a smaller angle β between the planes of the geminal dioxaborolane rings and to an increase in the O_1–O_2 repulsion. Thus, in **2**, a decrease in the interaction between the O-atoms lying across the cyclobutane ring inevitably increase the geminal interactions. The calculated geometries of **1a** and **2a** reflect these lone-pair interactions and support the qualitative considerations presented above. In **2a**, $\alpha = 121.7°$ and $\beta = 116.6°$. In **1a**, α increases to 126.0°. The O_1–O_3 separation in **1a** (3.16 Å) is, therefore, significantly larger than in the propellane **2a** (2.98 Å). The O_1–O_2 separation is essentially the same in both isomers (2.30 Å in **1a** and 2.32 Å in **2a**).

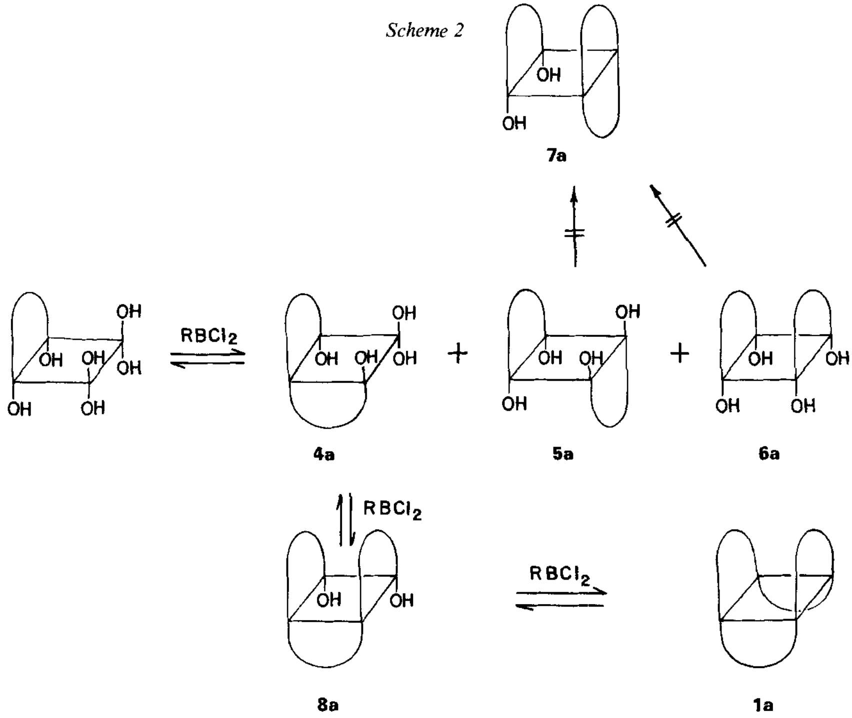
The dependence of α on the lone-pair interactions is further exemplified in comparing **5a** and **6a**. In **6a**, the two dioxaborolane rings are *syn* and $\alpha = 119.1°$, larger than for the *anti*-isomer **5a** ($\alpha = 116.6°$). To conclude this point, we note that although the geometrical changes in α are significant, the resulting energy changes in the lone-pair interactions are not all that significant (*e.g.* note the similar energies of **5a** and **6a**) as compared to the geminal ones.

A third factor to be considered in any system containing an O–C–O moiety is the anomeric effect. A *gauche* assignment of an oxygen lone-pair and a geminal C–O bond stabilizes the system [9]. Indeed, in all our systems which contain freely rotating OH groups (*i.e.* **3a**–**8a**), these adopt the *gauche*-conformation. In **1a** and **2a**, the B–O–C–O dihedral angles are fixed by structural constraints. As the anomeric effect has significant energetic consequences, it must be asked to what extent its geometrical constraints in **1a** and in **2a** determines their relative energies. Calculations give B–O–C–O dihedral angles of 134° and 111° in **1a** and **2a**, respectively. The highest degree of 'anomeric stabilization' is obtained for B–O–C–O dihedral angles of 60° and 120°. The dihedral angles in **1a** and **2a** deviate by roughly the same degree, *i.e.* by 14° and 9°, respectively. We, therefore, conclude that the anomeric effect plays a minor role, if any, in determining the energy difference between **1a** and **2a**.

The synthesis of compounds of type **1** proceeds *via* a thermodynamically controlled stepwise reaction [5], but it is not known at which stage the fate of the product is determined. We attempt to address this provocative question by calculating energies of models (**3a**–**8a**) to the possible intermediates **3**–**8** *(Scheme 2)*. MNDO and STO-3G calculations agree reasonably well, but we base our discussion on the STO-3G results which we consider to be more reliable.

First *(Scheme 2)* consider formation of the second dioxaborolane ring. The calculations show **5a** to be the favored product at this stage, but **4a** and **6a** are also accessible, being only 1–2 kcal·mol^{-1} higher in energy than **5a**. The only product thermodynamically

Scheme 2



excluded is the propellane **3a** that lies higher in energy by 8.1 kcal·mol^{-1}. Thus, after the second addition step it is still possible to obtain both the propellane **2** and the actual product obtained **1**. The product **4a** may yield only **1a**, **5a** may give only **2a**, and **6a** may lead to either **1a** or **2a**. The final product is determined only after the third dioxaborolane ring is formed. Formation of a propellane moiety leads to considerable destabilization so that **7a** is less stable than **8a** by 9.1 kcal·mol^{-1} (STO-3G). The energy difference between **7a** and **8a** is roughly half the energy difference between **1a** and **2a**, when a second propellane moiety is introduced. The calculations, therefore, suggest that at the third stage of the reaction sequence only **8a** is produced. This reacts further to give only the non-propellane product **1a**.

We note that the X-ray structure of the pyridine adduct of **1b** has been determined [2][6]. Unfortunately, the X-ray structure cannot be compared directly with our calculations, because the pyridine adduct and the isolated molecule are different both sterically and electronically. First, the pyridine ligands in **1b** push the substituents R which are attached to the B-atoms out of the plane of the dioxaborolane rings, thus increasing their steric requirements. Second, electron donation from the pyridine ligands reduces the electrophilicity of the B-atoms. This is expected to have a significant effect on the geometry. In general, it is difficult to predict the detailed geometrical changes due to pyridine attachment, but such prediction is possible for certain parameters. For example, the complexed B–O bonds are expected to be shorter in the free molecule than in the corresponding pyridine adduct due to a stronger allylic conjugation (see **10**) in the former.

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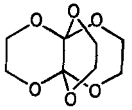
[6] We thank Dr. *R. Goddard*, MPI für Kohlenforschung, Mülheim/Ruhr, for the experimental data.

Indeed, we calculate shorter B–O distances in **1a** as compared to those measured in the pyridine complex of **1b**[6]). The major flaw in the MNDO calculations is probably in the C–C bond lengths which are calculated (in **1a**) to be longer by *ca.* 0.05 Å than those measured in the pyridine complex of **1b**[6]). This seems to be a general problem of MNDO with multiple O-substituted bonds. Thus for *cis*-1,2-dihydroxycyclobutane, we calculate 1.608 Å, 1.568 Å, and 1.541 Å for the C(1)–C(2), C(2)–C(3), and C(3)–C(4) bond lengths, respectively. A detailed evaluation of the reliability of the MNDO structures must await further experimental and theoretical studies.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It is of interest to note that in a hexaoxa[4.4.4]propellane structure **13** [10], the relationship between lone-pairs on geminal O-atoms appears to be analogous to that obtained in the dioxaboralanes **2**. However, examination of molecular models reveals the basic difference between **13** (which exists) and **2** (which does not). The non-planarity of the six-membered rings in **13** vis-à-vis planarity of the dioxaboralane rings allows relief of the O–O 2p-2p repulsive interactions in the latter.

Conclusion. – Our calculations reasonably explain the behavior of the reactants in their refusal to form a bis-propellane structure, which is significantly less stable than the one actually formed mainly due to O–O lone-pair repulsions.

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