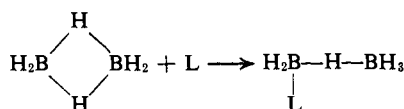
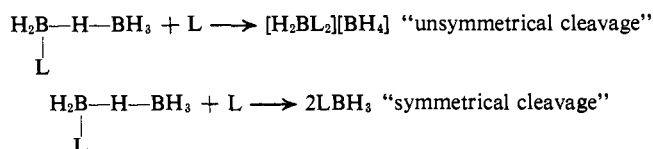


pose that diborane reacts with a ligand in a stepwise fashion, the first step involving the displacement of one hydrogen from the bridge position.



The second step, involving displacement of hydrogen from the remaining bridge, would determine the type of product produced.



Such a scheme is consistent with the observation that with increasing steric bulk of methyl-substituted amine the yield of symmetrical cleavage product increases.⁴

It has been suggested that reactions of diborane with Lewis bases at low temperature can involve unsymmetrical cleavage, but that the product can readily rearrange to a symmetrical cleavage product, depending upon which form is more stable, thermodynamically, at a particular temperature.⁶ There is no evidence for facile rearrangements in amine diborane systems. Thus, H_3NBH_3 and $[\text{H}_2\text{B}(\text{NH}_3)_2][\text{BH}_4]$ show no tendency toward interconversion in liquid ammonia.⁵

Boron-11 nmr spectra of singly hydrogen-bridged boranes are markedly temperature dependent. At about -25° each spectrum consists of a broad singlet, suggesting rapid proton exchange. As the temperature is lowered, fine structure in the spectrum becomes evident, until at about -60° seven lines can be observed. The BH_3 group produces a quartet which overlaps a triplet produced by the BH_2 group. In each spectrum the B-H coupling constant for the quartet appears to be significantly smaller than that for the triplet.¹¹ Figure 1 shows a typical low-temperature spectrum. Table I reports chemical shifts and coupling constants

Table I. Boron-11 Nmr Data at -65°

	$\delta, \pm 0.5 \text{ ppm}^a$	$J(\text{BH}_3), \pm 3 \text{ cps}^b$
$\text{H}_2\text{B}-\text{H}-\text{BH}_3$	-17.7	84
$\begin{array}{c} \text{NH}_3 \\ \\ \text{H}_2\text{B}-\text{H}-\text{BH}_3 \end{array}$	-18.0	89
$\begin{array}{c} \text{NH}_2\text{CH}_3 \\ \\ \text{H}_2\text{B}-\text{H}-\text{BH}_3 \end{array}$	-17.0	91
$\begin{array}{c} \text{N}(\text{CH}_3)_3 \\ \\ \text{H}_2\text{B}-\text{H}-\text{BH}_3 \end{array}$		

^a $\text{BF}_3\text{O}(\text{C}_2\text{H}_5)_2$ external reference. ^b The coupling constant $J(\text{BH}_2)$ is not reported at this time because of difficulty in locating the exact positions of the outer peaks of the triplet.

observed. Bridge hydrogen is expected to couple with each boron with the coupling constant for the

(9) D. F. Gaines, *Inorg. Chem.*, **2**, 523 (1963).

(10) R. W. Parry, R. W. Rudolph, and D. F. Shriver, *ibid.*, **3**, 1479 (1964).

(11) Gaines⁹ observed a seven-line spectrum for diborane in ether solutions at elevated temperatures and suggested that all six B-H hydrogens are equivalent. Considering the temperatures at which his work was performed plus the fact that only one coupling constant was observed for the seven-line spectrum, his interpretation is reasonable and does not conflict with the present study.

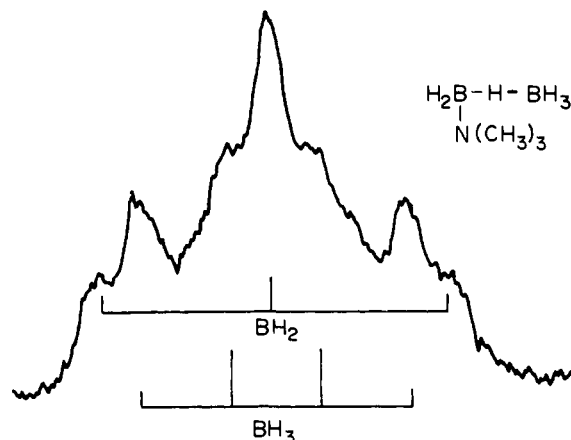


Figure 1. Boron-11 nmr spectrum at -65° in methylene chloride.

B-H-B bond being smaller than that for the B-H bond. Each component of the quartet and of the triplet should, therefore, be split into a doublet. Such coupling appeared to be present on one sample of **2** in which each component of the quartet was split into a doublet, with an apparent coupling constant of only several cycles. In general, however, coupling with bridge hydrogen was not detected.¹²

Acknowledgment. Support of this work by the National Science Foundation is gratefully acknowledged.

(12) Bridge coupling was not detected in $\text{H}_2\text{B}-\text{H}-\text{BH}_3^-$.⁹

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The "Size" of a Lone Pair of Electrons. Evidence for an Axial *t*-Butyl Group¹

Sir:

For some years there has been interest in the effective size of a lone pair of electrons.² Recently evidence has accumulated that the lone pair is smaller than a bonded hydrogen atom,^{3,4} although a contrary indication has also been recorded.⁵ We present here a striking demonstration that the space requirements of a free pair are, in fact, much smaller than those of a bonded hydrogen atom, the evidence being that *cis*-2-alkyl-5-*t*-butyl-1,3-dioxanes (I, Figure 1) exist very largely in the conformation Ia in which the *t*-butyl group is axial. Apparently this is the first instance where a *t*-butyl group is found to assume the axial position in a six-membered ring system.

Equilibration of *cis*- and *trans*-2-alkyl-4-methyl-1,3-dioxanes⁶ (Figure 2) indicates that the conformational

(1) This work was supported by National Science Foundation Grant GP-2096 and by a grant from the Air Force Office of Scientific Research (AF-AFOSR-772-65).

(2) Cf. E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis," Interscience Division, John Wiley and Sons, Inc., New York, N. Y., 1965, p 245.

(3) N. L. Allinger and J. C. Tai, *J. Am. Chem. Soc.*, **87**, 1227 (1965); N. L. Allinger, J. G. D. Carpenter, and F. M. Karkowski, *ibid.*, **87**, 1232 (1965).

(4) R. J. Bishop, L. E. Sutton, D. Dineen, A. Y. Jones, and A. R. Katritzky, *Proc. Chem. Soc.*, 257 (1964); K. Brown, A. R. Katritzky, and A. J. Waring, *ibid.*, 257 (1964).

(5) J. B. Lambert and R. G. Keske, *J. Am. Chem. Soc.*, **88**, 620 (1966).

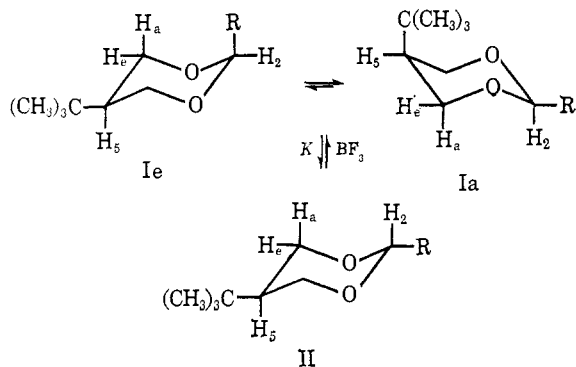


Figure 1. Configurational and conformational equilibria in 2-alkyl-5-*t*-butyl-1,3-dioxanes.

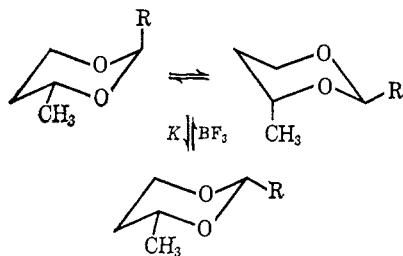


Figure 2. Configurational and conformational equilibria in 2-alkyl-4-methyl-1,3-dioxanes.

free energy of a methyl group in the 2 or 4 position of the dioxane system or of an ethyl group in the 2 position is *ca.* 3 kcal/mole.⁷ This free energy difference is considerably greater than the corresponding difference in cyclohexane:⁸ 1.56–1.75 kcal/mole for methyl, 1.67–1.86 kcal/mole for ethyl, presumably as a result of the greater proximity of the *syn*-axial positions at C₂ and C₄ in a 1,3-dioxane as compared to the *syn*-axial positions in cyclohexane, the difference resulting from the shorter C–O distance (1.43 Å) as compared to C–C (1.53 Å).

Table I. Conformational Equilibrium Constants and Free Energy Differences (at 25°) for 2-Alkyl-4-methyl-1,3-dioxanes (Figure 2)

R	K	–ΔG°, kcal/mole ^a
CH ₃	152	3.0 (3.4)
C ₂ H ₅	108	2.8 (3.2)
(CH ₃) ₃ C	127	2.9

^a Figure in parentheses is corrected for the assumption that the two conformations of the *trans* isomer are equally populated.

In view of the reluctance of the 2-methyl group to occupy the axial position (Table I), it came as a surprise that the free energy difference (–ΔG°) between *cis*- and *trans*-2-methyl-5-*t*-butyl-1,3-dioxane (Table II, entry 1) is only 1.5 kcal/mole. Light was shed on this apparent mystery when it was found (Table II, entries

(6) The dioxanes were prepared from appropriate aldehydes and diols. Equilibration was effected by boron trifluoride etherate in ether and analysis by glpc on 12- to 30-ft columns of 1,2,3-triscyano-2-ethoxypropane. Diastereoisomeric pairs were separated by preparative gas chromatography and subjected to elemental analysis (all analyses were within the normal limits of ±0.3%). Glpc response ratios and nmr spectra were recorded for all pure compounds.

(7) Alternatively, these systems may escape into the skew-boat conformation: J. Delmau and J. Duplan, *Tetrahedron Letters*, 2693 (1966).

(8) E. L. Eliel and T. J. Brett, *J. Am. Chem. Soc.*, **87**, 5039 (1965).



Figure 3. Configurational equilibrium in 2,5-dialkyldioxanes.

2–4) that –ΔG° is nearly the same for the 2-ethyl, 2-isopropyl, and even 2-*t*-butyl analogs. Clearly it is not the (variable) 2-alkyl group which changes position in the configurational equilibration of these compounds but the (constant) 5-*t*-butyl group which must thus occupy the axial position in the *cis* isomer (Ia, Figure 1).

Table II. Conformational Equilibrium Constants and Free Energy Differences (at 25°) for 2,5-Dialkyl-1,3-dioxanes (Figures 1 and 3)

Entry	R'	R	K	–ΔG°, kcal/mole
1	(CH ₃) ₃ C	CH ₃	11.9	1.5
2	(CH ₃) ₃ C	CH ₃ CH ₂	11.2	1.4
3	(CH ₃) ₃ C	(CH ₃) ₂ CH	10.8	1.4
4	(CH ₃) ₃ C	(CH ₃) ₂ C	9.9	1.4
5	CH ₃	(CH ₃) ₃ C	3.9	0.80
6	C ₂ H ₅	(CH ₃) ₃ C	3.1	0.67
7	C ₂ H ₅	C ₂ H ₅	3.4	0.72

This striking finding is supported by the nmr spectra of the 2-alkyl-5-*t*-butyl-1,3-dioxanes (Figure 1). Shown in Table III are salient data regarding the chemical shifts of the 2-proton and the 5-*t*-butyl groups and coupling constants between the proton at C₅ and protons at C₄. The chemical shift differences between the 2 protons in the *cis* and *trans* isomers of the 2-alkyl-5-*t*-butyl-1,3-dioxanes (Figure 1) are less than 10 cps in all cases, rather than the *ca.* 25 cps expected⁹ between Ie and Ia. All the *cis* isomers show the methyl protons of the *t*-butyl group at –62 to –63 cps. This is incompatible with an equatorial *t*-butyl group at C₅ found at –53 cps. The coupling constants *J*_{4,5} are 1.1–1.3 cps for e,e coupling and 3.9–4.0 cps for e,a coupling in I, whereas they are 10.6–12.1 cps for a,a coupling and 4.4–5.6 for e,a coupling in II. The coupling in I is incompatible with conformation Ie (which should show the same *J*_{4,5} values as II) or with a boat or skew-boat conformation.¹⁰ The remarkably constant coupling constants for the four different 2-alkyl-5-*t*-butyl-1,3-dioxanes are, however, entirely compatible with the assumption that *all* these compounds exist largely in conformation Ia.

The facility with which the *t*-butyl group moves into the axial position in this case as compared with its reluctance to do so in corresponding cyclohexane systems (which prefer to escape into boat forms instead¹¹) must be largely a reflection of the small space requirement of the axial (?) electron pairs on the oxygens in

(9) C. Barbier, M. Davidson and J. Delmau, *Bull. Soc. Chim. France*, 1046 (1964).

(10) H. Booth and G. C. Gidley, *Tetrahedron Letters*, 1449 (1964); see also H. Feltkamp, N. C. Franklin, M. Hanack, and K.-W. Heinz, *ibid.*, 3535 (1964); M. Anteunis, E. Coene, and D. Tavernier, *ibid.*, 4579 (1966).

(11) N. L. Allinger and L. A. Freiberg, *J. Am. Chem. Soc.*, **82**, 2393 (1960); R. D. Stolow and M. M. Bonaventura, *ibid.*, **85**, 3636 (1963). See, however, G. N. Zhizhin, K. E. Sterin, N. I. Tyun'kina, and A. L. Liberman, *J. Struct. Chem. (USSR)*, **6**, 793 (1965).

Table III. Chemical Shift and Coupling Constant Data for 2-Alkyl-5-*t*-butyl-1,3-dioxanes^a (Figure 1)

R	J_{H_3, H_4}		$-\nu_{H_2}$	$-\nu_{t-Bu}$
	4-c	4-a		
<i>trans</i> Isomers				
CH ₃	5.6	10.6	264.6	52.6
C ₂ H ₅	4.4	11.2	252.1	52.5
(CH ₃) ₂ CH	4.5	11.3	242.1	52.6
(CH ₃) ₃ C	4.7	12.1	231.5	53.0
<i>cis</i> Isomers				
CH ₃	1.3	4.0	273.5	62.3
C ₂ H ₅	1.1	3.9	261.9	63.1
(CH ₃) ₂ CH	1.1	4.0	248.5	63.0
(CH ₃) ₃ C	1.1	3.9	239.7	62.7

^a All values in cycles per second; chemical shifts are recorded at 60 Mcps with tetramethylsilane standard in carbon tetrachloride.

the 1,3-dioxane as compared with a much larger space requirement of the axial hydrogens in cyclohexane. The small conformational energies of other 5-alkyl groups (Figure 3 and Table II, entries 5-7) are in agreement with this assumption.

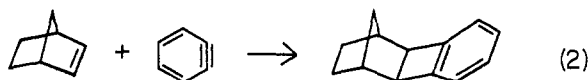
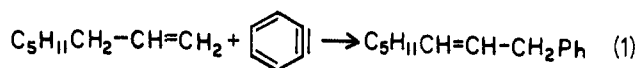
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The Electronic Structure and Reactivity of Small-Ring Compounds. II. The Reaction of Bicyclobutane with Benzyne¹

Sir:

It has been demonstrated recently that the known chemical and physical properties of bicyclobutane can be correlated with two models for the electronic structure of this molecule.¹ Although all the carbon-carbon bonds contain π character, the 1,3 bond exhibits the greatest degree of unsaturation. To demonstrate the olefinic nature of this bond further, we have investigated the course of the reaction of benzyne with bicyclobutane.

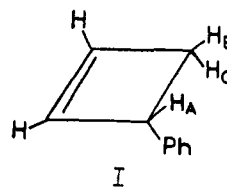
Benzyne is known to react with simple olefins, containing readily accessible allylic hydrogens, by the Alder "ene" synthesis (substitutive addition)²⁻⁴ or, in the absence of such hydrogens, by cycloaddition (eq 1 and 2).^{3,4}



When bicyclobutane⁵ is allowed to react with an equimolar amount of *o*-benzenediazoniumcarboxylate in ethylene chloride at 40-45°, a 40-60% yield of two products, in the ratio of 6-7:1, is obtained.

The major product was identified as 3-phenylcyclobutene (I) in the following way. Its nmr spectrum

(τ values) shows five aromatic hydrogens at 2.5 ppm, two vinyl hydrogens as a singlet at 3.5 ppm, and hy-



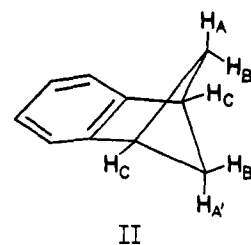
drogens A, B, and C each as a double doublet at 5.8, 6.85, and 7.55 ppm, respectively, $J_{AB} = 5.0$ cps, $J_{AC} = 2.2$ cps, and $J_{BC} = 15.3$ cps.⁶

Catalytic hydrogenation results in the uptake of 1 equiv of hydrogen and gives a product whose nmr spectrum is consistent with the phenylcyclobutane structure, five aromatic hydrogens at 2.4 ppm, one benzylic hydrogen centered at 6.2 ppm, and six aliphatic hydrogens as a broad multiplet between 7.3 and 8.3 ppm. The infrared spectrum, which is extremely similar to that reported for this compound,⁸ also supports this assignment.

Thermal rearrangement of 3-phenylcyclobutene⁹ affords *trans*-1-phenyl-1,3-butadiene, whose infrared and nmr spectra are identical with those of authentic material prepared by the method of Grummitt¹⁰ and which upon hydrogenation gives *n*-butylbenzene.

3-Phenylcyclobutene was also prepared by an independent route. Photolysis (100-w G.E. mercury lamp H100-A4/T; Pyrex filter) of *trans*-1-phenyl-1,3-butadiene initially gives a mixture of *cis*- and *trans*-phenylbutadiene, rich in the *cis* isomer, but on prolonged irradiation 3-phenylcyclobutene is formed.

The minor product from the reaction of benzyne with bicyclobutane was shown to be benzobicyclo[2.1.1]hexene (II). The mass spectrum shows the



parent peak at m/e 130, indicating a molecular formula of C₁₀H₁₀.¹¹ The nmr spectrum shows a symmetrical four-proton A₂B₂ aromatic multiplet centered at 3.0 ppm. In addition, the bridgehead protons (H_C) appear as a triplet at 6.86 ppm, the *exo*-hydrogens (H_B) as a complex multiplet at 7.25 ppm, and the *endo*-hydrogens (H_A) as a double doublet at 7.66 ppm (Figure 1; the peaks between 7.4 and 7.5 ppm are due to an impurity).

The spectrum, as can be seen from Figure 1, could be reproduced rather well with the aid of a computer program using the following coupling constants:

(6) The assignment follows that for 1,3-diphenylcyclobutene made by Masamune.⁷

(7) S. Masamune, *Tetrahedron Letters*, 945 (1965).

(8) N. A. Donskaya, V. K. Potapov, Yu. S. Shabarov, and R. Ya. Levina, *J. Org. Chem. USSR*, **1**, 1835 (1965).

(9) The thermal rearrangement was effected in a gas chromatograph with the injector temperature at 230° and the column temperature at 160°.

(10) O. Grummitt and E. I. Becker, *Org. Syn.*, **30**, 75 (1950); O. Grummitt and F. J. Christoph, *J. Am. Chem. Soc.*, **73**, 3479 (1951).

(11) We wish to thank Mr. J. Bayless for obtaining the mass spectrum.

(1) Part I: M. Pomerantz and E. W. Abrahamson, *J. Am. Chem. Soc.*, **88**, 3070 (1966).

(2) E. M. Arnett, *J. Org. Chem.*, **25**, 324 (1960).

(3) H. E. Simmons, *J. Am. Chem. Soc.*, **83**, 1657 (1961).

(4) J. A. Berson and M. Pomerantz, *ibid.*, **86**, 3896 (1964).

(5) We wish to thank Professor L. Friedman and Mr. J. Bayless for details of the preparation of bicyclobutane.