view of the much higher basicity of the conjugate base.[11] The much larger effect in the sulfone series of substituting a phenyl group for a β-methyl group appears to be worthy of additional study.

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[11] Part of this larger difference may be due to a solvent effect.[7]

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Steric Hindrance to the Formation of and Protonation of the Nitronate Ion from 2-Aryl-1-nitrocyclohexanes

Sir:

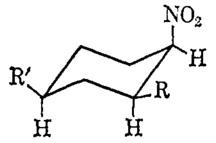
A study of the rates of nitronate ion formation from nitrocyclohexanes and related compounds (Table I) has revealed the presence of a sizable and unexpected steric effect of an equatorial 2-aryl substituent on an axial, *but not* an equatorial, hydrogen atom.

Table I. Rates of Nitronate Ion Formation from Nitroalkanes and Sodium Methoxide in Methanol at 25°

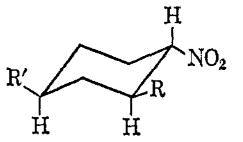
Compd	Nitroalkane	k, M^{-1} sec^{-1}	Relative rates	E_a[a]	ΔS^*
1	*cis*-4-*t*-Butyl-1-nitrocyclohexane[b]	1.0	220	16	−8
2	*cis*-2-*p*-Chlorophenyl-1-nitrocyclohexane[b]	1.9	410	16	−5
3	*cis*-2-*o*-Methylphenyl-1-nitrocyclohexane[b]	1.0	220	16	−7
4	*trans*-4-*t*-Butyl-1-nitrocyclohexane[b]	2.0×10^{-1}	44	16	−11
5	Nitrocyclohexane	3.3×10^{-1}	72		
6	2-Nitropropane	3.2×10^{-1}	70		
7	1-Phenyl-2-nitropropane	4.6×10^{-1}	100		
8	*trans*-2-*p*-Chlorophenyl-1-nitrocyclohexane[b]	9.3×10^{-3}	2.0	19	−6
9	*trans*-2-*o*-Methylphenyl-1-nitrocyclohexane[b]	4.6×10^{-3}	1.0	20	−5

[a] Calculated from measurements at two or more temperatures. [b] This sample was kindly furnished by Professor A. C. Huitric.

Examination of Table I shows that the rates of proton abstraction from *cis*-4-*t*-butyl-, *cis*-2-*p*-chlorophenyl-, and *cis*-2-*o*-methylphenyl-1-nitrocyclohexanes (**1**, **2**, and **3**, respectively) are all of a comparable order of magnitude.



1, R = H; R′ = *t*-Bu
2, R = *p*-ClC$_6$H$_4$; R′ = H
3, R = *o*-MeC$_6$H$_4$; R′ = H



4, R = H; R′ = *t*-Bu
8, R = *p*-ClC$_6$H$_4$; R′ = H
9, R = *o*-MeC$_6$H$_4$; R′ = H

trans-4-*t*-Butyl-1-nitrocyclohexane (**4**) reacts at a fivefold slower rate than the *cis* isomer, presumably because of the higher ground-state energy of the latter. The rate for nitrocyclohexane (**5**) is very close to that calculated from the Winstein–Holness equation,[1] using mole fraction values of 0.8 and 0.2 for the equatorial and axial conformers,[2] and the rate constants for **4** and **1** [relative rate = $(0.8 \times 44) + (0.2 \times 220) = 79$, *vs.* 72 observed].

Judging from the small rate effect of the β-aryl groups observed in **2** and **3** (compare with **1**) and the β-phenyl group in 1-phenyl-2-nitropropane (**7**) [compare with 2-nitropropane (**6**)], the inductive and steric effect of a β-aryl group on the rate of proton abstraction is normally small and accelerating. The 22-fold and 44-fold rate-*retarding* effects observed for the β-aryl groups in *trans*-2-*p*-chlorophenyl- and *trans*-2-*o*-methylphenyl-1-nitrocyclohexanes (**8** and **9**; compare with **4**) must, therefore, be attributed to the operation of a sizable steric effect. This is surprising since, in the perfect chair cyclohexane conformation, the (equatorial) β-aryl group in **8** or **9** has exactly the same skew relationship to the axial hydrogen atom as does the (axial) β-aryl group to the equatorial hydrogen atom in **2** or **3**. The most likely origin of this steric effect would appear to be the bending away from one another of the equatorial nitro and phenyl groups in **8** and **9**,[3] causing the cyclohexane ring to be deformed and allowing the aryl group to screen the axial hydrogen atom more effectively. (This is not possible in the *cis* isomers due to interference between the axial nitro group and the axial hydrogen atoms at C-3 and C-5.) This deformation must permit a considerable lowering of the ground-state energy of the *trans* isomer relative to the *cis* isomer, since introduction of a 2-phenyl substituent into nitrocyclohexane causes an apparent increase in the *A* value of the nitro group from 0.8 kcal/mole[2] to 2.7 kcal/mole.[4]

It follows that there must also be a sizable steric effect of an aryl group in the microscopic reverse of the proton-abstraction reaction. This requires that in the protonation of the nitronate ion derived from **2** (or **8**) or from **3** (or **9**) the proton enters preferentially into the equatorial position (equatorial:axial rate ratio = 205:1 for **2**:**8** and 220:1 for **3**:**9**). This reaction is not experimentally observable, since proton abstraction from the solvent by these nitronate ions is extremely slow. It has been observed, however, that in the closely related reaction, protonation of the nitronate ion from 2-phenyl-1-nitrocyclohexane under acidic conditions, the proton is delivered stereoselectively so as to give

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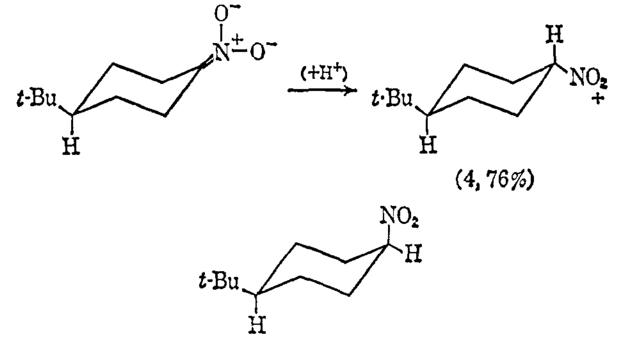
[1] See E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, pp 234–239, for a discussion.

[2] W. F. Trager and A. C. Huitric, *J. Org. Chem.*, **30**, 3257 (1965).

[3] E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis," Interscience Publishers, Inc., New York, N. Y., 1965, p 127.

[4] H. E. Zimmerman and T. E. Nevins, *J. Am. Chem. Soc.*, **79**, 6559 (1957).

almost exclusively the *cis* isomer (equatorial α-proton, axial nitro group).[4] It was suggested that this might be due to the greater steric hindrance (by the C-3 and C-5 axial hydrogen atoms) for approach of the proton donor from the "axial side." The present results suggested that the effect might lie in the steric effect of the phenyl group rather than in the steric effect of the C-3 and C-5 axial hydrogen atoms. To test this point the nitronate ion derived from 4-*t*-butyl-1-nitrocyclohexane (**1** or **4**) was protonated by acidifying to a congo red end point with ethanolic sulfuric acid, then treating with acetic acid–sodium acetate and finally with water.[2,4] The product was a mixture of 4-*t*-butylcyclohexanone, **1**, and **4**. The ratio of ketone to nitroalkanes varied considerably, depending on the reaction conditions, but the ratio **1**:**4** was in each instance 1:3.[5]



(1, 24%)

It appears, therefore, that in the absence of hindering groups at C-2 there is but little preference for "axial" or "equatorial" approach of the proton donor. When a substituent is present at C-2 it must exert a sizable steric effect. This does not mean that the original suggestion of Zimmerman[4] must be abandoned,[6] but merely that it must be modified. It does appear likely, however, that the C-2 substituent is in an axial position in the transition state for nitronate ion protonation,[6] since it would exert a much greater steric effect from this position than from an equatorial position.[4]

Acknowledgment. This work was sponsored by the National Science Foundation (GP-4208).

(5) A. T. Nielsen, *J. Org. Chem.*, **27**, 2001 (1962), observed that protonation of the nitronate ion from 1,4-dinitrocyclohexane gave 55% *cis*- and 45% *trans*-1,4-dinitrocyclohexanes.

(6) S. K. Malhotra and F. Johnson, *J. Am. Chem. Soc.*, **87**, 5493 (1965).

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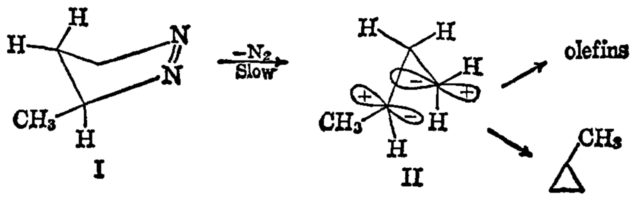
Thermolysis of *cis*- and *trans*-4-Deuterio-3-methyl-1-pyrazoline

Sir:

Thermolysis of simple alkyl-1-pyrazolines, in the gas phase, leads to a nitrogen-free intermediate.[1] On the basis of the olefin and cyclopropane products produced, structure II was proposed for the intermediate. We wish to report further evidence to support this structure.



The proposed intermediate (II) produced upon thermolysis of 3-methyl-1-pyrazoline (I) has a plane of symmetry through the four carbons. Such a structure has recently received theoretical support from extended Hückel molecular orbital calculations.[2] To test this symmetry we have prepared *cis*- and *trans*-4-deuterio-3-methyl-1-pyrazoline (III and IV), both being capable of producing the intermediate V. If V has a sufficient lifetime to become completely free of the nitrogen produced, then the product ratios will be independent of the initial stereochemistry. The intermediate V leads to predictions which are experimentally verifiable: (a) a 50:50 ratio of *cis*- and *trans*-2-deuteriomethylcyclopropane would be expected; (b) the yield of products, assuming a k_H/k_D ratio of 2.0 in the product-determining step,[1] should be that shown in Table I; (c) each olefin should exhibit the same k_H/k_D ratio irrespective of the initial source, III or IV.

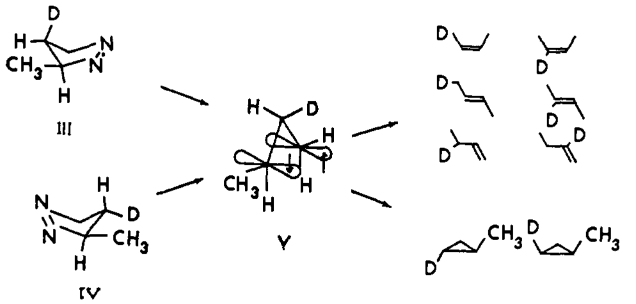
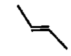


Table I. Product Proportions from the Pyrolysis of III and IV[a]

				
I, %	93.3 ± 0.6	1.9 ± 0.2	1.16 ± 0.12	3.7 ± 0.3
III and IV (predicted), %	94.9	1.4	0.9	2.8
III, %	95.1 ± 0.5	1.4 ± 0.2	1.0 ± 0.1	2.5 ± 0.3
IV, %	94.7 ± 0.5	1.5 ± 0.2	1.1 ± 0.2	2.7 ± 0.3

[a] Analysis carried out on a 20-ft column of silver nitrate and propanediol on Firebrick and a 20-ft column of dimethylsulfolane on Chromosorb.

The synthesis of III was achieved by the chlorination of *trans*-2-butene on a preparative scale using the procedure of Walling and Thaler.[3] Treatment of the *trans*-1-chloro-2-butene[4] with deuterium bromide in ether produced 3-bromo-1-chloro-2-deuteriobutane[5] which, upon treatment with hydrazine and oxidation of the

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(1) R. J. Crawford and A. Mishra, *J. Am. Chem. Soc.*, **88**, 3963 (1966).

(2) R. Hoffmann, Abstracts, 151st National Meting of the American Chemical Society, Pittsburgh, Pa., March 1966, Paper 109K.

(3) C. Walling and W. Thaler, *J. Am. Chem. Soc.*, **83**, 3877 (1961).

(4) The *trans*-1-chloro-2-butene was separated from the 3-chloro-1-butene produced by preparative glpc using a 20-ft silicone oil on Fluoropak column.

(5) The procedure used was essentially that of H. L. Goering and L. L. Sims, *ibid.*, **77**, 3465 (1955).