

such as to cause some loss of the product aldehyde³ **6**, probably by aldol condensation. The aldehyde was obtained as an oil in 50% yield. Its dinitrophenylhydrazone³ melted at 199–200°. The aldehyde was further characterized by oxidation with Jones' reagent, then hydrolysis of the nitrile, to give the diacid³ **7**, m.p. 196–197°. It was identical with a sample prepared from ketone **1** by permanganate oxidation.

The reaction conditions and course for the Beckmann cleavage are of interest. The rearrangement of oximes of 5- and 6-membered ketones is distinctly sluggish.¹⁰ The tosylate of oxime **4** required boiling for 12 hr. in pyridine for its rearrangement to proceed about seven-eighths to completion. From such conditions, we recovered **5** in yields up to 35% (after purification by chromatography), and 10% of pure oxime. It is possible that this sluggishness of reaction in our example is owing to slow formation of tosylate from hindered oxime, as conduct of the reaction on the mesylate proceeds to give 38% of product and no recoverable oxime in appreciably shorter time.

A third alternative method is to conduct the reaction in a novel manner suggested by a recent publication of Cross, *et al.*¹¹ Treatment of the oxime **4** in dioxane solution with dry, freshly prepared 2-chloro-1,1,2-trifluoroethyl-diethylamine for 30 min. at 70° affords the product **5** in quite variable yields up to 48%, and oxime recovery exceeds 20%. We suggest that this quite mild reaction proceeds as indicated in **8**.

Although such a formulation of the reaction course places it within the general framework characteristic of the second-order Beckmann rearrangement as suggested in Hill's valuable article,^{3a} this may be the first report¹² of such a rearrangement wherein the electron source which causes fragmentation is an unshared pair on sulfur. Hill refers to an article by Barltrop and Morgan¹³ as having reported such an example. They describe the rearrangement of some oximes having on the β -carbon a 2-nitrophenylthio group or a 2,4-dinitrophenylthio group. Even though some of the product amides were too unstable to characterize, they appear to have been formed in all cases, as acid hydrolysis was required for the liberation of product fragments which would correspond to those expected from the alternative course we describe. We suggest that the difference in reaction course between our results and those of Barltrop may be ascribed to the presence of a thioether so substituted with electron-withdrawing groups that the lone pair on sulfur required for our reaction is practically unavailable in his cases.

(10) For elegant work on the mechanistic details of the Beckmann rearrangement, consult the papers of R. Huisgen, *et al.*, *e.g.*, *Ann.*, **602**, 127 (1957); **604**, 191 (1957); *Ber.*, **90**, 1844, 1850 (1957)

(11) L. H. Knox, E. Velarde, S. Berger, D. Cuadriello, and A. D. Cross, *J. Org. Chem.*, **29**, 2187 (1964). We are indebted to Dr. Cross for a discussion of his results prior to publication.

(12) The first report may be that of E. Vinkler and K. Autheried, *Acta Univ. Szeged. Acta Phys. Chem.*, **2**, 105 (1948); *Chem. Abstr.*, **44**, 6399 (1950). We are unable to ascertain relevant details from the abstract.

(13) J. A. Barltrop and K. J. Morgan, *J. Chem. Soc.*, 4486 (1960).

(14) DuPont Fellow, summer 1963.

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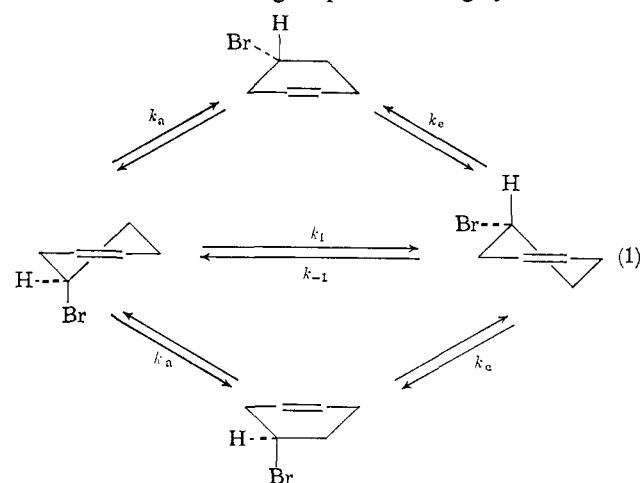
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The Interconversion Barrier and Conformational Preference of Bromine in 4-Bromocyclohexene

Sir:

The interconversion barriers of many cyclic compounds, *e.g.*, cyclohexane¹ and derivatives,^{2,3} have been determined using variable temperature n.m.r. spectroscopic methods. Related studies at low temperatures have been very fruitful in providing conformational preferences of groups substituted in cyclohexyl rings.⁴ One of the major remaining problems in conformational analysis is the cyclohexenyl ring; this report concerns the energy of the half-chair-half-chair interconversion of 4-bromocyclohexene and the conformational preference of the 4-bromo group in this ring system.



The various rate constants (eq. 1) were determined for a 30% by volume solution of 4-bromocyclohexene in perdeuteriovinyl chloride as solvent with tetramethylsilane (TMS) as internal standard using a Varian HR-60 spectrometer with a special low temperature probe.

At temperatures above -140° , the rate of the interconversion (eq. 1) is sufficiently rapid that a single, complex time average HCB \dot{r} resonance is observed. As the temperature is lowered below -145° , the HCB \dot{r} proton resonance broadens and separates into two peaks in a manner similar to that reported for cyclohexane¹ and the halocyclohexanes. In the case of 4-bromocyclohexene, the peaks are effectively completely separated at -159° with a broad signal occurring at 254.5 ± 0.9 c.p.s. downfield from TMS and a relatively sharp peak 281.8 ± 0.8 c.p.s. downfield from TMS. The upfield, broad peak was assigned to the axial hydrogen (equatorial bromine) and the downfield, sharper peak to the equatorial hydrogen on the basis of known chemical shifts of cyclohexyl axial and equatorial hydrogens⁵ and respective coupling constants as functions of dihedral angles between protons.⁶

The chemical shifts at various temperatures are reported in Table I.

From the observed separation of the peaks with temperature, the sum of the two residence times, τ (=

(1) F. R. Jensen, D. S. Noyce, C. H. Sederholm, and A. J. Berlin, *J. Am. Chem. Soc.*, **84**, 386 (1962).

(2) L. W. Reeves and K. O. Stromme, *Can. J. Chem.*, **38**, 1241 (1960).

(3) A. J. Berlin, Ph.D. Dissertation, University of California, Berkeley, 1961.

(4) A. J. Berlin and F. R. Jensen, *Chem. Ind.* (London), 998 (1960).

(5) R. U. Lemieux, R. K. Kullnig, H. G. Bernstein, and W. G. Schneider, *J. Am. Chem. Soc.*, **80**, 6098 (1958).

(6) M. Karplus, *J. Chem. Phys.*, **30**, 11 (1959).

Table I. Chemical Shifts of Axial-Equatorial Absorptions for CHBr in 4-Bromocyclohexene as a Function of Temperature

Temp., °C.	($\nu_a - \nu_e$) c/s ^a
-146.3	13.2 ± 1.5
-147.2	16.1 ± 1.0
-148.9	20.5 ± 0.7
-149.9	24.0 ± 0.4
-152.4	26.2 ± 0.4
-154.3	27.3 ± 0.3
-157.0	27.4 ± 0.5
-159.0	27.4 ± 0.4

^a Determined by the usual side-banding technique using TMS as internal standard.

$\tau_a + \tau_e$), of the conformers can be calculated.⁷ At three-quarters separation and $124.7 \pm 0.5^\circ\text{K}$., τ is 0.0125 sec., thus giving $k_1 = 47.7 \text{ sec.}^{-1}$ and $k_{-1} = 32.3 \text{ sec.}^{-1}$.⁸ Assuming that the interconversion (eq. 1) is partitioned to the same degree *via* the boat forms of 4-bromocyclohexene, a statistical factor of two is required in calculating the half-chair to half-boat transition. Utilizing this assumption, the rate constant for bromine axial to boat (k_a) is 95.4 sec.^{-1} at $124.7 \pm 0.5^\circ\text{K}$., from which is calculated by absolute rate theory $\Delta F_a^* = 5.93 \pm 0.10 \text{ kcal./mole}$. Statistical factors as in the cyclohexane case probably provide the principal contributions to ΔS^* .¹ There are two pathways in each direction (eq. 1), as compared to 12 for cyclohexane.¹ From this consideration $\Delta S^* \sim R \ln 2 = 1.4 \text{ e.u.}$, and $\Delta H_a^* \sim 6.1 \text{ kcal./mole}$.

The lower ΔF_a^* for 4-bromocyclohexene is in contrast with that of cyclohexyl bromide ($\Delta F^* = 10.5 \text{ kcal./mole}$) and cyclohexane ($\Delta F^* = 10.3 \text{ kcal./mole}$).³ By analogy with the similarity observed in barriers for cyclohexane and its derivatives, the ΔF^* for 4-bromocyclohexene should be a reasonable approximation of ΔF^* for cyclohexene. In fact, at approximately -165° , definite changes are observed in the spectrum of cyclohexene.

The ΔF (eq. 1) was determined by the chemical shift method^{4,9} and by area measurements. Both determinations were effected at $116.1 \pm 0.2^\circ\text{K}$. The ΔF (shift) was calculated making the assumption that ($\nu_a - \nu_e$) is independent of temperature. The "time-average" HCBBr resonance at 116.1°K . was obtained by a linear extrapolation of the positions of time-average HCBBr resonances from -38 to -138° . Thus, the " E_4 value," as defined by eq. 2, was found to

$$E_4 = -\Delta F = RT \ln K \quad (2)$$

be $0.101 \pm 0.050 \text{ kcal./mole}$ by the shift method¹⁰ and $0.077 \pm 0.015 \text{ kcal./mole}$ by area measurement.¹⁰ The E_4 value for the 4-position in cyclohexene is defined analogously to the A value¹¹ used in the cyclohexane system.

(7) "High Resolution Nuclear Magnetic Resonance," J. A. Pople, W. G. Schneider, and H. G. Bernstein, Ed., McGraw-Hill Book Co., Inc., New York, N. Y., 1959, p. 224.

(8) Some overlap of the peaks occurs as the axial and equatorial proton resonances separate. Consequently, it would be expected that the apparent center of the peak is farther downfield for the upfield peak than the actual center and *vice versa* for the downfield peak. Thus, the degree of overlap was determined and subtracted from the appropriate peak. A new center of the peak was determined, and it is this value which was used to calculate ΔF^* . This is probably a valid method because the axial and equatorial (H-C-Br) resonances are, to a first approximation, subject to AX type coupling and should be symmetrical.

(9) E. L. Eliel, *Chem. Ind.* (London), 568 (1959).

(10) Corrections were made for peak overlap (footnote 7).

Possible explanations of the lower ΔF in the cyclohexene series as compared to the cyclohexane series are the loss of steric interactions by introduction of a double bond into the ring and the intervention of a van der Waals attractive force between the π -electrons of the double bond and the bromine atom. Examination of a model of cyclohexyl bromide reveals that the 1,3-axial interactions between bromine and hydrogen are at a maximum, and no staggering occurs. However, in 4-bromocyclohexene, it is seen that one 1,3-interaction is eliminated and the remaining axial-axial interactions are slightly staggered.¹²

The lower ΔF^* for the interconversion as compared to cyclohexyl derivatives can be attributed to the presence of fewer eclipsing interactions in the transition state.

Acknowledgment. Acknowledgment is made to the National Science Foundation (GP-1713) for support of this work.

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(13) Alfred P. Sloan Fellow, 1961-1965.

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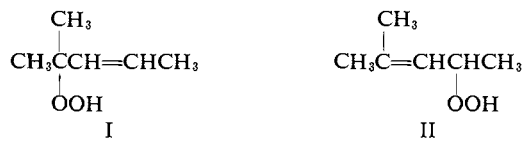
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The Isolation and Rearrangement of Pure Acyclic Allylic Hydroperoxides

Sir:

Investigations of the autoxidation of acyclic olefins, unlike those dealing with cyclic olefins and some hydrocarbons, have been handicapped by the unavailability of the pure hydroperoxide products and consequently by the lack of reliable information on their reactivity. This note reports the isolation, for the first time, of two isomeric unsaturated acyclic hydroperoxides and the results of the initial study of their properties.

Gas chromatography of the products from the autoxidation of *trans*-4-methyl-2-pentene, using diisodecyl phthalate adsorbent on a Fluoropak 80 support, yielded *trans*-2-methyl-3-pentenyl-2 hydroperoxide (I) and its allylic isomer 4-methyl-3-pentenyl-2 hydroperoxide (II) in purities of from 95 to 100%. Either



isolated hydroperoxide could be chromatographed under the conditions used for its isolation to give a single peak. Structures were proved by reduction of the hydroperoxides with aqueous sodium sulfite to the corresponding alcohols. Iodometric analysis, generally evaluated with available peroxides and assumed to give valid results with olefin hydroperoxides, was found in fact to give results consistent with the purity demonstrated by n.m.r. and g.c.

It was demonstrated that isomerization of either I or II to an equilibrium mixture containing approximately equal quantities of each hydroperoxide occurs readily in dilute solutions of hexane, carbon tetrachloride, or olefin at 40° . Negligible decomposition