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 ± 0.5°K., τ is 0.0125 sec., thus giving $k_1 = 47.7$ sec.$^{-1}$ and $k_{-1} = 32.3$ 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 ± 0.5°K., from which is calculated by absolute rate theory $\Delta F_a^* = 5.93 ± 0.10$ 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 $\Delta S^* \sim R \ln 2 = 1.4$ e.u., and $\Delta H_a^* \sim 6.1$ kcal./mole.

The lower ΔF_a^* for 4-bromocyclohexene is in contrast with that of cyclohexyl bromide ($\Delta F^* = 10.5$ kcal./mole) and cyclohexane ($\Delta F^* = 10.3$ 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 ± 0.2°K. The ΔF (shift) was calculated making the assumption that $(\nu_a - \nu_e)$ is independent of temperature. The "time-average" HCBr resonance at 116.1°K. was obtained by a linear extrapolation of the positions of time-average HCBr resonances from −38 to −138°. Thus, the "E_4 value," as defined by eq. 2, was found to

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

be 0.101 ± 0.050 kcal./mole by the shift method[10] and 0.077 ± 0.015 kcal./mole by area measurement.[10] The E_4 value for the 4-position in cyclohexene is defined analogously to the A value[11] 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.

(11) S. Winstein and N. J. Holness, J. Am. Chem. Soc., 77, 5562 (1955).
(12) D. H. R. Barton, R. C. Cookson, W. Klyne, and C. W. Shoppee, Chem. Ind. (London), 21 (1954).
(13) Alfred P. Sloan Fellow, 1961–1965.

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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

$$\begin{array}{cc}
\underset{\underset{OOH}{|}}{\overset{\overset{CH_3}{|}}{CH_3\underset{}{C}CH{=}CHCH_3}} & \underset{\underset{OOH}{|}}{\overset{\overset{CH_3}{|}}{CH_3C{=}CHCHCH_3}} \\
I & II
\end{array}$$

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

occurs under these conditions. This unusual rearrangement is slow in acetone-d_6 and does not appear to occur at all in 70% aqueous acetone. In methanol-d_4, sufficient decomposition occurs to obscure a slow rearrangement, while in the absence of solvent the hydroperoxides show only a slight tendency to isomerize.

Kinetics were investigated using both g.c. and n.m.r. analysis. The results appear to be complex, and it is not clear how sensitive they are to experimental technique. The rate of approach to equilibrium fits a log plot well only in CCl_4, but in all solvents except acetone (Table I) it appears that the rate of isomerization of I depends inversely on the total hydroperoxide concentration. Such an inverse dependency is, of course, compatible with the surprising stability of the pure neat hydroperoxide. The rearrangement is catalyzed by ultraviolet radiation and may be completely inhibited by 2,6-di-t-butyl-4-methylphenol. The following mechanism appears to explain these results adequately.

Initiation

RO· + ·OH ⟵— ROOH ⇌ (ROOH)$_n$ ⟶ decomposition

ROOH + RO· (·OH) ⟶ ROO· + ROH (H₂O)
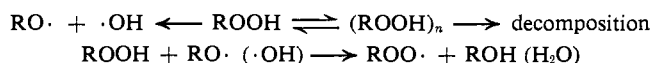
Propagation
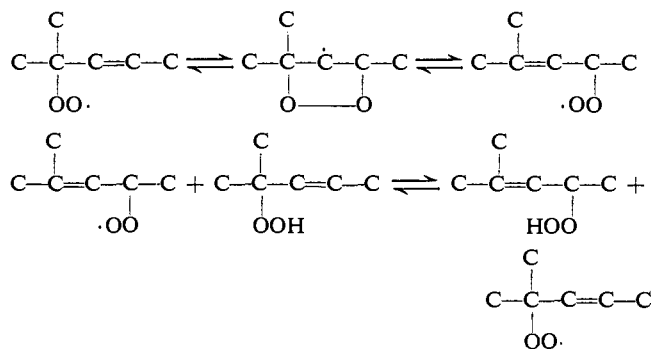
It is assumed that hydrogen is much less readily abstracted from the hydrogen bonded complex, (ROOH)$_n$, or from a solvent–hydroperoxide complex than from the unbonded hydroperoxide. Hydrogen bonding may also explain the apparently equal stability of the tertiary and secondary hydroperoxide. Both the n.m.r. and infrared spectra indicated strong hydrogen bonding in the dilute hydroperoxide solutions studied.

More pertinent for the understanding of the products produced by the autoxidation of olefins is the behavior of the pure hydroperoxides at the higher temperatures required for oxidation. At 100° decomposition becomes equally rapid for both I and II in olefin solvent, but it is clearly preceded by isomerization. In 70% aqueous acetone, in which rearrange-

Table I. Rate of Allylic Rearrangement of I or II to an Equilibrium Mixture

| Solvent | Anal. | I | | II | |
		Concn., M	$t_{1/2}$,[a] min.	Concn., M	$t_{1/2}$, min.
CCl₄	N.m.r.	0.50	180	0.97	
		0.12	65	0.32	170
				0.24	
Hexane	G.c.	0.21	110	0.15	80
		0.71	500		
4-Methyl-2-pentene	G.c.	0.65	2300[b]		
		0.22	920		
Acetone-d_6	N.m.r.	0.31	650		
		0.15	1400		

[a] From a log plot taking the equilibrium concentration of I as 60% in acetone-d_6 and 50% in the other solvents. [b] Rearrangement stopped at 15% I.

ment is retarded, the decomposition is more rapid, and II can be shown to be less stable than I with the over-all kinetics being complicated as expected. In cis-4-methyl-2-pentene at 100°, less than 10% of the reacted hydroperoxide produces epoxide by oxidation of the olefin solvent. More trans- than cis-epoxide is produced until the decomposition of the hydroperoxides is nearly complete, when an increase in the yield of cis-epoxide is detectable.

While allylic rearrangement has previously been observed for the single case of Δ^5-steroid 7-hydroperoxides,[1] the present work with a simpler system is the first demonstration of the equilibration of isomeric allylic hydroperoxides. It is not yet clear how general hydroperoxide isomerizations may be, but caution must be observed in interpreting the hydroperoxide products determined by the prevalent technique of reducing oxidation mixtures and identifying the alcohols formed.[2] It is small consolation that it can be shown that no rearrangement accompanies the reduction of I or II with sodium sulfite or sodium borohydride. Also, the reported formation of trans-hydroperoxide in the autoxidation of cis-olefin[2] which appears to demonstrate the lack of configurational stability for the cis-allyl radical may now be explained by the previously unsuspected rearrangements: cis-I → II ⇌ trans-I.

(1) G. O. Schenck, O. A. Neumuller, and W. Eisfeld, Ann., 618, 202 (1958).

(2) W. F. Brill, American Chemical Society, Division of Petroleum Chemistry, Preprints, Symposia 9, No. 4, D-73, Sept. 1964.

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