Oxyfunctionalization of Hydrocarbons. 1. Protolytic Cleavage-Rearrangement Reactions of Tertiary Alkyl Hydroperoxides with Magic Acid

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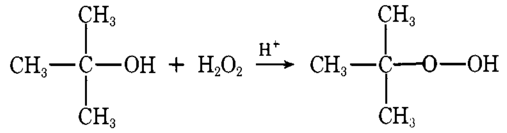
Abstract: Magic acid catalyzed cleavage-rearrangement reactions of a series of *tert*-alkyl hydroperoxides were studied. Similar reactions were achieved by treating directly the corresponding tertiary alcohols with hydrogen peroxide and magic acid. For *tert*-butyl hydroperoxide both O-O and C-O cleavage reactions were observed, depending on reaction conditions. The intermediate carboxonium ions generated from O-O cleavage reactions were examined by ^{13}C NMR spectroscopy.

Introduction

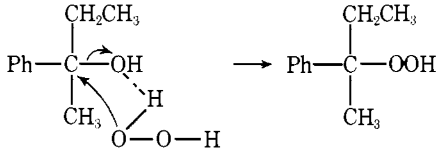
The reaction of hydrogen peroxide with tertiary alcohols in the presence of acid has long been used for preparation of hydroperoxides. For example, reaction of *tert*-butyl alcohol with hydrogen peroxide together with a catalytic amount of concentrated sulfuric acid at 0-5° gives *tert*-butyl hydroperoxide in good yield (eq 1).[2,3]



$$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-OH + H_2O_2 \xrightarrow{H^+} CH_3-\overset{CH_3}{\underset{CH_3}{C}}-O-OH \quad (1)$$

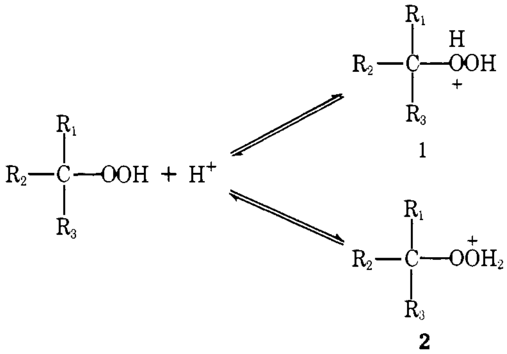
The reaction was assumed to proceed via an SN1 pathway (eq 2), although in some cases such as that of 2-phenylbutan-2-ol, partial participation of an SNi mechanism (eq 3) could not be completely ruled out.[4]

$$R_3COH \longrightarrow R_3C^+ \xrightarrow{H_2O_2} R_3COOH \quad (2)$$



(3)

Hydroperoxides themselves react with acids, depending upon conditions, and acid-catalyzed rearrangement and cleavage reactions of particularly alkaryl hydroperoxides such as cumyl hydroperoxide have been extensively investigated.[5] The initial step involves protonation at either oxygen atom, leading to the two conjugate acids **1** and **2** (eq 4).

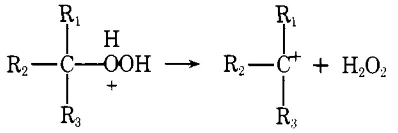


1

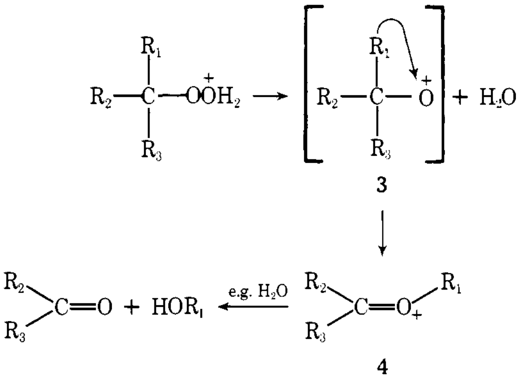
2

(4)

1 can undergo C-O heterolysis forming hydrogen peroxide and the corresponding carbenium ion (eq 5), while for **2** cleavage of the oxygen to oxygen bond results in formation of water and the corresponding highly energetic oxenium ion **3**; the latter immediately rearranges to the alkylated (arylated) ketone (carboxonium ion) **4** which then reacts further, depending on conditions employed (eq 6).



$$R_2-\overset{R_1}{\underset{R_3}{C}}-\overset{H}{\underset{+}{O}}OH \longrightarrow R_2-\overset{R_1}{\underset{R_3}{C^+}} + H_2O_2 \quad (5)$$

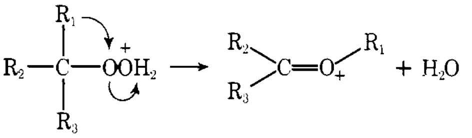


3

4

(6)

Oxenium ions of type **3** have never been observed as long-lived species in solution,[6] and it may well be that a concerted alkyl (aryl) shift and elimination (eq 7) follows the initial protonation.



(7)

The relative migratory aptitude of the R group shows the trend phenyl > vinyl > cyclopentyl > propyl > ethyl > methyl.[5] Hydrogen was shown to be ≃ propyl.[10]

tert-Butyl hydroperoxide is remarkably resistant to acid-catalyzed rearrangement. Sulfuric or perchloric acid in acetic acid failed to induce rearrangement, the reaction occurring via C-O heterolysis resulting in formation of 2-methylpropene and hydrogen peroxide.[8] In the presence of boron trifluoride, *tert*-butyl hydroperoxide yielded some acetone and methanol.[9] More recently, however, Deno, using 90-98% sulfuric acid at 25°, showed that exclusive O-O heterolysis occurred followed by methyl migration and hydrolysis, giving acetone and methanol.

$$(CH_3)_3COOH \xrightarrow{H_2SO_4} (CH_3)_2CO\ (100\%) + CH_3OSO_3H\ (100\%) \quad (8)$$

Table I. ^{13}C NMR Parameters of *tert*-Butyl Systems[a]

Compound	^{13}C chemical shift, ppm $-C-O-$	$-CH_3$
tert-Butyl hydroperoxide	80.73	25.89
tert-Butyl peroxide	78.15	26.69
tert-Butyl alcohol	68.68	30.99
Di-*tert*-butyl ether[b]	76.3	33.8

[a] $CDCl_3$, internal Me_4Si. [b] G. A. Olah and H. Lin, *Synthesis*, 315 (1975).

Interested in hydrocarbon functionalization reactions, we have now carried out a study of the reactions of *tert*-butyl hydroperoxide with superacids such as magic acid. We found that by varying the amount of acid used both pathways (eq 5 and 6) could be observed. Our studies were also extended to the effect of strong acids on other *tert*-alkyl hydroperoxides by both direct and indirect methods. The latter involved reacting the corresponding tertiary alcohol in situ with hydrogen peroxide[11] and magic acid, while in the former, the hydroperoxide itself was added to the acid solution. Moreover, use of superacid media enabled direct observation of the carbocationic intermediates formed in the acid-catalyzed transformations of hydroperoxides, thus allowing to unequivocally establish the mechanism of the reactions.

Results and Discussion

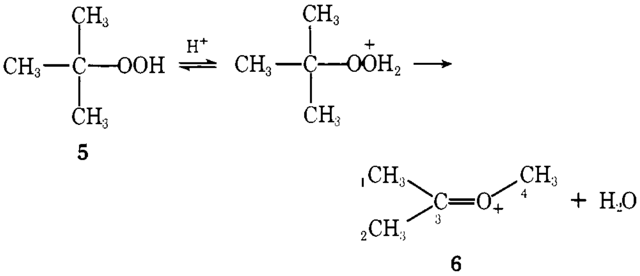
Preparation and Carbon-13 NMR Spectroscopic Analysis of Alkyl Hydroperoxides. The *tert*-alkyl hydroperoxides used in our study were usually prepared by the acid-catalyzed alkylation of hydrogen peroxide, and were analyzed as described by Hiatt.[12] Although this method is fairly reliable for hydroperoxide determinations, it tells nothing of the nature of any impurities present. Instrumental methods, e.g., ir, ^1H NMR, Raman, and uv spectroscopy have also been employed for identification of impurities such as alcohols and peroxides contained in hydroperoxides.[13] However, overlapping absorptions often make peak assignments difficult.

FT ^{13}C NMR spectroscopy was found to be a most convenient method for the analysis of alkyl hydroperoxides. The carbon shifts of the hydroperoxides are significantly different from those of the starting alcohols, as well as the corresponding peroxides. This is illustrated for the *tert*-butyl systems in Table I.

We were able to detect the presence of impurities at levels of about 5% or less. For example, 1% of *tert*-butyl alcohol could be detected in *tert*-butyl peroxide after ~400 transients. Furthermore, the ^{13}C NMR method has the advantage of determining the nature of the impurities. ^{13}C NMR parameters of the other hydroperoxides studied together with those for the corresponding alcohols are given in Table II.

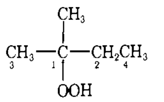
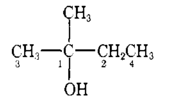
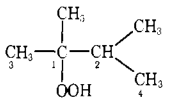
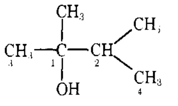
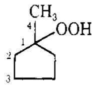
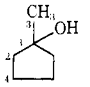
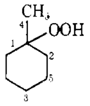
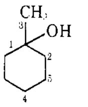
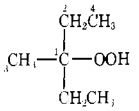
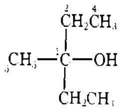
Reaction of Alkyl Hydroperoxides with Magic Acid. *tert*-Butyl Hydroperoxide. Careful addition of an equimolar amount of *tert*-butyl hydroperoxide (**5**) in SO_2ClF at −78° to a well-stirred solution of magic acid in SO_2ClF at −78° gave a vigorous reaction. ^1H and ^{13}C NMR spectra of the resultant clear pale yellow solution were consistent with reaction via O–O cleavage, as were the spectra obtained when a twofold excess of magic acid was employed. The latter spectra were more clearly defined as the protonated oxygenated species were "frozen out" under these conditions, the reaction occurring as shown in Scheme I.

Scheme I



^{13}C NMR 1, 27.01; 2, 32.2; 3, 245.21; 4, 68.81
^1H NMR 1,2, 3.37; 4, 5.20

Table II. ^{13}C NMR Chemical Shifts of *tert*-Alkyl Hydroperoxides[a]

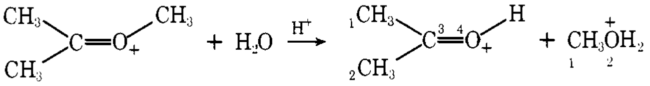
Compound	Peak number 1	2	3	4	5
	84.16	32.14	24.44	9.35	
	71.0	36.56	28.70	8.77	
	85.14	34.08	21.0	17.6	
	73.05	38.88	26.44	17.77	
	92.1	36.86	24.88	23.59	
	79.7	41.3	28.33	24.18	
	77.28	35.47	26.0	24.9	22.53
	69.76	39.66	29.67	26.0	22.88
	85.11	28.75	20.7	8.0	
	72.92	33.97	25.9	8.29	

[a] In $CDCl_3$, internal Me_4Si.

The water formed in this reaction (particularly when the concentration of excess superacid is lower) can readily hydrolyze the dimethylmethoxycarbenium ion (**6**) yielding acetone and methanol, both being observed as protonated species (Scheme II).

On reacting **5** with a fivefold excess of magic acid, ^1H and ^{13}C NMR showed formation of the trimethylcarbenium ion[14] (**7**), together with absorptions due to the intermediate ion **6**, protonated methanol, and protonated acetone. Formation of **7** which occurred to the extent of 15% implies that with a large excess of magic acid C–O cleavage com-

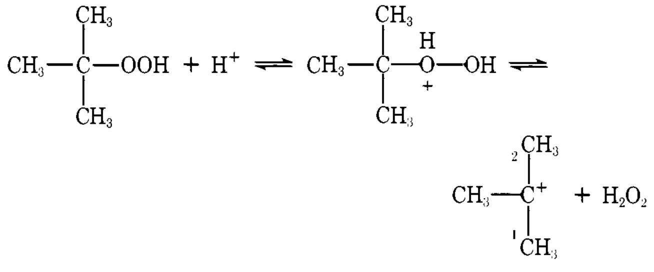
Scheme II



^{13}C NMR 1, 31.6; 2, 30.21; 3, 248.53, 1, 62.01
^{1}H NMR 1,2, 3.47; 4, 14.30, 1, 4.80, t, $J = 4$ Hz; 2, 9.50, q, $J = 4$ Hz

petes effectively with O-O cleavage, as shown in Scheme III.

Scheme III

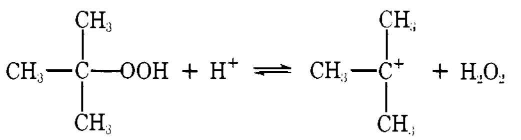


7

^{13}C NMR 1, 335.67; 2, 47.78
^{1}H NMR 2, 4.30

Whereas the reaction of *tert*-butyl hydroperoxide with perchloric acid yields products from C-O heterolysis[8] the reaction with a twofold excess of magic acid gives exclusive O-O cleavage, while a fivefold excess of magic acid yields products via both O-O (85%) and C-O (15%) cleavage pathways.

The differing reactivity can readily be explained as being due to the overall reversibility of the reaction shown in Scheme III, i.e.



$$(CH_3)_3C{-}OOH + H^+ \rightleftharpoons (CH_3)_3C^+ + H_2O_2$$

7

Under milder acid conditions,[8] the trimethylcarbenium ion (**7**) is readily lost to the equilibrium, isobutylene being formed via proton elimination. Under more severe acid conditions **7** is stable, and thus a true equilibrium can exist. Protonation of the end oxygen in **5** removes **5** from the equilibrium, consequently forcing the reaction to the left. This type of preequilibrium reaction is known to interfere with rate studies in the acid-catalyzed rearrangements of hydroperoxides,[15] and in some cases olefins and peroxides have been formed as by-products.[16]

With a large excess of magic acid, however, it is quite likely that hydrogen peroxide formed from C-O heterolysis will be protonated, and hence its nucleophilicity reduced, resulting in the observation of the trimethylcarbenium ion. That a large excess of acid is necessary to deactivate the hydrogen peroxide is not surprising since it has been estimated that hydrogen peroxide is more than a million times less basic than water.[17] It has also been shown that typical acids in strong hydrogen peroxide have about the same conducting power as their salts, suggesting that the proton has a normal mobility in hydrogen peroxide, in contrast to the abnormal conductance of the proton and hydroxyl ion in water.[18]

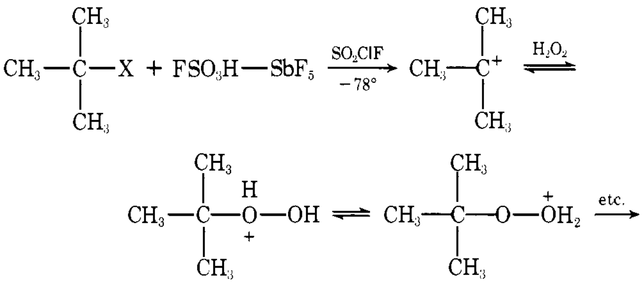
We subsequently studied the behavior of hydrogen peroxide in magic acid. The ^{1}H NMR spectrum of a usual sample of 1:1 magic acid shows the acid proton peak at δ 12.2 and generally a hydronium ion impurity peak at ca. δ 9.9. For the sample of magic acid used, the hydronium ion peak was ~8% of the acid peak. Addition of 0.02 g of hydrogen peroxide (98%)[19] to magic acid (1 g in SO_2ClF at $-78°$) increased the relative intensity of the hydronium peak to 11% of the acid peak and this was increased to 18% by addition of a further 0.04 g of hydrogen peroxide with no observable broadening or appreciable change in chemical shift. However, on addition of a further 0.04 g of hydrogen peroxide to the acid solution, the ^{1}H NMR spectrum showed broadening such that no peak was discernible from the baseline. Higher concentrations, ca. 0.1 g of hydrogen peroxide in 1 g of magic acid, show a single broad peak in the ^{1}H NMR spectrum at $-70°$ at δ 10.7. The ^{1}H NMR results indicate that at low concentrations (<0.06 g of H_2O_2 in magic acid) a rapid exchange is occurring between the hydronium ion and hydrogen peroxide, the equilibrium presumably being well to the left,

$$H_2O_2 + H_3O^+ \rightleftharpoons H_3O_2^+ + H_2O$$

while at the higher concentrations, complete exchange between hydrogen peroxide, the hydronium ion, and acid occurs. Thus the failure to observe static protonated hydrogen peroxide is in agreement with previous studies.[16,17]

The observation that the trimethylcarbenium ion was reacting reversibly with hydrogen peroxide under our reaction conditions prompted the carrying out of quenching experiments in which **7** generated under stable ion conditions was treated with hydrogen peroxide. The addition of a solution of *tert*-butyl chloride, *tert*-butyl alcohol, or isobutane, and hydrogen peroxide in SO_2ClF to an SO_2ClF solution of magic acid (2-3 molar excess) yielded the oxonium ion (**6**) together with some acetone and methanol (Scheme IV).

Scheme IV

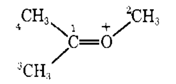
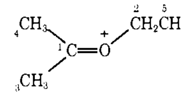
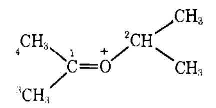
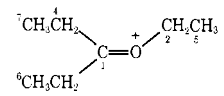
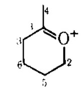
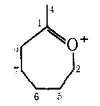
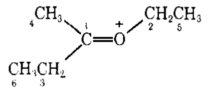
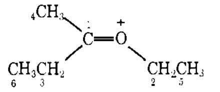


X = OH, Cl, H

Similar results were obtained when the trimethylcarbenium ion was added directly to an SO_2ClF solution of hydrogen peroxide. This latter method, however, can result in explosive reactions[20] and therefore in the studies of other tertiary alkyl hydroperoxide systems the former method was used.

In the reactions of other *tert*-alkyl hydroperoxides studied under similar conditions described for *tert*-butyl hydroperoxide, we failed to detect any carbenium ion intermediates, reflecting the high stability of the trimethylcarbenium ion.[21] The spectra obtained from these reactions were consistent with products formed from O-O heterolysis. However, we were able to observe the intermediate carboxonium ions in the rearrangement reaction of a number of *tert*-alkyl hydroperoxides. Identical intermediates were also formed when the corresponding tertiary alcohol was treated with hydrogen peroxide and magic acid, and indeed this later method often gave cleaner ^{13}C NMR spectra. However, ^{1}H NMR spectra obtained from the reactions employing hydrogen peroxide usually showed poor resolution due to dis-

Table III. ^{13}C NMR Parameters of Intermediate Carboxonium Ions

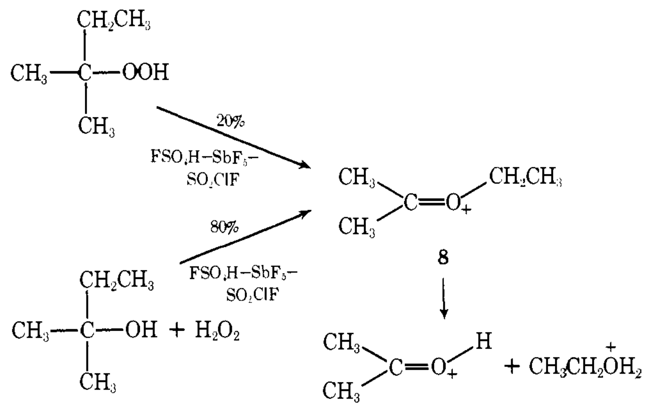
Oxonium ion	Structure	Chemical shift, ppm[a]						
		1	2	3	4	5	6	7
6		245.1	68.81	32.2	27.01			
8		243.13	82.47	32.37	27.27	13.03		
9		240.72	95.09	32.68	26.72	20.76		
12		247.92	80.74	34.3	28.72	13.04	11.03	8.05
13		241.8	84.63	37.73	30.17	20.46	14.72	
15		248.61	87.35	40.24	32.83	28.38	25.23	21.49
19		243.64	81.57	39.86	25.27	12.05	5.25	
20		246.57	80.52	33.80	28.70	12.05	7.49	

[a] SO_2ClF, external Me_4Si, -40°.

solved oxygen. The ^{13}C NMR is not affected by broadening since carbons have longer relaxation times than protons. The studied reactions are described subsequently and the ^{13}C NMR parameters of the intermediate carboxonium ions are summarized in Table III.

***tert*-Amyl Hydroperoxide.** *tert*-Amyl hydroperoxide was reacted with magic acid as outlined in Scheme V. *tert*-Amyl alcohol with hydrogen peroxide and magic acid behaved similarly; however, in this system the intermediate carboxonium ion (**8**) was less affected by hydrolytic cleavage. No products arising from methyl migration could be found. This was the case in all systems studied where there was a choice of migrating group.

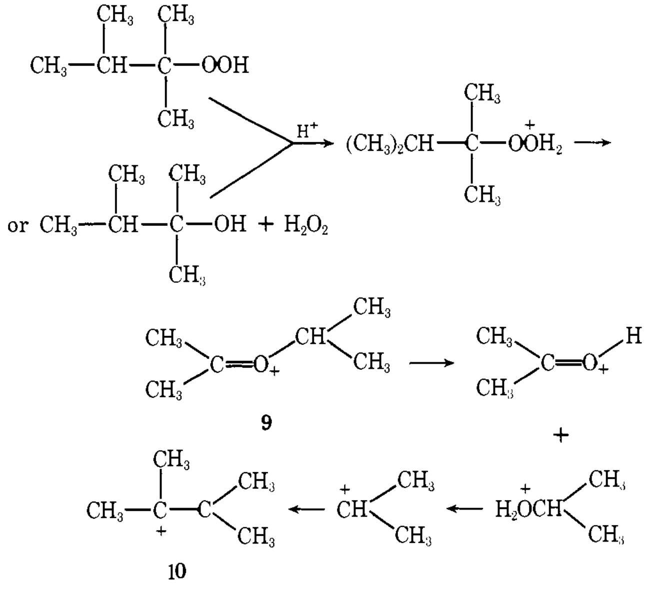
Scheme V



2,3-Dimethyl-2-butyl Hydroperoxide. The carboxonium ion intermediate (**9**) was obtained by protolysis of the hydroperoxide or via the alcohol-hydrogen peroxide route. The reaction was complicated by isopropyl alcohol formed from hydrolysis of **9**, reacting further to yield the *tert*-hexyl cation etc.[23] (Scheme VI).

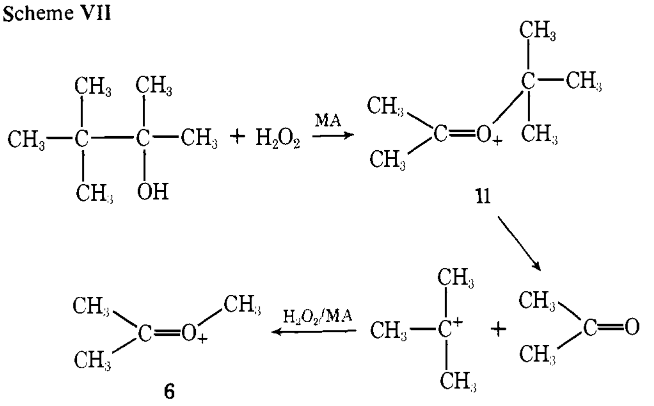
3,3,2-Trimethyl-2-butyl Hydroperoxide. The procedure described by Winstein and Hedaya[24] for the preparation of

Scheme VI



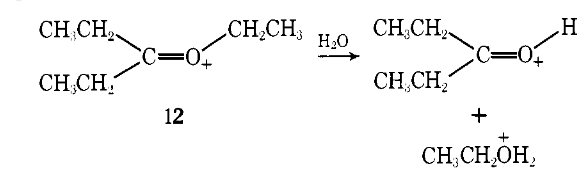
3,3,2-trimethyl-2-butyl hydroperoxide gave low yield. However, the rearrangement reaction of the 3,3,2-trimethylbutyl system was studied by way of the reaction of 3,3,2-trimethylbutan-2-ol and hydrogen peroxide with magic acid. As expected, the *tert*-butyl group migrated to the total exclusion of methyl migration. The initial carboxonium ion (**11**) formed in this reaction was not stable and readily cleaved to give acetone and the trimethylcarbenium ion. The latter underwent further reaction with excess hydrogen peroxide present in the system, yielding the oxonium ion **6**, (Scheme VII).

Scheme VII



1,1-Diethylpropyl Hydroperoxide. The ^{13}C NMR spectra of the resultant solution from the reaction of 1,1-diethylpropanol with hydrogen peroxide and magic acid showed clearly the presence of the intermediate diethylethoxycarbenium ion (**12**) together with its hydrolysis products pentan-3-one and ethanol (Scheme VIII).

Scheme VIII



The ^{1}H NMR spectrum of the solution showed broad unresolved signals. However, the chemical shifts for the methylene protons in ethanol and in **12** were sufficiently displaced (δ 5.17, 5.50 ppm, respectively) to allow integration which showed the ion **12** to be present to the extent of approximately 50%.

Some small impurity peaks were also observed in the ^{13}C NMR spectra. In particular one peak at $\delta_{^{13}C}$ 194 (10% of the peak height of the carbonyl carbon in **12**), suggested the presence of an ester moiety. An ester would be an expected by-product in this reaction, since it could be formed via the Baeyer-Villiger oxidation of pentan-3-one. The feasibility of this side reaction was shown in separate experiments in which we induced the Baeyer-Villiger oxidation of a number of ketones under similar conditions employed for the alcohol/hydrogen peroxide/magic acid reactions.

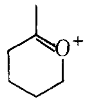
The ^{1}H NMR and ^{13}C NMR spectra of the final reaction mixture for the ketones studied gave the results indicated in Table IV.

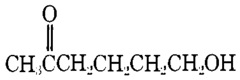
Table IV. Baeyer-Villiger Oxidation of Ketones

Ketone	% yield of ester and hydrolysis products
Butan-2-one	40
Pentan-3-one	66
Heptan-4-one	10

1-Methylcyclopentyl and 1-Methylcyclohexyl Hydroperoxides. The acid-catalyzed rearrangements of 1-methylcyclopentyl hydroperoxide[25] and 1-methylcyclohexyl hydroperoxide[26] have previously been reported. Reaction was induced in concentrated sulfuric acid, and the products isolated were, for 1-methylcyclopentyl hydroperoxide, unspecified yield of 7-hydroxyheptan-2-one. Deno[10] observed a similar reaction upon the addition of 1-methylcyclopentanol and 1-methylcyclohexanol, respectively, to solutions of $K_2S_2O_8$ in 20-60% H_2SO_4, obtaining the cyclic carboxonium ions **13** and **15**.

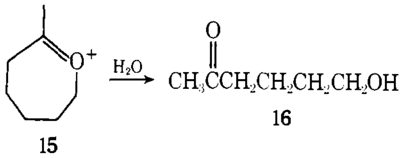
We examined these systems by both addition of the hydroperoxide to magic acid and by reaction of the alcohols with hydrogen peroxide and magic acid. For the 1-methylcyclopentyl systems the spectra obtained were consistent with exclusive formation of the cyclic carboxonium ion **13**. The spectra do not indicate the presence of the ring-opened hydroxy ketone **14**.


13

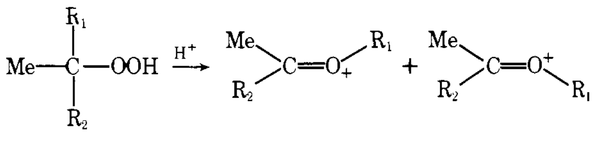

$CH_3\overset{\overset{\displaystyle O}{\|}}{C}CH_2CH_2CH_2CH_2OH$
14

In the acyclic systems studied (particularly for the hydroperoxides where the amount of water in the system is necessarily less than for the alcohol-hydrogen peroxide system), the ketone and alcohol hydrolysis products of the intermediate carboxonium ions were always observed as protonated species for temperatures lower than ca. −40°.

For the reaction of 1-methylcyclohexanol with hydrogen peroxide and magic acid, the ^{13}C NMR spectrum of the reaction mixture indicated the presence of one species, the cyclic carboxonium ion **15**. **15** was also the major species formed (80%) when 1-methylcyclohexyl hydroperoxide was treated with magic acid, but the solution also contained a number of other species, one of which is the hydrolysis product of **15**, heptan-6-on-1-ol (**16**).

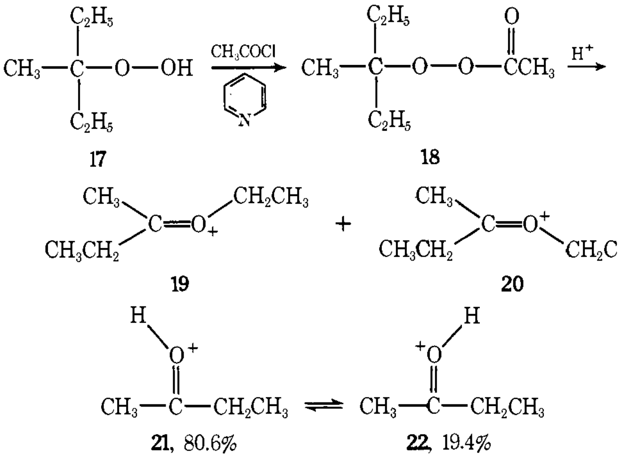


For systems in which the parent compound has only one methyl group, the intermediate carboxonium ion can exist as cis and trans isomers, viz.



We decided to check this experimentally. Taking the simplest case, 3-methylpentane 3-hydroperoxide (**17**), we found that both the hydroperoxide **17** and the corresponding alcohol-hydrogen peroxide system gave only the hydrolysis products from the oxonium ion(s), namely butan-2-one and ethanol. The problem of hydrolysis was resolved by starting from the peroxy ester 3-methylpentane 3-peroxyacetate (**18**). The cleavage product in the acid-catalyzed rearrangement reaction of **18** and acetic acid gives little or no products arising from acetolysis of the oxonium ions.[22] The ^{13}C NMR spectra of the resultant solution when **18** was treated with magic acid in SO_2ClF was consistent with formation of the two carboxonium ions **19** and **20** (Scheme IX). We assigned **19** as the major isomer on the basis of the known isomeric distribution for protonated butan-2-one **21** and **22**.[26]

Scheme IX



Conclusions

We have examined the reaction of a number of tertiary hydroperoxides and/or tertiary alcohols-hydrogen peroxide with magic acid. In these reactions ^{13}C NMR spectroscopy proved to be a useful mechanistic probe for observing intermediate species. We are currently extending this work in a number of directions, including preparative applications, and will report our observations subsequently.

Experimental Section

Magic acid (1:1 FSO_3H-SbF_5) used was spectrograde from Cationics, Inc., Columbia, S.C. Hydrogen peroxide (98%) was obtained from F.M.C. Corp., Buffalo, N.Y. Sulfuryl chloride fluoride was spectrograde Cationics. *tert*-Butyl hydroperoxide (Matheson Coleman and Bell) was purified by repeated distillation. *tert*-Amyl hydroperoxide and 2,3-dimethyl-2-butyl hydroperoxide were prepared by acid-catalyzed alkylation of hydrogen peroxide, according to a literature procedure.[24]

1-Methylcyclopentyl hydroperoxide, 1-methylcyclohexyl hydroperoxide, and 3-methyl-3-pentyl hydroperoxide were prepared analogously. The ^{13}C NMR parameters for the hydroperoxides used are given in Tables I and II.

3-Methyl-3-pentyl peroxyacetate was prepared in an analogous manner to that used by Yablokov, Shushunov, and Kolyaskina[27] for the preparation of cumyl peroxyacetate.

General Procedure for Acid-Catalyzed Rearrangement of Hydroperoxides. To a vigorously stirred (Vortex mixer) solution of a 2-5 molar excess of magic acid in SO_2ClF at dry ice-acetone temperature (ca. −78 °C) a solution of the hydroperoxide (ca. 0.5 g) was added slowly in small portions. The resulting solution was then transferred at the same temperature into the precooled NMR probe for study.

General Procedure for Alcohol-Hydrogen Peroxide-Magic Acid Systems. A 2-3 molar excess of magic acid in SO_2ClF was stirred (magnetic stirrer) in a 50-ml Erylenmeyer flask held at dry ice-acetone temperature. To this was added, with great caution, a homogeneous solution of the alcohol (1 g) with a 1.5-2 molar excess of 98% hydrogen peroxide in SO_2ClF. The latter solution was kept at ice-salt temperature (~−20 °C) as hydrogen peroxide solidified at temperatures below ca. −30 °C. On addition of a few drops of the alcohol-hydrogen peroxide solution to the magic acid solution, a vigorous reaction occurred. When this subsided addition was continued. Usually addition of the alcohol-hydrogen peroxide solution took 5-10 min. The resulting solution was then studied by NMR spectroscopy.

Baeyer-Villiger oxidation reactions of ketones were carried out in an analogous manner. However, the magic acid-SO_2ClF solution in these reactions was held at ~−40°.

NMR Spectroscopic Study ^1H NMR spectra were obtained on a Varian Associates Model A56/60-A spectrometer equipped with a variable-temperature probe.

^{13}C NMR spectra were obtained on a Varian Associates Model XL-100 spectrometer equipped with a broad band decoupler and variable-temperature probe. The instrument operates at 25.2 MHz for carbon-13, and is interfaced with a Varian 620L computer. The combined system was operated in the pulse Fourier transform mode, employing a Varian Fourier transform accessory.

Typically 1-2000 pulses, with a pulse width of 20 μsec and pulse delay of 1.5 s, were required to give satisfactory signal to noise ratios. Field frequency stabilization was maintained by locking on the fluorine-19 external sample of fluorobenzene. Chemical shifts were measured from the carbon-13 signal of 5% carbon-13 enriched tetramethylsilane in a 1.75-mm capillary held concentrically inside the standard 12-mm sample tube.

Precursor hydroperoxides were run in $CDCl_3$ with internal tetramethylsilane.

Peak assignments were aided by off resonance spectra.

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References and Notes

(1) (a) Postdoctoral research fellow; (b) Visiting scientist from the Societa Italiana Resine, Milan, Italy.

(2) R. Criegee and H. Dietrich, *Justus Liebigs Ann. Chem.*, **560**, 135 (1948).

(3) A. G. Davies, R. V. Foster, and A. M. White, *J. Chem. Soc.*, 1541 (1953).

(4) A. G. Davies, *J. Chem. Soc.*, 4288 (1962).

(5) (a) D. Swern, "Organic Peroxides", Vol. II, Wiley, New York, N.Y., 1971, p 65; (b) J. B. Lee and B. C. Leff, *Q. Rev., Chem. Soc.*, 429 (1967); (c) A. G. Davies, "Organic Peroxides", Butterworths, London, 1961; (d) E. G. Hawkins, "Organic Peroxides", Van Nostrand, New York, N.Y., 1961.

(6) The species $(CH_3)_3CO^+$ has been detected in the mass spectrometer from the thermal decomposition of *tert*-butyl peroxide.[7] The species was derived from the *tert*-butoxy radical.

(7) G. K. Lavsovskaya, M. I. Markin, and V. L. Talioze, Jr., *Komiss. Anal. Khim., Akad. Nauk SSSR*, **13**, 474 (1963).

(8) J. E. Leffler, *Chem. Rev.*, **45**, 385 (1949).

(9) G. A. Razuvaev and N. A. Kartashova, *Zh. Org. Khim.*, **3**, 993 (1967); *Chem. Abstr.*, **67**, 107983 (1967).

(10) N. C. Deno, W. E. Billups, K. E. Kramer, and R. R. Lastomivsky, *J. Org. Chem.*, **35**, 3080 (1970).

(11) Kharasch reacted a number of alkaryl alcohols with hydrogen peroxide and perchloric acid to obtain O-O cleavage products; cf. M. S. Kharasch and J. G. Burt, *J. Org. Chem.*, **15**, 150 (1950).

(12) R. Hiatt, T. Mill, K. C. Irwin, and J. K. Castleman, *J. Org. Chem.*, **33**, 1421 (1968).

(13) R. D. Mair and R. T. Hall, ref 5a, Chapter 6.

(14) G. A. Olah and A. M. White, *J. Am. Chem. Soc.*, **91**, 5801 (1969).

(15) D. E. Bissing, C. A. Matuszak, and W. E. McEwen, *Tetrahedron Lett.*, 763 (1962).

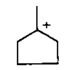
(16) Cf. A. W. Van Stevenik and E. C. Koogman, *Recl. Trav. Chim. Pays-Bas*, **79**, 413 (1960).

(17) A. G. Mitchell and W. F. K. Wynne-Jones, *Discuss. Faraday Soc.*, **No. 15**, 161 (1953); *Trans. Faraday Soc.*, **51**, 1690 (1955).

(18) E. S. Shanley in "Peroxide Reaction Mechanisms", J. O. Edwards, Ed., Interscience, New York, N.Y., 1962.

(19) This is the maximum yield of hydrogen peroxide that could theoretically be obtained (from C-O cleavage) in our experiment for the reaction of *tert*-butyl hydroperoxide with a fivefold excess of magic acid.

(20) A detonation resulted when the 1-methylcyclopentylcarbenium ion (A) in magic acid-SO_2ClF solution was added to an SO_2ClF solution of hydrogen peroxide.



A

(21) A study of the related acid-catalyzed rearrangement reaction of *tert*-alkyl peroxy esters[22] underlines this result. *tert*-Butyl peroxyacetate gave with a fivefold excess of magic acid ~80% O-O cleavage products via the oxonium ion **6** and acetic acid, and ~20% C-O cleavage products, viz. the trimethylcarbenium ion and peroxyacetic acid. Other peroxy esters studied, such as *tert*-amyl peroxy ester, gave only O-O cleavage products.

(22) G. A. Olah, D. G. Parker, and N. Yoneda, submitted for publication.

(23) G. A. Olah and A. M. White, *J. Am. Chem. Soc.*, **91**, 5801 (1969).

(24) E. Hedaya and S. Winstein, *J. Am. Chem. Soc.*, **89**, 1661 (1967).

(25) E. G. E. Hawkins, *J. Chem. Soc.*, 2801 (1950).

(26) W. Pritzkow and K. A. Müller, *Chem. Ber.*, **89**, 2321 (1956).

(27) V. A. Yablokov, V. A. Shushunov, and L. V. Kolyaskina, *Zh. Obshch. Khim.*, **32**, 2714 (1962); taken from *J. Gen. Chem. USSR* (*Engl. Transl.*), **32**, 2671 (1962).