(q, 4 H); ir (neat) ν C≡C 2190 cm^{-1}; MS M$^+$ *m/e* (rel intensity) 254 (72), 185 (16), 156 (28), 141 (100), 128 (15), 115 (36).

1-Ethoxy-1-(*p*-anisylethynyl)cyclopropane 8 (X = OCH$_3$; R = CH$_2$CH$_3$): NMR (CCl_4) δ 1.02 (m, 4 H), 1.05–1.30 (t, 3 H, J = 7 Hz), 3.50–3.85 (q, 2 H, J = 7 Hz), 3.75 (s, 3 H), and 6.65–7.35 ppm (q, 4 H); ir (neat) ν C≡C 2185 cm^{-1} (very strong); MS M$^+$ *m/e* (rel intensity) 216 (3), 201 (6.5), 188 (41), 172 (20), 159 (100), 144 (35), 116 (20), 115 (15), 88 (20).

1-(2′,2′,2′-Trifluoroethoxy)-1-(*p*-anisylethynyl)cyclopropane 8 (X = OCH$_3$; R = CH$_2$CF$_3$): NMR (CCl_4) δ 1.10–1.20 (m, 4 H), 3.75 (s, 3 H), 3.80–4.20 (q, 2 H, J = 8.7 Hz), and 6.70–7.30 ppm (q, 4 H); ir (neat) ν C≡C 2190 cm^{-1}; MS M$^+$ *m/e* (rel intensity) 270 (24.5), 201 (100), 187 (47), 173 (30), 171 (27), 159 (89), 145 (36), 144 (32), 128 (38), 116 (28), 115 (24.5), 57 (32), 55 (45).

2-Methylene-4-*p*-anisyl-3-butyn-1-ol 10 (X = OCH$_3$): NMR (CCl_4) δ 3.75 (s, 3 H), 4.20 (m, 2 H), 5.50 (m, 2 H), and 6.70–7.40 ppm (q, 4 H); ir (neat) ν C≡C 2185 cm^{-1}; MS M$^+$ *m/e* (rel intensity) 188 (7.5), 159 (100), 144 (4), 116 (3), 57 (4), 55 (2.8).

1-(2′,2′,2′-Trifluoroethoxy)-2-methylene-4-*p*-anisyl-3-butyne 10 (X = OCH$_3$; R = CH$_2$CF$_3$): NMR (CCl_4) δ 3.75 (s, 3 H), 3.80–4.20 (q, 2 H, J = 8.7 Hz), 4.15 (m, 2 H), 5.55 (m, 2 H), and 6.70–7.40 ppm (q, 4 H); ir (neat) ν C≡C 2180 cm^{-1}; MS M$^+$ *m/e* (rel intensity) 270 (70), 172 (25.5), 157 (100), 135 (25.5), 57 (60), 55 (29.5).

Kinetic procedures have been described in the preceding report.[1]

Acknowledgment. The author is grateful to Professor J. M. Conia for his interest and constant encouragement throughout this work.

Registry No.—**3**, 57951-60-7; **4**, 60512-41-6; **5**, 60512-42-7; **6**, 13837-45-1; **8** (X = CH$_3$), 60512-43-8; **8** (X = OCH$_3$), 60512-44-9; **8** (X = H; R = CH$_2$CF$_3$), 60512-45-0; **8** (X = CH$_3$; R = CH$_2$CH$_3$), 60512-46-1; **8** (X = CH$_3$; R = CH$_2$CF$_3$), 60512-47-2; **8** (X = OCH$_3$; R = CH$_2$CH$_3$), 60512-48-3; **8** (X = OCH$_3$; R = CH$_2$CF$_3$), 60512-49-4; **9** (X = CH$_3$), 766-97-2; **9** (X = OCH$_3$), 768-60-5; **10** (X = H; R = CH$_2$CF$_3$), 60512-50-7; **10** (X = CH$_3$), 60512-51-8; **10** (X = CH$_3$; R = CH$_2$CH$_3$), 60512-52-9; **10** (X = CH$_3$; R = CH$_2$CF$_3$), 60512-53-0; **10** (X = OCH$_3$), 60512-54-1; **10** (X = OCH$_3$; R = CH$_2$CF$_3$), 60512-55-2; 1,1-dibromo-2-*p*-tolylethylene, 60512-56-3; 1,1-dibromo-2-*p*-anisylethylene, 60512-57-4; tosyl chloride, 98-59-9.

References and Notes

(1) Part 1: J. Salaun, *J. Org. Chem.*, **41**, 1237 (1976).
(2) J. A. Berson and S. S. Olin, *J. Am. Chem. Soc.*, **92**, 1087 (1970).
(3) J. A. Landgrebe and L. W. Becker, *J. Am. Chem. Soc.*, **89**, 2505 (1967); see also ref 9.
(4) J. D. Roberts and V. C. Chambers, *J. Am. Chem. Soc.*, **73**, 5034 (1951).
(5) R. B. Woodward and R. Hoffmann, *J. Am. Chem. Soc.*, **87**, 395 (1965); C. H. Depuy, L. G. Schnack, J. W. Hausser, and W. Wiedemann, *ibid.*, **87**, 4006 (1965).
(6) H. H. Wassermann, R. E. Cochoy, and M. S. Baird, *J. Am. Chem. Soc.*, **91**, 2375 (1969).
(7) H. Taniguchi, M. Mathai, and S. Miller, *Org. Synth.*, **50**, 97 (1970).
(8) E. J. Corey and P. L. Fuchs, *Tetrahedron Lett.*, 3769 (1972).
(9) B. A. Howell and J. G. Jewett, *J. Am. Chem. Soc.*, **93**, 798 (1971).
(10) C. H. Depuy, *Acc. Chem. Res.*, **1**, 33 (1968); D. H. Gibson and C. H. Depuy, *Chem. Rev.*, **74**, 605 (1974).
(11) M. D. Schiavelli, S. C. Hixon, and H. W. Moran, *J. Am. Chem. Soc.*, **92**, 1082 (1970).
(12) C. H. Depuy, L. G. Schnack, and J. W. Hausser, *J. Am. Chem. Soc.*, **88**, 3343 (1966).
(13) J. Salaun and M. Hanack, *J. Org. Chem.*, **40**, 1994 (1975).
(14) L. L. Miller and D. A. Kaufman, *J. Am. Chem. Soc.*, **90**, 7282 (1968).
(15) C. A. Grob and R. Spaar, *Helv. Chim. Acta*, **53**, 2119 (1970).
(16) E. Grunwald and S. Winstein, *J. Am. Chem. Soc.*, **70**, 846 (1948).
(17) For definitions and a discussion of k_s, k_Δ, and k_c see P. v. R. Schleyer, J. L. Fry, L. K. M. Lam, and C. J. Lancelot, *J. Am. Chem. Soc.*, **92**, 2542 (1970).
(18) J. L. Fry, C. J. Lancelot, L. K. M. Lam, J. M. Harris, R. C. Bingham, D. J. Raber, R. E. Hall, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **92**, 2538 (1970); D. J. Raber, R. C. Bingham, J. M. Harris, J. L. Fry, and P. v. R. Schleyer, *ibid.*, **92**, 5977 (1970), and references cited therein.
(19) P. v. R. Schleyer, W. F. Sliwinski, G. W. Van Dine, U. Schollkopf, J. Paust, and K. Fellenberger, *J. Am. Chem. Soc.*, **94**, 125 (1972).
(20) P. G. Gassman and A. F. Fentiman, Jr., *J. Am. Chem. Soc.*, **92**, 2549 (1970); H. C. Brown and M. Ravindranathan, *ibid.*, **97**, 2895 (1975).
(21) H. G. Richey, J. C. Phillips, and L. E. Rennick, *J. Am. Chem. Soc.*, **87**, 1381 (1965).
(22) C. U. Pittman, Jr., and G. A. Olah, *J. Am. Chem. Soc.*, **87**, 5632 (1965); G. A. Olah, R. J. Spear, P. W. Westerman, and J. M. Denis, *J. Am. Chem. Soc.*, **96**, 5855 (1974).
(23) M. D. Schiavelli, R. P. Gilbert, W. A. Boynton, and C. J. Boswell, *J. Am. Chem. Soc.*, **94**, 5061 (1972).
(24) T. L. Jacobs, C. Hall, D. A. Barre, and P. Prempree, *J. Org. Chem.*, **32**, 2283 (1967).
(25) M. M. Otto, *J. Am. Chem. Soc.*, **56**, 1393 (1934).
(26) E. Bergmann and A. Boudi, *Chem. Ber.*, **66B**, 278 (1933).

Oxyfunctionalization of Hydrocarbons.[1a] 5. Protolytic Cleavage–Rearrangement Reactions of Tertiary Alkyl (Arylalkyl) Peroxy Esters in Superacids

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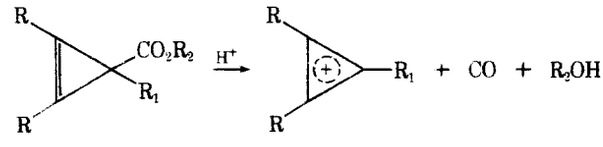
In continuation of our work on superacid induced cleavage–rearrangement reactions of hydroperoxides,[2a] we have undertaken a study of the superacid induced cleavage–rearrangement reactions of peroxy esters. Studies included those of *tert*-alkyl peroxyacetates, as well as various other *tert*-butyl peroxy esters. Particularly, *tert*-butyl peracetate was found to be unique in that both O–O and C–O cleavage products were observed, depending upon conditions. The yield of O–O and C–O cleavage products from various peroxy esters is discussed in terms of the inactivation (via protonation) of peroxy acid and the relative migratory aptitude of alkyl groups. The direct observation of the reaction intermediates, including the dimethylphenoxycarbenium ion **24** in the reactions of cumyl peroxy esters, is discussed.

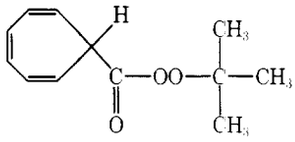
Unlike the related acid-catalyzed cleavage–rearrangement reaction of hydroperoxides (**1**)[2] those of peroxy esters are considerably less studied.

Protolysis of peroxy esters has been employed as a means of preparation of stable carbenium ions. Thus Farnum et al., upon decarboxylation of the peroxy ester, obtained the corresponding cyclopropenium ion **2**.[3]



1 **2**

Similarly Rüchardt and Schwarzer obtained the tropylium ion **4** from the peroxy ester **3**.[4]



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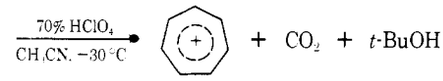
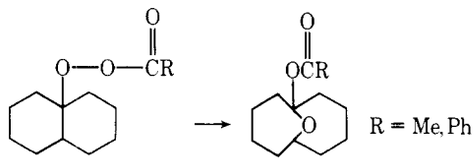


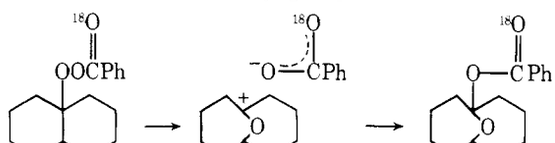
4

Ionic cleavage–rearrangement reactions of peroxy esters have also been known for some time. Criegee,[5] in 1944, observed that the acetate and benzoate esters of *trans*-9-decalyl hydroperoxide **5** rearranged on standing to give isomeric esters of type **6**.



5 **6**

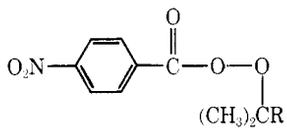
It was shown subsequently that the Criegee rearrangement, which competes effectively with homolytic decomposition, is facilitated by polar solvents,[6,7] added salt,[8] and with increased electron-withdrawing power of R.[6] Furthermore, the rearrangement was shown to proceed intramolecularly since incorporation of the *p*-nitrobenzoate or *p*-bromobenzoate group into the product, when *trans*-9-decalyl perbenzoate was decomposed in the presence of added lithium *p*-nitrobenzoate[7] or sodium *p*-bromobenzoate,[8] did not occur. That the oxygens in the carboxylate group are nonequivalent during the rearrangement of **7** was shown by the almost complete retention of an ^{18}O label in the carbonyl group of **9**.[9]



7 **8** **9**

These results were interpreted in terms of a highly structured tight ion-pair intermediate **8**, which collapsed to the product before equilibration of the oxygens of the carboxylate anion.[10]

The most detailed investigation to date of the Criegee rearrangement is that of Winstein and Hedaya,[11] who solvolyzed



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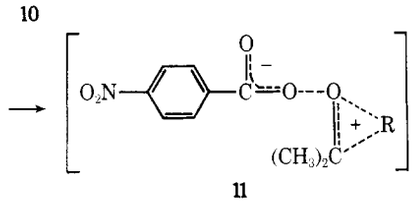

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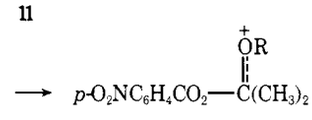
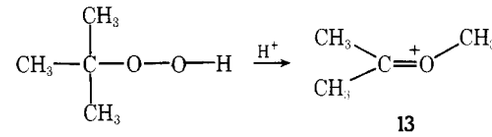


12

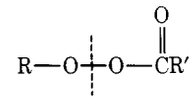
a series of 2-substituted 2-propyl *p*-nitroperbenzoates **10**. Steric acceleration was found to be negligible and they concluded that the relative rate order R = CH_3 < CH_2CH_2Ph < CH_2CH_3 < $CH(CH_3)_2$ < CH_2Ph < $CH_2C_6H_4OCH_3$-*m* < $CH_2C_6H_4OCH_3$-*p* < 4-camphyl < C_6H_5 < $C(CH_3)_3$ is best described in terms of a nonclassical type bridged transition state **11** which collapsed to an α-alkoxy carbenium ion **12**.

We have shown previously[2a] that for the acid-induced cleavage–rearrangement reaction of *tert*-alkyl hydroperoxides in superacid media intermediates analogous to **12** could be observed by NMR spectroscopy, e.g., **13**.



13

Furthermore, it was found that by using the corresponding peracetate the intermediates showed little or no further reaction and were conveniently observed. Among the hydroperoxides studied *tert*-butyl hydroperoxide was found to be unique in that it gave products from both O–O and C–O cleavage. We decided, therefore, to further study the reactions of peroxy esters in superacids, with particular emphasis on the effect of varying the nature of the alkyl (a) and acyloxy (b) groups.



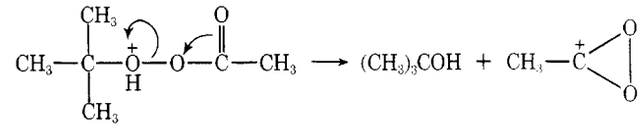
(a) (b)

Results and Discussion

The preparation of the peroxy esters used in this study is described in the Experimental Section. The esters were characterized and their purity checked by both ^1H and ^{13}C NMR spectroscopy. ^{13}C NMR parameters for the *tert*-butyl peroxy esters studied are given in Table I.

***tert*-Butyl Peracetate (14).** The ^1H NMR and ^{13}C NMR spectra of the resultant solution from the reaction of **14** with a fivefold excess of magic acid in SO_2ClF at −78 °C showed the dimethylmethoxycarbenium ion **13** and protonated acetic acid in 60% yield, together with 40% of the trimethylcarbenium ion **15** and peracetic acid. The former products are the result of O–O cleavage, route a of Scheme I, while the latter are the result of C–O cleavage, route b of Scheme I.

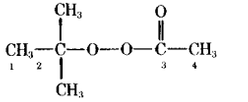
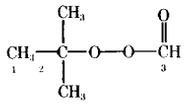
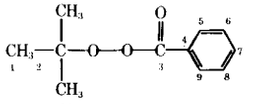
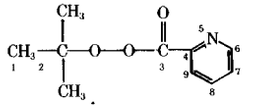
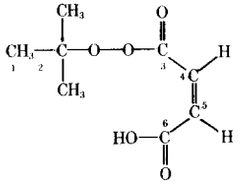
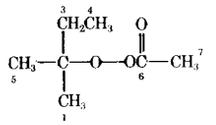
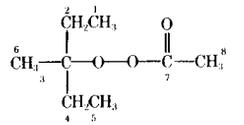
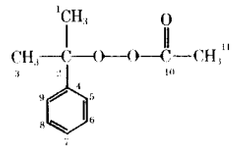
Ion **13** showed no sign of solvolytic cleavage under the conditions employed. The third alternative cleavage path for b, namely, cleavage to the acetyloxy cation, the cyclic form of which could be significantly stabilized,[12] was not indicated by the experimental data.



Treatment of **14** with a twofold excess of magic acid resulted in exclusive reaction via route a, as found previously for *tert*-butyl hydroperoxide.[2a] Furthermore, reaction products of **14** with an equimolar amount of magic acid, in SO_2ClF at −78 °C, gave the ion **13** and acetic acid together with a third species, which on the basis of its ^{13}C NMR data is regarded as protonated *tert*-butyl peracetate **16**, the expected primary protonation product.

These results may be explained by the reasoning used in the case of the *tert*-butyl hydroperoxide/magic acid systems, that an excess of magic acid is required to deactivate peracetic acid to act as a nucleophile, thus enabling direct observation of

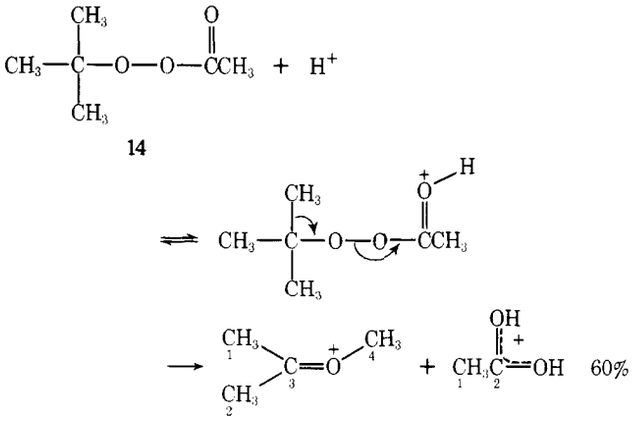
Table I. ^{13}C NMR Chemical Shifts for Peroxy Esters Studied

Registry no.	Compd		Chemical shift[a] 1	2	3	4	5	6	7	8	9	10	11
107-71-1			25.3	83.21	168.16	16.75							
		b	26.14	83.16	168.21	17.61							
819-50-1			25.36	84.23	161.39								
614-45-9			27.68	85.29	165.73	134.9	130.52	130.17	134.9	130.17	130.52		
60512-72-3		*b*	23.48	83.39	161.83	144.7		148.19	124.65	137.24	127.26		
1931-62-0			26.29	84.24	163.91	132.92		165.56					
690-83-5			23.77	85.36	31.60	8.23	23.77	168.03	17.63				
60512-73-4			7.19	29.27	87.65	29.27	7.19	20.94	167.7	17.71			
34236-39-0			26.36	85.63	26.36	144.0	128.15	125.1	127.35	125.1	128.15	167.35	17.80

[a] $CDCl_3$, internal ambient temperature unless otherwise stated. [b] SO_2ClF, external Me_4Si, −40 °C.

Scheme I

route a

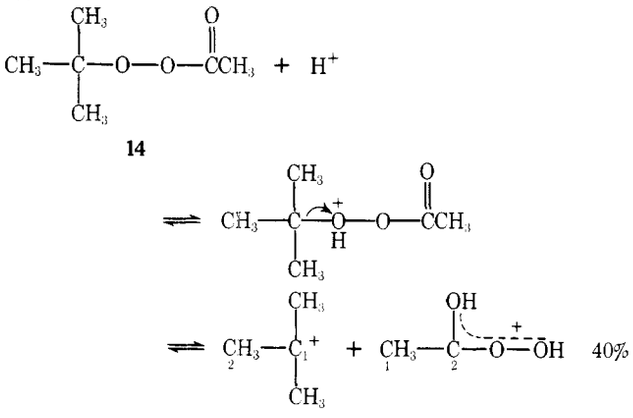


14

13

^{13}C NMR: 1, 26.83; 2, 32.1; 3, 245.48; 4, 68.87
^{1}H NMR: 1, 2, 3.40; 4, 5.23
^{13}C NMR: 1, 20.08; 2, 144.68
^{1}H NMR: 1, 3.27; 2, 13.07, 12.27

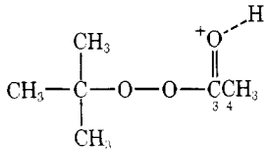
route b



14

15

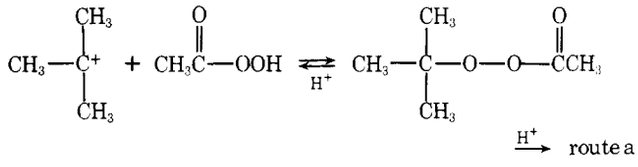
^{13}C NMR: 1, 335.7; 2, 47.78
^{1}H NMR: 2, 4.30
^{13}C NMR: 1, 16.90; 2, 192.30
^{1}H NMR: 1, 3.27; 2, 13.57, 13.33



16

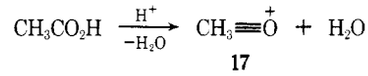
^{13}C NMR: 1, 24.94; 2, 86.66; 3, 177.28; 4, 17.19 [$\delta_{^{13}C}$ (Me_4Si)]

C–O cleavage. At lower acid concentrations the peroxy ester readily re-forms and can then react via O–O cleavage.



Indeed the rearrangement reaction of peroxy esters is so facile that alkylation of peroxy acids cannot be used as a method of preparation of peroxy esters.[13]

The equilibrium character of the solution obtained from the reaction of *tert*-butyl peracetate with a fivefold excess of magic acid was proven by gently warming the solution to −10 °C in the NMR probe. This shifted the equilibrium to the right, resulting in loss of the trimethylcarbenium ion with subsequent increase in the amount of carboxonium ion **13** and acetic acid in solution. After ~30 min at −10 °C no trace of the trimethylcarbenium ion remained, and at this temperature acetic acid was dehydrated to yield the acetylium ion **17**.[14]



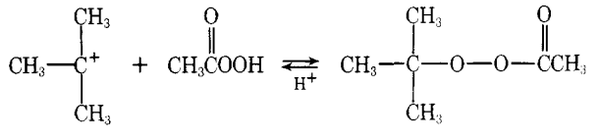
17

Our success in trapping products from both C–O and O–O heterolysis in the reaction of **14** with a fivefold excess of magic acid led us to examine the reaction of other peroxy esters under similar conditions to check if this pathway was characteristic only of the *tert*-butyl system as found previously for a series of *tert*-alkyl hydroperoxides.[2a]

Our attention was first turned to variation of the acyloxy group in *tert*-butylperoxy esters. Reactions of these peroxy esters with a fivefold excess of magic acid are summarized in Table II.

It is apparent that the nature of the acyl group played a considerable part in determining the course of the reactions. As seen from Table II, there is an increase in the percentage of reaction via O–O cleavage.

This can be interpreted in terms of the relative ease of deactivation of the peroxy acid as a nucleophile. The more acidic the peroxy acid, the less readily it will be protonated. Thus for the least acidic of the three studied systems, peroxyacetic acid, trapping of the C–O cleavage reaction is facilitated since the reaction of the formed carbenium ion with peroxy acid will be inhibited.



Though the basicities of these peroxy acids were not known, the order of basic strengths would be expected to correspond to those of model compounds with the same RC=O groups. Of the related carboxylic acids [RC(=O)OH], acetic acid (R = CH_3) is more basic (pK_b = −6.10) than benzoic acid (R = Ph, pK_b = −7.26).[15] Of the related ketones, RC(=O)CH_3 and RC(=O)Ph, the order of basic strengths is R = CH_3 > Ph > H.[16a,b] Based on extrapolations, the order of base strength of the peroxy acids would be peracetic > perbenzoic > performic acid. The latter two peroxy acids would be increasingly less capable of deactivation on the carbonyl oxygen of the COOOH group.

Next our attention was directed to the variation of the alkyl group of the *tert*-alkyl peracetates. Addition of *tert*-amyl peracetate **18** to a fivefold excess of magic acid, in SO_2ClF at −78 °C, yielded exclusively the dimethylethoxycarbenium ion **19** and acetic acid, the expected products from O–O cleavage. No trace of C–O cleavage products, i.e., the dimethylethylcarbenium ion and peracetic acid, was found. Furthermore, the ethyl group migrated to the total exclusion of methyl migration, Scheme II.

Scheme II

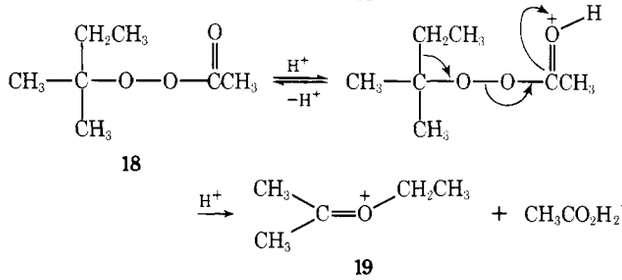


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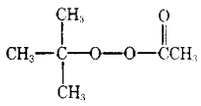
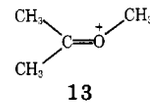
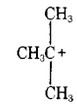
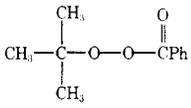
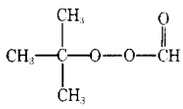
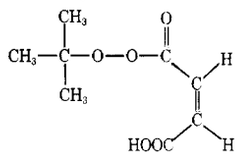
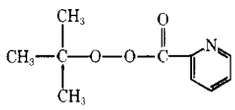
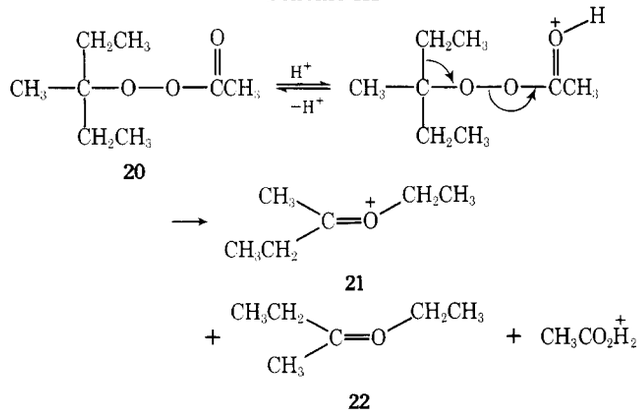
Table II. Reactions of *tert*-Butyl Peroxy Esters with Magic Acid[a]

Peroxy ester	% O–O[b] cleavage	% C–O[b] cleavage	Observed products[c]		
	60	40	 13	 15	Acetic acid Peracetic acid
	85	15	13	15	Benzoic acid Perbenzoic acid[d]
	>95	<5	13	15	Formic acid[e]
	>95	<5	13	15	Maleic acid[f] Fumaric acid
	100	0	13		α-Picolinic acid[g]

[a] All reactions carried out in fivefold excess of magic acid to peroxy esters in SO_2ClF at −78 °C. [b] Yields determined by integration of the ^1H NMR spectra. [c] Product was analyzed using ^1H and ^{13}C NMR. [d] Carbonyl and C_{ipso} could be distinguished from those of benzoic acid: benzoic acid, C=O 182.54, C_i 119.64 ppm; perbenzoic acid, C=O 181.55, C_i 116.76 ppm. [e] Only one C=O absorption was detected in ^{13}C NMR. If peroxyformic acid were present two carbonyl signals would be expected.[14b] [f] Showed two C=O absorptions in ^{13}C NMR due to the two isomeric acids. [g] Only one C=O absorption was detected in the ^{13}C NMR spectrum.

Similar treatment of 3-methylpentyl 3-peracetate **20** also gives exclusive O–O cleavage (Scheme III). **21** is regarded as the major isomer.[2a]

Scheme III

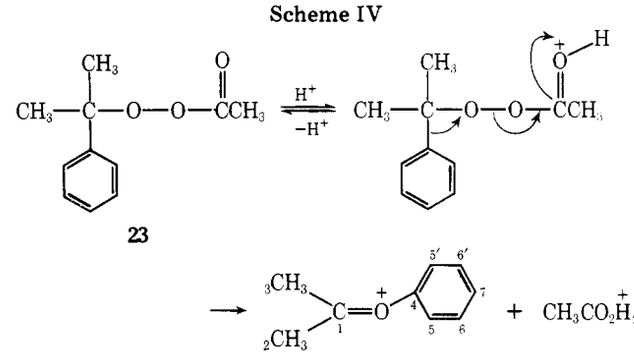


We were also unable to detect any evidence for C–O cleavage on treating cumyl peracetate **23** with a fivefold excess of magic acid. However, the blood-red solution produced in the above reaction showed (by NMR) the carboxonium ion **24** which we believe to be the first direct observation of this significant intermediate (Scheme IV), which is of course also the key to the cumene hydroperoxide rearrangement.

Previous attempts using cumyl hydroperoxide **25** failed to yield observable **24** upon treatment with magic acid.[14b] The dark green solution so obtained contained the decomposition products of **24**, namely phenol and acetone, indicating that **24** is easily susceptible to hydrolysis (Scheme V). Indeed both phenol and acetone were also observed as minor products from the decomposition of **23**.

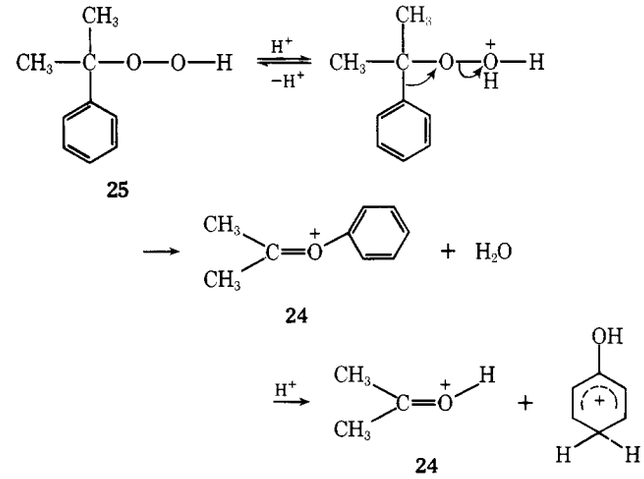
For the related reactions of *tert*-alkyl hydroperoxides,[2a] we

Scheme IV

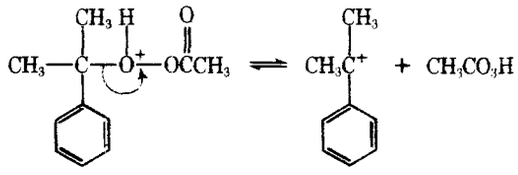


^{13}C NMR: 1, 248.27; 2, 32.22; 3, 29.10; 4, 154.16; 5,5′, 118.03; 6,6′, 131.95; 7, 131.14 [$\delta_{^{13}C}$ (Me_4Si)]

Scheme V



attributed the singular behavior of the *tert*-butyl system to the relative stability of the trimethylcarbenium ion **15**. This, however, cannot be the main factor since the dimethylphenylcarbenium ion **26** which would result from C–O cleavage of cumyl peracetate is a more stable species than **15**.[14b]



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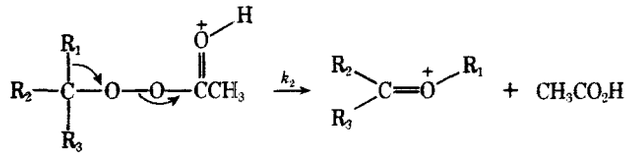
We therefore now consider that the important feature of these reactions is the relative migratory aptitude of the migrating alkyl (aryl) group.

In all systems studied in which an alkyl (aryl) group migrates to oxygen the methyl group has been found to have the lowest migratory aptitude.[2] For the peroxyacetates investigated in the present study the observed order of relative migratory aptitude is phenyl > ethyl > methyl, in good accord with the observations of Hedaya and Winstein in solvolytic systems.[11] Thus, in the reactions of



the increase in k is on the order of $R_1R_2R_3 = Et_2Me > EtMe_2 > Me_3$ and $R_1R_2R_3 = PhMe_2 > Me_3$. This relative migratory aptitud is one of the factors which determine the ratio of O–O and C–O cleavage, as well as the basicity of peroxy acids produced by the reaction.

In conclusion the protolytic cleavage–rearrangement reactions of peroxy esters in superacidic media are clearly related to the analogous reaction of hydroperoxides,[2a] and, as with the hydroperoxides, only the *tert*-butyl systems were found to give both O–O and C–O cleavage products. Our studies allowed the direct observation of the carboxonium ion intermediates key to both processes.

Experimental Section

Preparation of Peroxy Esters. Cumyl peracetate was prepared according to the method of Yablokov, Shushunov, and Kolyaskipa.[17] ***tert*-Butyl, *tert*-amyl,** and **3-methylpentyl 3-peracetate** were prepared analogously. This method gave good yields, ca. 70%, of high purity (>95%) peroxy ester. ***tert*-Butyl performate** was prepared according to the method of Rüchardt and Hecht.[18] Double distillation failed to remove the *tert*-butyl hydroperoxide impurity which was present to the extent of ~15%. ***tert*-Butyl perpicolinate,** 95%, was prepared by treating the 1,4-diazobicyclo[2.2.2]octane (Dabco) salt of *tert*-butyl hydroperoxide with 2-picolyl chloride hydrochloride. ***tert*-Butyl perbenzoate,** 99%, and ***tert*-butyl permaleate,** 98%, were obtained from Lucidol Corp., Buffalo, N.Y.

General Procedure for Reactions of Peroxy Esters with Magic Acid. To a vigorously stirred (vortex mixer) solution of a 5-mol excess of magic acid (1:1 FSO_3H–SbF_5) in SO_2ClF at dry ice–acetone temperature (ca. −78 °C) an SO_2ClF solution of the peroxy ester (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.

NMR Spectroscopic Study. ^1H NMR spectra were obtained in 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. Operational parameters were as described previously.

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Registry No.—Magic acid, 23854-38-8; *tert*-butyl hydroperoxide Dabco salt, 60512-74-5; picolinic acid chloride HCl, 39901-94-5.

References and Notes

(1) (a) Part 4: G. A. Olah, N. Yoneda, and D. G. Parker, *J. Am. Chem. Soc.*, in press. (b) Postdoctoral Fellows.
(2) (a) G. A. Olah, D. G. Parker, N. Yoneda, and F. Pelizza, *J. Am. Chem. Soc.*, **98**, 2245 (1976); (b) N. C. Deno, W. E. Billups, K. E. Kramer, and R. R. Lastomirsky, *J. Org. Chem.*, **35**, 3080 (1970); (c) D. Swern, "Organic Peroxides", Vol. II, Wiley, New York, N.Y., 1971, p 65; (d) J. B. Lee and B. C. Off, *Q. Rev., Chem. Soc.*, **21**, 429 (1967); (e) A. G. Davies, "Organic Peroxides", Butterworths, London, 1961; (f) B. C. Hawkins, "Organic Peroxides", Van Nostrand, Princeton, N.J., 1961.
(3) D. G. Farnum, G. Mehta, and R. G. Silberman, *J. Am. Chem. Soc.*, **89**, 5048 (1967).
(4) C. Rüchardt and H. Schwarzer, *Chem. Ber.*, **99**, 1861, 1871, 1878 (1966).
(5) R. Criegee, *Ber.*, **77**, 722 (1944).
(6) R. Criegee, *Justus Liebigs Ann. Chem.*, **560**, 127 (1948).
(7) H. L. Goering and A. C. Olsen, *J. Am. Chem. Soc.*, **75**, 5853 (195).
(8) P. D. Bartlett and J. C. Kice, *J. Am. Chem. Soc.*, **75**, 5591 (1953).
(9) D. B. Denney and D. G. Denney, *J. Am. Chem. Soc.*, **79**, 4806 (1957).
(10) S. Winstein and G. C. Robinson, *J. Am. Chem. Soc.*, **80**, 169 (1958).
(11) E. Hedaya and S. Winstein, *J. Am. Chem. Soc.*, **89**, 1661 (1967).
(12) M. T. Reetz and W. Maier, personal communication, *Theor. Chim. Acta*, in press.
(13) L. A. Singer in "Organic Peroxides", Vol. I, D. Swern, Ed., Wiley, New York, N.Y., 1971.
(14) (a) G. A. Olah and A. M. White, *J. Am. Chem. Soc.*, **89**, 3591 (1967); (b) Unpublished results.
(15) D. D. Perrin, "Dissociation Constants of Organic Bases in Aqueous Solution", Butterworths, London, 1965.
(16) (a) *Prog. Phys. Org. Chem.*, **1**, 223 (1963); (b) E. M. Arnett, K. P. Quirk, and J. W. Larsen, *J. Am. Chem. Soc.*, **92**, 3877 (1970).
(17) 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).
(18) C. Rüchardt and R. Hecht, *Chem. Ber.*, **97**, 2716 (1964).