The shift to low field is consistent with the deshielding effect of the 7-*syn* hydroxyl group and the inductive effect of the 2-*endo* hydroxyl group.

7-Phenyl-2-norbornanon-7-*anti*-ol (13). The pyridine complex from 5 g of chromium trioxide was prepared. To it was added 1 g of **5**. The ketone was isolated in the same way as described for **11**. The product was crystallized twice from hexane–ether mixture, mp 109°.

Anal. Calcd for $C_{13}H_{14}O_2$: C, 77.20; H, 6.98. Found: C, 77.14; H, 7.01.

A sample of the ketone **13** weighing 0.47 g was reduced with lithium aluminum hydride. The isolated diol was crystallized from hexane–ether mixture. It was identical in every respect with the starting diol **5**.

Test for Internal Return. Compound **2** was subjected to hydrolysis conditions previously described for a period of 4 hr. Among the products isolated the only tosylate ester found was **2**. The hydrolysis of **14** was complete after the reaction had proceeded for 1 hr. No trace of **2** or **14** could be found in the product mixture.

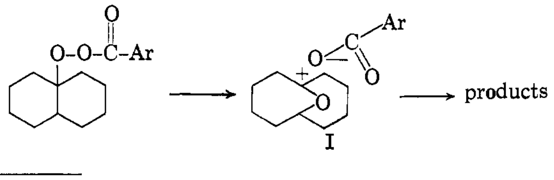
The Ionic Decomposition of 2-Substituted 2-Propyl *p*-Nitroperbenzoates. Migration to Electron-Deficient Oxygen and Anchimeric Acceleration of Peroxide-Bond Heterolysis[1]

E. Hedaya[2] and S. Winstein

Contribution from the Union Carbide Research Institute, Tarrytown, New York, and the Department of Chemistry, University of California, Los Angeles, California. *Received December 2, 1966*

Abstract: A number of 2-substituted 2-propyl *p*-nitroperbenzoates have been prepared and solvolyzed in methanol solvent. The products from the *p*-nitroperbenzoates which were substituted with alkyl groups larger than methyl were those derived from exclusive migration of the alkyl group; these were *p*-nitrobenzoic acid, acetone and its dimethyl ketal, and the alcohol, olefin, and methyl ether derived from the migrating group. The amount of ether or olefin derived from the migrating group was negligible for the ethyl and isopropyl groups, but was substantial for the *t*-butyl or benzyl migrating groups. The relative rates of heterolysis were found to depend markedly on the nature of the migrating group. They were CH_3, 1; $CH_2CH_2C_6H_5$, 14.9; CH_2CH_3, 45.0; $CH(CH_3)_2$, 2.94×10^3; $CH_2C_6H_5$, 1.63×10^3; $CH_2C_6H_4OCH_3$-*m*, 1.54×10^3; $CH_2C_6H_4OCH_3$-*p*, 5.32×10^4; 4-camphyl, 1.42×10^4; C_6H_5, 1.18×10^5; $C(CH_3)_3$, 2.28×10^5. Evidence is presented which shows that steric acceleration of ionization is negligible and that the relative rate order is best interpreted in terms of a nonclassical-type, bridged transition state which collapses to an α-alkoxy carbonium ion intermeditae. In terms of neighboring group theory, these relative rates of heterolysis or migration aptitudes can be considered measures of anchimeric acceleration of ionization. A comparison of neopentyl tosylate and *t*-butyl pertosylate solvolysis leads to an anchimeric acceleration factor for the methyl-substituted perester of about 10^{23} in terms of rate. This enormous anchimeric acceleration coupled with the very large relative rate spectrum observed for the alkyl-substituted *p*-nitroperbenzoates imply that unrearranged *t*-alkoxy cations are very unstable and that there is considerable distribution of positive charge on carbon rather than on oxygen in the transition state for perester solvolysis. The high relative rate for the 4-camphyl-substituted perester furthermore shows that tetrahedral hybridization of the migrating group is retained in the transition state. That there is, nevertheless, considerable positive charge distributed within the migrating group in the transition state was demonstrated by the substantial rate-enhancing effect of *p*-methoxy substitution on the benzyl migrating group. In contrast, *m*-methoxy substitution leads to no rate enhancement compared to benzyl and thus Ar_2-4 type participation for benzyl is ruled out. Furthermore, Ar_1-3, Ar_1-4, and Ar_2-5 styles of participation are probably unimportant on the basis of the solvolysis products and the relatively small, rate-enhancing effect of the 2-phenylethyl substituent. Finally, a comparison of the relative rates of fragmentation of the corresponding *t*-alkoxy radicals with the relative rates of perester solvolysis indicate that the former process is best not rationalized in terms of a bridged transition state as for the latter process.

The ionic decomposition of peresters, involving a 1,2 rearrangement of carbon to electron-deficient oxygen, has been the subject of a number of mechanistic investigations. The general features of the rearrangement were first discovered by Criegee,[3] who studied the decomposition of 9-decalyl peresters. A relatively polar mechanism was indicated by the nature of the products and the enhanced rate of rearrangement in polar solvents and with more acidic leaving groups. Later workers showed that ion-pair exchange with foreign anions[4a,b] did not occur and that the carboxylate oxygens of the leaving group did not equilibrate.[4c] These results were interpreted in terms of a



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[1] Research supported in part by the National Science Foundation.

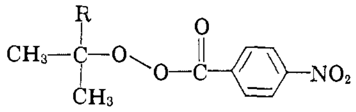
[2] U. S. Rubber Company Foundation Fellow in Chemistry, 1960–1961. Presently at the Union Carbide Research Institute.

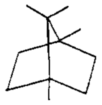
[3] R. Criegee, *Ann.*, **560**, 127 (1948).

[4] (a) P. D. Bartlett and J. L. Kice, *J. Am. Chem. Soc.*, **75**, 5591 (1953); (b) H. L. Goering and A. C. Olson, *ibid.*, **75**, 5853 (1953); (c) D. B. Denney and D. G. Denney, *ibid.*, **79**, 4806 (1957); (d) S. Winstein and G. T. Robinson, *ibid.*, **80**, 169 (1958); (e) P. D. Bartlett and T. G. Traylor, *ibid.*, **83**, 856 (1961); (f) E. Hedaya, R. L. Hinman, L. Kibler, and S. Theodoropulos, *ibid.*, **86**, 2727 (1964); (g) T. Koenig and W. Brewer, *ibid.*, **86**, 2729 (1964).

highly structured, tight ion-pair intermediate I.[4a-d] More recently, Bartlett and Traylor[4e] showed that *t*-butyl pertosylate undergoes the Criegee rearrangement exclusively and very rapidly at even ambient temperatures. Similarly, *t*-butyl N-succinimidepercarboxylate[4f,g] was found to decompose heterolytically in even relatively nonpolar solvents like chlorobenzene to give Criegee-type products.

Despite the effort expended on the study of this reaction, little quantitative data have been obtained on the effect of variation of migrating group structure on the rate of heterolysis of the perester peroxide bond, in contrast to the related acid-catalyzed rearrangement of hydroperoxides[5] and the Baeyer-Villiger reaction.[6] However, in these latter rearrangements, the results are complicated by prequilibrium steps involving non-isolable intermediates which give the rearranged products. Consequently, kinetic studies designed to explore structure-reactivity relationships, while instructive, must cope with the problem of the nature of the preequilibrium step and the variation of the equilibrium constant with structure. Relative reactivities of migrating groups derived from product studies are also equivocal because migration occurs necessarily from different origins for each group.



IIa, R = CH_3
b, R = CH_2CH_3
c, R = $CH(CH_3)_2$
d, R = $C(CH_3)_3$
e, R = $CH_2CH_2C_6H_5$
f, R = $CH_2C_6H_5$
g, R = $CH_2C_6H_4OCH_3$-*m*
h, R = $CH_2C_6H_4OCH_3$-*p*
i, R =  (4-camphyl)

Preliminary results of Nelson[7] indicated that a detailed investigation of the general perester system II would be fruitful since for R = methyl, isopropyl, and *para*-substituted phenyl, decomposition occurred in acetic acid at a rate which was highly sensitive to changes in R. Also, another attractive feature of perester II is that comparisons with the analogous neopentyl system, where C-O heterolysis and Wagner-Meerwein rearrangement occurs, can readily be made.

Results

Preparation of Peresters. The key step in the synthesis of the *p*-nitroperbenzoates II was the preparation of the hydroperoxides from the corresponding alcohols. The hydroperoxides with R = $CH(CH_3)_2$ and R = CH_2CH_3 were prepared from the corresponding alcohols by using acidified 50% hydrogen peroxide in refluxing chloroform.[8] The other hydroperoxides (excluding *t*-butyl hydroperoxide, which is commercially available) were obtained by stirring the alcohol in excess 90% hydrogen peroxide at room temperature or below. The addition of sulfuric acid catalyst, as prescribed by Criegee,[3] was found to be unnecessary for the hydroperoxides with R = $C(CH_3)_3$ or 4-camphyl. The remaining hydroperoxides were obtained only by adding catalytic amounts of sulfuric acid. The yields of hydroperoxide prepared from 90% hydrogen peroxide were approximately 80%, while the yields obtained with 50% hydrogen peroxide were no better than 30%. While 90% hydrogen peroxide can be used for the preparation of all of the above hydroperoxides, its use with the lower molecular weight alcohols (R = $CH(CH_3)_2$ or CH_2CH_3) apparently gave hazardous reaction mixtures. Explosions were observed both by Criegee[3] and Nelson[5] when dimethylisopropylcarbinol was combined with cold, acidified 90% hydrogen peroxide. In general, extreme caution should be exercised in carrying out any of these reactions with 90% hydrogen peroxide.

The preparation of the alcohols and the acylation of the hydroperoxides were both straightforward reactions. The former involved the reaction of the appropriate Grignard reagent with acetone or the reaction of methyl Grignard with the appropriate ketone or ester. An exception was the preparation of 4-camphyldimethylcarbinol which could only be prepared in low yield by the reaction of methyllithium with methyl 4-camphylcarboxylate. The acylation reaction of the hydroperoxides was routinely carried out using purified *p*-nitrobenzoyl chloride in dry pyridine at low temperatures.

The peresters themselves are all relatively stable substances at room temperature. Only IId (R = $C(CH_3)_3$) and IIi (R = 4-camphyl) decomposed on standing at room temperature for days or in the refrigerator for weeks. Again only IId and IIi decomposed violently on heating.

The purity of the peresters was established by melting point comparisons (for peresters IIa, b, and c which were known), C, H analysis, infrared spectrum, kinetic behavior, and yields of solvolysis products. Iodometric analysis for active oxygen after prior transesterification of the perester with sodium methoxide[9] appeared to be stoichiometric only for *t*-butyl *p*-nitroperbenzoate (IIa). In general, the per cent of active O for each of the other peresters varied from 5% less than the stoichiometric amount to 10% greater.

Kinetics and Products. The rates of decomposition of peresters II were measured generally in methanol solvent by titration of generated acid and were checked by titration of remaining active oxygen (Table I). In all cases good first-order rate constants were obtained over 10-70% reaction except for *t*-butyl *p*-nitroperbenzoate (IIa) where the derived rate constant drifted sharply upwards after *ca.* 15% reaction. However, good first-order rate constants were obtained

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(5) (a) A. G. Davies, "Organic Peroxides," Butterworth, Inc., Washington, D. C., 1961, p 147; (b) A. W. De R. Van Stevenick and E. C. Kooyman, *Rec. Trav. Chim.*, 79, 413 (1960).

(6) (a) C. H. Hassall, *Org. Reactions*, **9**, 73 (1957); (b) M. F. Hawthorne, W. D. Emmons, and K. McKallum, *J. Am. Chem. Soc.*, **80**, 6393 (1958).

(7) K. L. Nelson, unpublished work.

(8) J. H. Raley, F. F. Rust, and W. E. Vaughan, U. S. Patent 2,573,-947 (1951).

(9) T. G. Traylor, private communication; such transesterification can be quite rapid depending on the structure of the perester and the solvent composition. For example, we have observed rapid transesterification of some of the peresters studied here in methanol which had been dried with calcium hydride or magnesium and thus which contained small amounts of ammonia. In general, our dry alcohol solvents were redistilled from anhydrous sulfanilic acid.

Table I. Rates of Decomposition of 2-Substituted 2-Propyl *p*-Nitroperbenzoates II[a]

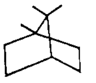
R	Solvent	Concn, *M*	Temp, °C[b]	k, sec^{-1}
CH_3[c]	AcOH	0.03	50.00	$(1.40 \pm 0.09) \times 10^{-7}$
CH_3[c]	AcOH	0.03	75.00	$(3.20 \pm 0.06) \times 10^{-7}$
CH_3[c]	AcOH	0.03	100.00	$(5.03 \pm 0.20) \times 10^{-5}$
CH_3	MeOH	0.0271	75.00	*Ca.* 4×10^{-6}
CH_3	MeOH	0.0270	100.00	*Ca.* 77×10^{-6}
CH_3CH_2	MeOH	0.0309	50.00	$(4.90 \pm 0.03) \times 10^{-6}$
CH_3CH_2	MeOH	0.0276	75.00	$(9.20 \pm 0.11) \times 10^{-5}$
CH_3CH_2[c]	MeOH	0.0296	75.00	*Ca.* 8×10^{-5}
$(CH_3)_2CH$[d]	MeOH	0.0295	25.00	$(1.03 \pm 0.02) \times 10^{-5}$
$(CH_3)_2CH$	MeOH	0.0228	50.00	$(2.55 \pm 0.03) \times 10^{-4}$
$(CH_3)_3C$	MeOH	0.0187	25.00	$(7.94 \pm 0.04) \times 10^{-4}$
$(CH_3)_3C$	MeOH	0.0200	15.00	$(2.12 \pm 0.02) \times 10^{-4}$
$(CH_3)_3C$[c]	MeOH	0.0227	25.00	$(7.0 \pm 0.4) \times 10^{-4}$
$(CH_3)_3C$	EtOH	0.01	25.00	$(3.50 \pm 0.10) \times 10^{-4}$
$CH_2C_6H_5$	MeOH	0.01	25.00	$(5.68 \pm 0.04) \times 10^{-6}$
$CH_2C_6H_5$[d]	MeOH	0.01	50.00	$(1.36 \pm 0.01) \times 10^{-4}$
$CH_2C_6H_4OCH_3$-*p*	MeOH	0.00597	25.00	$(1.86 \pm 0.05) \times 10^{-4}$
$CH_2C_6H_4OCH$-*m*[d]	MeOH	0.00631	25.00	$(5.41 \pm 0.3) \times 10^{-6}$
$CH_2C_6H_4OCH_3$-*m*	MeOH	0.00609	50.00	$(1.08 \pm 0.04) \times 10^{-4}$
$CH_2CH_2C_6H_5$[d]	MeOH	0.00568	75.00	$(5.21 \pm 0.20) \times 10^{-5}$
$CH_2CH_2C_6H_5$	MeOH	0.00602	90.02	$(2.88 \pm 0.09) \times 10^{-4}$
4-Camphyl	EtOH	0.01	25.00	$(2.19 \pm 0.07) \times 10^{-5}$
4-Camphyl[d]	EtOH	0.01	50.00	$(4.85 \pm 0.13) \times 10^{-4}$

[a] Measured by titration of evolved acid unless noted. [b] Precision was ±0.02°. [c] Measured by disappearance of active O. [d] Measurement of active oxygen for one or two kinetic points indicated correspondence with acid titers.

for the latter perester in acetic acid. Essentially quantitative acid generation was observed in alcoholic solvents for all the peresters studied, again except for *t*-butyl *p*-nitroperbenzoate where only 65% *p*-nitrobenzoic acid was obtained along with about 23% methyl *p*-nitrobenzoate. The other products from *t*-butyl *p*-nitroperbenzoate in methanol were small amounts of acetone and its dimethyl ketal along with substantial amounts of formaldehyde and a mixture of *t*-butyl alcohol and *t*-butyl hydroperoxide.

Products for peresters II in methanol are summarized in Table II. These were determined by vpc, and the acetone yields are those found after hydrolysis of the reaction mixture. Considerable amounts (70 ± 10%) of the dimethyl ketal of acetone were present before hydrolysis. The yields of the other products from the R fragment of the perester did not vary on hydrolysis, and methyl ether could not be detected before hydrolysis. Only the acetone yield after hydrolysis was determined for the peresters IIe, g, h, and i, and this was found to be essentially quantitative. Again, considerable amounts of the dimethyl ketal of acetone were present before hydrolysis (70 ± 10%).

Table II. Products from the Decomposition of 2-Substituted 2-Propyl *p*-Nitroperbenzoates[a]

R	%			
	$(CH_3)_2C{=}O$[b]	ROH	ROMe	Olefin
CH_2CH_3	94 ± 5, 100 ± 1[c]	87 ± 3	0	...
$CH(CH_3)_2$	100 ± 2, 98 ± 1[c]	86 ± 3	0	+[d]
$C(CH_3)_3$	96 ± 3, 98 ± 1[c]	59 ± 3	17 ± 2	~20[e]
$CH_2C_6H_5$	99 ± 2	88 ± 3	8.4 ± 8	...
$CH_2C_6H_4OCH_3$-*p*	100 ± 5 ...	...	...	...
$CH_2C_6H_4$-OCH_3-*m*	100 ± 5 ...	...	...	...
$CH_2CH_2C_6H_5$	95 ± 5 ...	...	...	...
	93 ± 2 ...	...	...	...

[a] Analysis by glpc unless noted. [b] Concentration of acetone after hydrolysis of the reaction mixture. In general 70 ± 10% dimethyl ketal was present before hydrolysis. [c] Analysis by gravimetric determination of the 2,4-DNP derivative. [d] Small quantities of propene were detected. [e] Isobutylene.

Control experiments showed that alcohol (ROH) did not form ether (ROMe) or olefin under the product analysis conditions, nor did ether (ROMe) give alcohol (ROH). Furthermore, acetone was not converted to ketal.

Discussion

Products and General Reaction Scheme. The product analysis data for perester solvolysis possess the following general features, excluding the results for the decomposition of *t*-butyl *p*-nitroperbenzoate in methanol. In all cases acetone and/or its dimethyl ketal and *p*-nitrobenzoic acid were generated essentially quantitatively, implying nearly quantitative migration of the R group. The stable products generated from the R group were alcohol, olefin, and ether with the proportion of the latter products increasing with the size of the R group. From these data, we can rule out homolytic decomposition processes since in no case was there any alcohol derived from the radical $RC(CH_3)_2O\cdot$. Also, formaldehyde, which would result from radical attack on the solvent, was not detected. Moreover, the quantitative yield of acid is inconsistent with what is known about carboxyl radicals. Decarboxylation predominantly occurs with almost all carboxyl radicals except in the presence of very efficient scavengers.[10] Consequently, our results are formally completely consistent with a Criegee ionic decomposition.

The reaction scheme given in Figure 1 most logically accounts for the products observed and serves as a framework for illustrating some specific points of

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(10) G. S. Hammond and L. M. Soffer, *J. Am. Chem. Soc.*, 72, 4711 (1950).

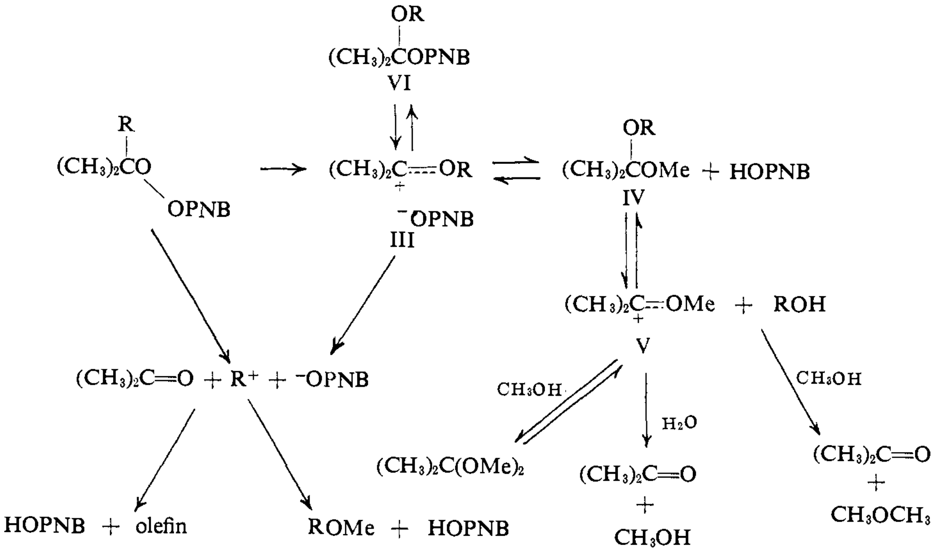

Figure 1. Ionic decomposition of 2-alkyl-2-propyl *p*-nitroperbenzoates (II) in methanol.

interest. First, since the products derived from the R group were the same before and after deliberate hydrolysis of the reaction mixture, and since there was no vpc evidence for any mixed ketal IV, the latter must be unstable toward methanol exchange under the reaction conditions. Similar, but more deep-seated exchanges involving mixed ortho ester intermediates previously were observed in the ionic decomposition of 2-alkoxy-2-propyl *p*-nitroperbenzoates.[11]

The significant quantities of ether and/or olefin derived from the migrating group for R = $C(CH_3)_3$ (IId) and for R = $CH_2C_6H_5$ (IIf) can be accounted for by two alternate pathways. One involves direct fragmentation of the perester while the second involves solvolysis of the intermediate alkoxycarbonium ion III. Experimental evidence bearing on this question could be obtained by preparing the intermediate ion as a tetrafluoroborate salt by Meerwein's methods[12] or by generating it from an acylal of type VI. It is interesting that the ratio of ether and olefin (about 50:50) for IId is close to that observed for *t*-butyl chloride solvolysis in ethanol (56:46) and is quite different from that observed for *t*-butylsulfonium perchlorate in the same solvent (82:18).[13] Solvolysis of the latter salt is considered to give a product resembling that from fully dissociated *t*-butyl cation, and on this basis, it was concluded that at least 73% of the elimination occurring in *t*-butyl chloride solvolysis involves the chloride ion as part of an ion pair.[13] The apparent correspondence between the ether:olefin ratio from *t*-butyl chloride and IId solvolysis suggests that the *t*-butyl carbonium ion derived from the latter also reacts predominantly in the form of an ion pair. However, the absence of *t*-butyl *p*-nitrobenzoate, which is stable under the reaction conditions, indicates that such an ion pair does not collapse to covalent products derived from the anion.

The apparent quantitative migration of the R group implies that the migration aptitude of the R group is at least 50 times that of methyl. Actually, when R = CH_2CH_3 (IIb), one might expect from the relative rates of perester solvolysis (see below) that some methyl migration should be detected. Detection of small quantities of 2-butanone, which is the anticipated methyl migration product from perester IId in methanol, was precluded because of the closely similar retention times of 2-butanone and acetone at our glpc conditions. However, when IIb was decomposed in acetic acid, 3% methyl acetate and 93% ethyl acetate were detected, indicating that a small but significant amount of methyl migration does occur in this case. Finally, the apparent absence of significant quantities of dimethyl ether implies that hydrolysis of carbonium ion V must occur. Our solvent contained a maximum concentration of water of about 0.03 *M*, and since comparable concentrations of perester were employed in the product analysis experiments, such hydrolysis can be significant.

Table III. Relative Rates for the Solvolysis of $(CH_3)_2CROOPNB$ in Methanol at 25°

R	Relative rate	$\Delta H^{\ddagger}$, kcal mole^{-1}	$\Delta S^{\ddagger}$, eu
CH_3[a]	1	27.6	−6.7
$CH_2CH_2C_6H_5$[b]	14.9	27.9	−0.3
CH_2CH_3[b]	45.0	25.6	−5.8
$CH(CH_3)_2$	2.94×10^3	24.0	−3.0
$CH_2C_6H_5$	1.63×10^3	22.9	−7.6
$CH_2C_6H_4OCH_3$-*m*	1.54×10^3	23.0	−7.3
$CH_2C_6H_4OCH_3$-*p*	5.32×10^4	...	...
 [c]	1.42×10^4	23.5	−3.0
C_6H_5[d]	1.18×10^5	...	...
$C(CH_3)_3$	2.28×10^5	21.9	−1.3

[a] Extrapolated from rates at higher temperatures in acetic acid; $k = 3.5 \times 10^{-9}$ sec^{-1}. [b] Calculated from rates at higher temperatures. [c] Estimated from the rate of solvolysis in ethanol and rates of solvolysis of IId (R = $C(CH_3)_3$) in methanol and ethanol. [d] Estimated from data of J. L. Kice (Ph.D. Dissertation, Harvard University, 1954).

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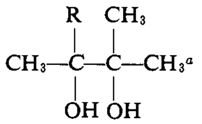
[11] E. Hedaya and S. Winstein, *Tetrahedron Letters*, 563 (1962).

[12] H. Meerwein, *Arch. Pharm.*, **291**, 541 (1958).

[13] M. Cocivera and S. Winstein, *J. Am. Chem. Soc.*, **85**, 1702 (1963).

Table IV. Migration Aptitudes for Some 1,2 Rearrangements

System	Me	Et	*i*-Pr	*t*-Bu	$CH_2C_6H_5$	C_6H_5
 $CH_3-\underset{OH}{\overset{R}{C}}-\underset{OH}{\overset{CH_3}{C}}-CH_3$[a]	1	17	...	~4000	...	...
$(CH_3)_2CRCH_2OTS$	1	...	5.3[b]	...	0.16[c]	335[d]
C_6H_5COR[e]	Very small	0.07	1.9	39	1.3	...
$RCO\bar{N}OCOC_6H_5$[f]	<0.03	1	14.9	12.0	...	12.2
$(CH_3)_2CROOPNB$ (II)	1	45.0	2.9×10^3	2.3×10^5	1.6×10^3	1.1×10^5

[a] M. Stiles and R. D. Mayer, *J. Am. Chem. Soc.*, **81**, 1497 (1959); pinacol rearrangement. [b] P. S. Magee, Ph.D. Dissertation, University of California at Los Angeles, 1955; relative gross acetolysis rates uncorrected for methyl migration. [c] W. H. Saunders, *J. Am. Chem. Soc.*, **85**, 4095 (1963); net relative acetolysis rate corrected for methyl migration. [d] W. H. Saunders, *ibid.*, **83**, 883 (1961); net relative acetolysis rate corrected for methyl migration. [e] Reference 6; Baeyer-Vililger oxidation. [f] D. C. Brandt and H. Schecter, *J. Org. Chem.*, **29**, 916 (1964); Lossen rearrangement.

Relative Rates of Perester Solvolysis. Migration Aptitudes. The kinetic data listed in Table I for the perester IIa-i can be summarized in terms of relative rates of perester solvolysis and these are given in Table III. The major difficulty in setting up Table III was to estimate the rate of ionic decomposition of *t*-butyl *p*-nitroperbenzoate in methanol. The presence of methyl *p*-nitrobenzoate and some *t*-butyl hydroperoxide as products indicates that one complication is transesterification with solvent.[9] Subsequent homolysis of the hydroperoxide could account for the *t*-butyl alcohol and formaldehyde. Alternatively, it is conceivable that homolysis or induced homolysis of the perester peroxide bond itself occurs. Finally, the sharply drifting rate constants indicate buildup of a species which catalyzes the perester decomposition. While it would be possible to sort out the relative importance of the various decomposition pathways, we have instead used the rate constants in acetic acid as a measure of the rate of ionic decomposition of *t*-butyl *p*-nitroperbenzoate. The decomposition in acetic acid appears to be predominantly ionic on the basis of the products and comparison with other peresters,[14] and the rate difference for heterolysis in acetic acid and methanol is predicted to be small compared to the magnitude of the rate spread in Table III. For example, the rate of heterolysis or 9-decalyl perbenzoate is only 2.5 times greater in acetic acid than in methanol.[3]

Since the products derived from the solvolysis of all the peresters except *t*-butyl *p*-nitroperbenzoate can be accounted for by the scheme given in Figure 1, where essentially quantitative migration of the R group to electron-deficient oxygen occurs (Criegee rearrangement), these relative rates quantitatively represent migration aptitudes. The correspondence of rates determined by loss of active oxygen and appearance of acid furthermore rules out fast rearrangement to acylal (VI) followed by its slower decomposition.

A comparison of our data in Table III with similar data for other systems (Table IV) indicates that the rate of solvolysis in the perester system is much more sensitive to the nature of the migrating group and implies greater involvement of the migrating group in the transition state. Actually the data for some of the systems require certain assumptions before being considered quantitative migration aptitudes, or are incomplete. In the pinacol rearrangement it is necessary to assume that the equilibrium constant for protonation does not vary with structure. The relative rate for isopropyl in the solvolysis of the neopentyl derivatives is only a gross relative rate measurement while the numbers given for benzyl and phenyl are derived from both product studies and kinetics and thus represent migration aptitudes quantitatively. The Baeyer-Villiger data are alkyl:phenyl migration product ratios and consequently one must assume that phenyl migrates from different origins with the same rate before considering these values as quantitative measures of migration aptitudes.

Electronic and Steric Effects for the Migrating Group. The migrating R group would be expected to have an important electronic effect on the stability of the transition state. As the number of α-methyl groups increase in R, both inductive and resonance (including hyperconjugative) mechanisms should more effectively stabilize electron deficiency at the migrating carbon atom and thus in the transition state. Besides an electronic effect, steric effects can also be envisioned. As the R group increases in size, steric crowding in the ground-state perester and subsequent relief of strain in the transition state could conceivably lead to rate enhancement of R group migration. Such steric crowding would have to be important in conformations such as VII.

The relative importance of steric and electronic effects can be indirectly evaluated from a plot of log k *vs.* N_α, the number of α-methyl groups in R (Figure 2). The unquestionable linearity of the correlation indicates that log k will be a linear function of any property of the R group which is itself linear in N_α. The two most pertinent energetic measures of steric effects for the alkyl group (E_s and A values)[15,16] are clearly not linear in N_α (E_s: Me = 0.00, Et = −0.07, *i*-Pr = −0.47, *t*-Bu = −1.54; A value: Me = 1.8, Et = 1.8, *i*-Pr = 2.3, *t*-Bu > 5.4). The steric effect for *t*-butyl is proportionately much larger than that for methyl. The absence of a linear free energy relationship between

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(14) E. Hedaya, Ph.D. Dissertation, University of California at Los Angeles, 1962; the major products were 72% methyl acetate and 80% acetone along with ≥70% *p*-nitrobenzoic acid. No *t*-butyl alcohol or *t*-butyl acetate was detected. Also the activation parameters (Table I) were quite different from that for *t*-butyl perbenzoate in acetic acid ($\Delta H^{\ddagger}$ = 40.7 kcal mole^{-1}, $\Delta S^{\ddagger}$ = 23.7 eu) which were calculated from data of Blomquist (A. F. Blomquist and S. A. Bernstein, *J. Am. Chem. Soc.*, **73**, 5546 (1951).

(15) R. Taft, "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1956, p 561.

(16) (a) S. Winstein and N. J. Holness, *J. Am. Chem. Soc.*, 77, 5562 (1955); (b) A. H. Lewin and S. Winstein, *ibid.*, **84**, 2464 (1962).

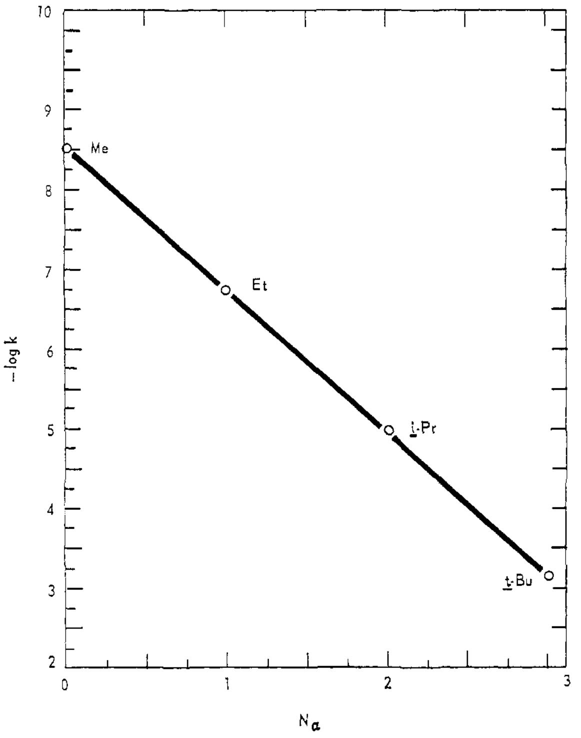
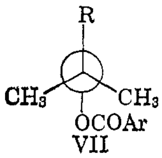


Figure 2. Log *k* *vs.* N_α for the ionic decomposition of $(CH_3)_2$-CROOPNB (II) in methanol at 25.00°.

log *k* and these measures of steric effects for R suggest that such effects are relatively unimportant.

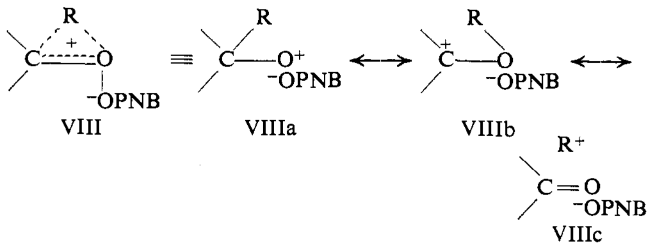
Other comparisons which indicate that steric effects are relatively unimportant are the relative rates given for R = CH_2CH_3, $CH_2CH_2C_6H_5$, $C(CH_3)_3$, and 4-camphyl. On the basis of steric acceleration of solvolysis the 2-phenylethyl group would be predicted to be a better migrating group than ethyl because of its greater steric effect, in contrast to what is observed (Table III). On the same basis, 4-camphyl would be predicted to be a better migrating group than $-C(CH_3)_3$, but the opposite was observed.



VII

In contrast substituent constants which are measures of inductive and resonance effects of alkyl groups (σ^I and σ^R)[17] are both linear in N_α. However, it must be noted that these parameters were derived from systems where electron deficiency was not generated directly within the substituent and, consequently, because of the relative importance of C–C and C–H hyperconjugation, the *t*-butyl group is less electron donating than the methyl group.[17] Another pertinent comparison is that between relative rates of perester decomposition and the stability of the carbonium ion derived from the R group. Such stabilities can be derived from ionization potential measurements[18] or can be calculated.[19] The comparison shows that only a qualitative correlation exists since the effect of methyl substitution on methyl is greater than the effect of methyl substitution on isopropyl.[18,19] The apparent lack of correlation suggests that the migrating group cannot be considered a fully developed planar carbonium ion in the transition state.

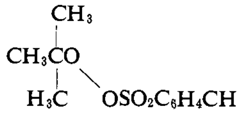
The Transition State in Terms of the Theory of Neighboring Group Participation. Instability of RO$^+$. The apparent importance of electronic effects rather than steric can best be understood in terms of neighboring group theory[20] where the large rate enhancements observed in perester II solvolysis represents anchimeric acceleration of ionization by the migrating alkyl group. The transition state will then be represented by the bridged, electron-deficient structures VIII. In the explicit application of neighboring group theory, the anchimeric acceleration for perester solvolysis (k_Δ/k_s) will be approximated by the product of the relative rates of Table III(k/k_{Me}) and the anchimeric acceleration for *t*-butyl *p*-nitroperbenzoate heterolysis (k_Δ^{Me}/k_s^{Me}) where k_Δ is the rate constant for the anchimerically accelerated ionization and k_s is the rate constant for the anchimerically unaccelerated process (eq 1).



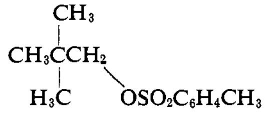
VIII VIIIa VIIIb VIIIc

$$k_\Delta/k_s = (k_\Delta^{Me}/k_s^{Me})(k/k^{Me}) \qquad (1)$$

An estimate of k_Δ^{Me}/k_s^{Me} can be obtained most conveniently from the solvolysis rates of *t*-butyl pertosylate (IX) and neopentyl tosylate (X) in acetic acid (Table V) and from the estimated differences in energies of heterolysis of peroxide and carbon–oxygen bonds ($\Delta\Delta E_H$).



IX



X

The latter quantity will be approximated by eq 2 where the first term is the difference in homolytic dissociation energies between peroxide and carbon–oxygen bonds and the second term is the ionization potential difference between oxygen and carbon. The latter term predominates and substitution of the appropriate quantities leads to the conclusion that peroxide heterolysis should be more costly by about 22 kcal. Neglecting anchimeric acceleration of solvolysis of neopentyl tosylate in acetic acid and assuming that the enthalpy of activation is a measure of the energy of heterolysis of a carbon–oxygen bond, then $\Delta H_s^{\ddagger}$ for peroxide heterolysis should be about 52 kcal (Table V). If entropy differences between assisted and unassisted solvolysis are ignored this value leads to a k_Δ^{Me}/k_s^{Me} of about 10^{23} for *t*-butyl pertosylate and we assume a similarly large ratio for

$$\Delta\Delta E_H = (\Delta E_{OO} - \Delta E_{CO}) + (I_O - I_C) \qquad (2)$$

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[17] R. Taft and E. Lewis, *Tetrahedron*, **5**, 210 (1959).

[18] (a) R. B. Bernecker and F. A. Long, *J. Phys. Chem.*, **65**, 1565 (1961); (b) F. H. Field and J. L. Franklin, "Electron Impact Phenomena," Academic Press Inc., New York, N. Y., 1957.

[19] R. Hoffman, *J. Chem. Phys.*, **40**, 2480 (1964).

[20] (a) S. Winstein and E. Grunwald, *J. Am. Chem. Soc.*, 70, 828 (1948); (b) S. Winstein, *Bull. Soc. Chim. France*, **18**, 55 (1951).

Table V. Solvolysis of Neopentyl Tosylate and *t*-Butyl *p*-Pertosylate at 25° in Acetic Acid

Compound	k, sec^{-1}	$\Delta H^{\ddagger}$, kcal mole^{-1}	$\Delta S^{\ddagger}$, eu
Neopentyl tosylate	3.41×10^{-11}[a]	30.0[a]	−2.5
t-Butyl *p*-pertosylate	6.30×10^{-4}	20.9	−3.1

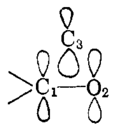
[a] Extrapolated from data at higher temperatures: S. Winstein, B. K. Morse, E. Grunwald, K. C. Schreiber, and J. Corse, *J. Am. Chem. Soc.*, **74**, 1113 (1952).

the *p*-nitroperbenzoate ester IIa. Consequently on the basis of these crude calculations the actual anchimeric acceleration (k_Δ/k_s) is approximately a factor of 10^{23} greater than that indicated by the relative rates of Table III. The conclusion that $k_\Delta{}^{\text{Me}}/k_s{}^{\text{Me}}$ is very large is perhaps more simply derived by noting that, even though carbon–oxygen ionization is favored by 22 kcal compared to peroxide ionization on the basis of eq 2, the latter process in *t*-butyl pertosylate solvolysis is actually more facile by 9 kcal.

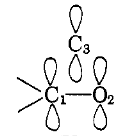
The obvious enormous anchimeric acceleration for perester heterolysis, even though only approximated here, is indicative of the very powerful driving forces toward rearrangement *via* transition state VIII, with a corresponding distribution of positive charge on carbon rather than on oxygen. Explicitly, structure VIIIa must be relatively unimportant. An important conclusion closely related to this discussion is that unrearranged alkoxy cations (RO^+) or the ion ^+OH written in simplified representations of peracid oxidations of aromatics[21] are very unstable and do not represent actual intermediates.

Previous evidence for the lack of stability of intermediate alkoxy cations was reported by Bassey and co-workers.[22] When α-phenylethyl hydroperoxide was decomposed in sulfuric acid solution containing H_2O^{18} they found that the recovered hydroperoxide did not contain O^{18}, indicating that ionization of the peroxide bond does not occur without inevitable migration of neighboring phenyl. The lack of equilibration of carbonyl O^{18} in the Baeyer–Villiger reaction has also been interpreted as evidence against RO^+ intermediates.[22b] More recently, unsuccessful attempts to generate the *t*-butoxy cation from *t*-butyl hypochlorite have been described.[22c]

The Bridgehead Perester and the Configuration of the Migrating Group. The high relative rates given in Table III for IIi (R = 4-camphyl) shows that the restriction of the migrating group to a pyramidal configuration does not significantly retard the rate of ionization. Previously, Hawthorne[6] reported that bridgehead migration in the Baeyer–Villiger oxidation of phenyl alkyl ketones occurs to the same extent as *t*-butyl migration. Also Bartlett and Knox[23] earlier observed that 1-apocamphyl is a facile migrating group in the Hoffman rearrangement. Similar observations have been made in the Curtius reaction.[24] This result can best be rationalized by comparing the two transition-state models XI and XII where the bridging group (C_3) is tetrahedrally and trigonally hybridized, respectively.



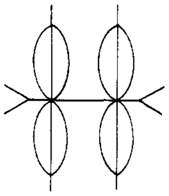
XI



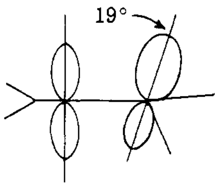
XII

Qualitatively one may anticipate that XI would be more stable than XII because of the greater overlap of a sp^3 orbital compared to a carbon 2p orbital. Simple molecular orbital calculations of the type previously described for the corresponding Wagner–Meerwein bridged ion[25] confirms this even when one takes into account the increased electronegativity of sp^3-hybridized carbon compared to trigonal carbon (2p orbital). These calculations furthermore show that the tendency of RO^+ to form a bridged species is greater than that for the corresponding carbonium ion and that increase in the electronegativity of the migrating carbon by electron-withdrawing substituents retards bridging.

One might suppose, because of the tetrahedral hybridization of the migrating carbon, that resonance stabilization (unsaturation or hyperconjugation) of electron deficiency at this site would be unimportant. This can be evaluated by considering structures XIII and XIV where π overlap involves 2p orbitals or 2p and sp^3 orbitals, respectively. A simple calculation shows that overlap in XIV is only 17% less than that in XIII. Consequently, resonance stabilization of electron deficiency at the migrating carbon is still of relative importance and definitely cannot be eliminated from consideration.



XIII



XIV

It is probable that the small decrease in relative rate observed for the 4-camphyl migrating group compared to *t*-butyl reflects a compromise between increased stabilization of electron deficiency by inductive mechanisms and a decrease in stabilization by hyperconjugative mechanisms. The former results from the increased alkyl substitution in 4-camphyl compared to *t*-butyl and the latter results from the greater hyperconjugation of C–H bonds compared to C–C bonds.[17] Also, to the extent that there is a steric requirement for hyperconjugation,[26] the pertinent rigid C–H bonds in 4-camphyl are not as well disposed as those in *t*-butyl.

The Benzyl and 2-Phenylethyl Substituents. Distribution of Electron Deficiency in the Transition State. The greatly enhanced rate of solvolysis of perester IIe (R = benzyl) and its methoxy derivatives (Table III) can be rationalized on an *a priori* basis in terms of a variety of transition states and intermediates, depending

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(21) H. Hart and C. A. Buehler, *J. Org. Chem.* **29**, 2397 (1964).

(22) (a) M. Bassey, C. A. Bunton, A. G. Davies, T. A. Lewis, and D. R. Llewellyn, *J. Chem. Soc.*, 2471 (1955); (b) C. A. Bunton, T. A. Lewis, and D. R. Llewellyn, *ibid.*, 1226 (1956); (c) D. Martin, A. Weise, and J. Becker, *Chem. Ber.*, **99**, 1266 (1966).

(23) P. D. Bartlett and L. H. Knox, *J. Am. Chem. Soc.*, **61**, 3184 (1939).

(24) U. Schollkopf, *Angew. Chem.*, **72**, 147 (1960).

(25) R. J. Piccolini and S. Winstein, *Tetrahedron*, 423 (1963).

(26) (a) V. J. Shiner, *J. Am. Chem. Soc.*, **83**, 240 (1961); (b) V. J. Shiner and J. S. Humphrey, Jr., *ibid.*, **85**, 2416 (1963).

on whether the aryl group interacts (Figure 3) directly with electron-deficient carbon or oxygen in the transition state. The various possibilities are depicted by structures XV–XIX. Each of these could be visualized to lead to the intermediate benzyloxy carbonium ion XX or to the various phenonium-type intermediates XXI–XXIVa. For example, XVIII could collapse to either XXa or to the phenonium ion in intermediate XXIIIa.

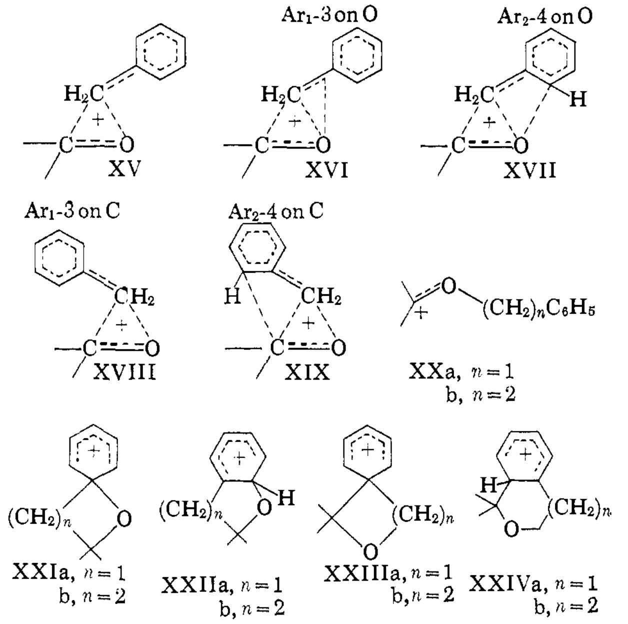


Figure 3. Possible transition states and intermediates for solvolysis of peresters IIe–f.

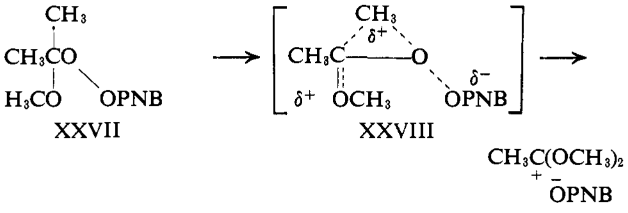
Of the rate-enhancing effects of migrating benzyl *vs.* methyl visualized by XV–XIX, the simplest is the one involving conjugation in the migrating group (XV). The rate acceleration by a *p*-methoxyl group,[27] but not by a *m*-methoxyl, would be consistent with such an explanation. So is the slower rate with migrating 2-phenylethyl compared to ethyl.

Of the possible direct interactions between the benzene ring of the migrating benzyl and either C or O in the transition state, as visualized in structures XVI–XIX, the Ar₂-4[28] type contribution and the corresponding phenonium ions depicted by XVII and XIX and XXIIa and XXIVa, respectively, may be ruled out on the basis of the rate-retarding effect of *m*-methoxyl. On the other hand, the methoxyl group effects would be consistent with structures XVI or XVIII with an Ar₁-3[28] contribution on O or C. Such an Ar₁-3 contribution in the case of benzyl would also be consistent with the slow rate of 2-phenylethyl. With the latter group, aryl participation would need to be Ar₁-4 or Ar₂-5, and neither of these modes is very effective compared to the Ar₁-3 type.[29] Transition states XVI and XVIII, reflecting Ar₁-3 aryl participation on O or C, could conceivably give rise to not only XX, but also XXI and XXIII. However, the quantitative yields of acetone after hydrolysis and the high yields of its dimethyl ketal before hydrolysis clearly rule out intermediates XXI or XXIII. In methanol XXI, for example, would most likely give 1,1-dimethyl-1-phenoxy-2-methoxyethane (XXV) or for the case of IIe (R = $CH_2CH_2C_6H_5$) the corresponding propane XXVI. Also, products corresponding to those obtained in the analogous carbon systems where ring expansion of a spiro-cationic intermediate occurs[29] apparently are not observed, and this further rules out intermediate XXI or XXIII.

$CH_3OCH_2C(CH_3)_2OC_6H_5$ XXV $\qquad$ $CH_3OCH_2CH_2C(CH_3)_2OC_6H_5$ XXVI

To summarize, if partial aryl participation contributes to the IIe–h transition states, they still lead to intermediate XX. Until more information is available, these solvolyses may be interpreted most simply by means of transition state XV. Because of the substantial overlap of the phenyl π-electron system with a tetrahedral migrating carbon atom it seems probable that the benzyl migrating group retains a predominantly tetrahedral hybridization in the transition state. This conclusion is reinforced by noting that any flattening of the migrating group will result in a compensating decrease in transition-state stability owing to decreasing s character in the apex orbital. However, it is conceivable that detailed molecular orbital calculations might indicate an optimum hybridization intermediate between tetrahedral and trigonal.

Evidence for the importance of stabilization of electron deficiency at the migration origin can be obtained from the rates of solvolysis of perester XXVII. Previous work[11] has shown that exclusive migration of methyl to give a dialkoxy carbonium ion occurs in this model of the Bayer–Villiger intermediate. The observed rate enhancement (relative rate = 1.12 × 10^3 on the scale of Table III), which is uncorrected for inductive retardation of solvolysis owing to the alkoxy substituent, indicates that XXVIII is the most logical transition-state model. This model clearly depicts the role alkoxy substituents play in stabilizing electron deficiency at the migration origin.



XXVII XXVIII

Previously Van Steveninck and Kooyman[5] concluded that since the observed second-order rate of acid-catalyzed decomposition of 1-phenylethyl hydroperoxide was only one-fifth that of cumyl hydroperoxide, little electron deficiency was generated at the migration origin. However, their second-order rate constants are products of an equilibrium constant for hydroperoxide protonation and a first-order rate constant for decomposition of the protonated intermediate. It is probable that a compensating increase in the ratio of equilibrium constants for 1-phenylethyl hydroperoxide and cumyl hydroperoxide protonation leads to a net second-order rate comparison indicating little effect of α-methyl substitution. Their comparison is further

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(27) Explicitly *p*-methoxybenzyl migration occurs about 30 times faster than benzyl or *m*-methoxybenzyl, leading to an approximate ρ value of −2 on the σ^+ scale or −5.5 on the σ scale.

(28) S. Winstein, R. Heck, S. Lapporte, and R. Baird, *Experientia*, **12**, 138 (1956).

(29) R. Heck and S. Winstein, *J. Am. Chem. Soc.*, **79**, 3105 (1957).

complicated by considerable hydrogen migration (35%) for 1-phenylethyl hydroperoxide.

Comparison of the Relative Rates of Fragmentation of 2-Substituted 2-Propylalkoxy Radicals and the Relative Rates of Solvolysis of 2-Substituted 2-Propyl *p*-Nitroperbenzoates II. Numerous workers[30] have studied the relative rates of fragmentation of *t*-alkoxy radicals, and a comparison with our data is pertinent and interesting. In Table VI we have collected the relative rates obtained by Walling and Padwa[30b] for 2-substitued 2-propylalkoxy radicals generated from hypochlorite photolysis. These data were obtained by measuring acetone:alcohol ratios generated from the fragmentation of the alkoxy radical (k_d) and the concurrent abstraction of hydrogen (k_a) from cyclohexane. If one assumes that the abstraction reaction rate is independent of *t*-alkoxy radical structure, then the relative rates of fragmentation ($k_d/k_d^{CH_3}$) can be obtained and these are listed. The first noteworthy feature is that entropy differences are significant and lead to a smaller, relative rate spectrum than that implied from the activation energy differences. Secondly the difference between methyl and any other alkyl group is quite large both in terms of rate and activation energy, while the difference between higher alkyl groups is relatively small. In contrast, as Table III and Figure 2 shows, perester ionization rates increase regularly with increasing size of the migrating group. Thirdly, phenyl is one of the better migrating groups in perester solvolysis, while phenyl fragmentation was not observed from the corresponding alkoxy radical. In fact, 2-phenyl substitution led to substantial rate enhancement for methyl fragmentation from the corresponding alkoxy radical. Finally, benzyl is the best fragmenting group on the basis of activation energy, but is a poorer fragmenting group on the basis of relative rate because of an unfavorable entropy factor.

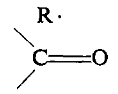
Table VI. Decomposition of $RC(CH_3)_2OCl$ in CCl_4 in the Presence of Cyclohexane (R′H)[a]

R	k_d/k_a	$k_d/k_d^{CH_3}$	$E_d - E_a$, kcal mole^{-1}	$10^{-3}(PZ)_d/(PZ)_a$
CH_3	0.002	1	10.0	500
CH_2Cl	0.051	25.5	4.6	0.13
C_6H_5[b]	0.242	121	5.1	1.72
C_2H_5	1.140	570	3.3	0.42
$C_6H_5CH_2$	1.80	900	0.7	0.006
i-C_3H_7	61.5	30,750	1.7	1.15
t-C_4H_9	7300	>150,000	...	...

[a] k_d/k_a were obtained at 0°. Conditions and details are given in ref 30b. [b] Methyl fragments rather than phenyl.

Another pertinent comparison is that between norbornyl fragmentation and 4-camphyl migration. Greene and co-workers[30c] showed that the ratio of norbornyl fragmentation to methyl fragmentation from the dimethyl-(1-norbornyl)alkoxy radical is only 4:1 in contrast to 4-camphyl migration which is greatly enhanced compared to methyl in perester ionization.

On the basis of these data it is reasonable to conclude that the transition state for *t*-alkoxy radical fragmentation probably is best represented by an unsymmetrical structure such as XXIX where R–O bonding is considerably weaker than in the corresponding transition state for perester ionization. The most compelling evidence for this is the fairly good correlation with radical (R·) and ketone stability. Furthermore, simple molecular orbital considerations of the type described above suggest that the bridged neutral species is less stable than the unrearranged alkoxy radical, in contrast to the *t*-alkoxy cation where the bridged species is more stable.



XXIX

Experimental Section

Solvents and Reagents. Acetic Acid. Anhydrous acetic acid containing 0.01 *M* acetic anhydride was prepared as previously described.[31]

Brom Phenol Blue Indicator. A saturated solution of brom phenol blue indicator was made up in distilled glacial acetic acid and neutralized to dry acetic acid. Alternatively, 0.1 g of brom phenol blue was dissolved in absolute ethanol and neutralized to dry methanol.

Cyclohexane. Eastman White Label cyclohexane was washed with concentrated sulfuric acid, dried by refluxing over calcium hydride, and finally distilled.

Dioxane. Dioxane was purified by the method described in Fieser[32] and was obtained from Dr. S. G. Smith.

Anhydrous Ethanol. Absolute ethanol was refluxed overnight over calcium hydride and then distilled through a 10-in. Vigreux column. The solvent was dry to Karl Fischer reagent.

Ether. Mallinckrodt anhydrous ether was used without further purification.

***p*-Hydroxyazobenzene Indicator.** *p*-Hydroxyazobenzene (0.1 g), which was prepared by Dr. E. Freidrich, was dissolved in 100 ml of reagent grade benzene and neutralized to dry methanol.

Anhydrous Methanol. Calcium hydride (10 g) was dissolved in 500 ml of reagent grade methanol and then concentrated by distillation to about 200 ml. This 200-ml portion was poured into 1.5 l. of methanol, and the mixture was refluxed overnight. Distillation gave a middle fraction of methanol which was dry to Karl Fischer reagent, but still slightly basic to *p*-hydroxyazobenzene indicator. The residual ammonia was removed by refluxing the dry methanol solvent under dry nitrogen flow or by redistillation from anhydrous sulfanilic acid.[33] The recovered solvent was both dry to Karl Fischer reagent and apparently neutral. Use of this solvent in kinetics resulted in quantitative evolution of acid for all peresters except Ia (R = Me).

Pentane. Commercial pentane solvent was distilled through a 2-ft, bubble-plate column. A 200-ml forerun was discarded.

Pyridine. Eastman White Label pyridine was refluxed over calcium hydride overnight and distilled through a 10-in. Vigreux column, bp 114°.

Standard Sodium Acetate in Acetic Acid. A 0.2088 *M* solution of sodium acetate in acetic acid was made up by dissolving analytical grade, dry sodium carbonate in 1 l. of distilled acetic acid. Portions of this solution were diluted as needed with dry acetic acid to give a 0.02088 *M* solution.

Standard Sodium Methoxide. Enough metallic sodium was added to about 3 l. of regent grade methanol to make a 0.02–0.03 *M* solution of sodium methoxide. The solution was standardized with a freshly prepared solution of potassium hydrogen phthalate using phenolphthalein as an indicator. This was checked with pure *p*-nitrobenzoic acid in methanol using *p*-hydroxyazobenzene as an indicator.

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(30) (a) C. Walling and A. Padwa, *J. Am. Chem. Soc.*, **83**, 2207 (1961); (b) C. Walling and A. Padwa, *ibid.*, **85**, 1593 (1963); (c) F. D. Greene, M. L. Savitz, F. D. Osterholtz, H. H. Law, W. N. Smith, and P. M. Zanet, *J. Org. Chem.*, **28**, 55 (1963); other leading references are cited in the above papers.

(31) S. Winstein and A. H. Fainberg, *J. Am. Chem. Soc.*, **78**, 2763 (1956).

(32) L. F. Fieser, "Experiments in Organic Chemistry," 3rd ed, D. C. Heath and Co., Boston, Mass., 1955, p 292.

(33) H. Goldschmidt and A. Theussen, *Z. Prakt. Chem.*, **81**, 31 (1952).

Standard Sodium Thiosulfate. Approximately 0.07 *M* solutions of sodium thiosulfate were prepared from freshly redistilled water and reagent grade salt. Sodium carbonate and chloroform were added as preservatives.[34] The usual textbook procedure for standardization involving the reduction of dichromate was used.[35] The molarity of the solution was periodically checked.

Preparation of Alcohols. *t*-**Amyl Alcohol.** Eastman practical grade *t*-amyl alcohol was distilled, and the fraction boiling at 101–102° was collected.

2,3-Dimethyl-2-butanol was prepared by the reaction of isopropylmagnesium bromide and acetone. Material with bp 116° (lit.[36] bp 117–122°) was used.

2,3,3-Trimethyl-2-butanol was prepared by the reaction of methylmagnesium iodide and pinacolone. The alcohol, bp 127–129°, was converted to the crystalline hemihydrate, mp 82° (lit.[37] mp 82–83°).

Dimethylbenzylcarbinol was prepared by the reaction of methylmagnesium iodide with ethyl phenylacetate. Material with bp 97–98° (12 mm) was used [lit.[38] bp 99.5–102° (14 mm)].

α,α-Dimethyl-β-phenylethylcarbinol was obtained from the reaction of β-phenylethylmagnesium bromide and acetone. Material with bp 128° (17 mm) was used [lit.[39] bp 124–125° (15 mm)].

1-(4-Methoxyphenyl)-2-methyl-2-propanol was prepared by the reaction of methylmagnesium iodide and methyl *p*-methoxyphenylacetate. The pure alcohol had mp 42.5°.

Anal. Calcd for $C_{11}H_{16}O_2$: C, 73.30; H, 8.94. Found: C, 72.89; H, 8.84.

1-(3-Methoxyphenyl)-2-methyl-2-propanol was obtained as above from the reaction of methylmagnesium iodide and methyl *m*-methoxyphenylacetate. The purified alcohol had bp 131° (9.5 mm).

Anal. Calcd for $C_{11}H_{16}O_2$: C, 73.30; H, 8.94. Found: C, 73.68; H, 8.90.

4-Camphyldimethylcarbinol. A three-necked flask equipped with condenser, dropping funnel, and magnetic stirrer was dried by flame under argon flow. Upon cooling, about 40 ml of dry ether was added and 2.0 g of lithium ribbon was cut directly into the flask. Distilled, Eastman White Label methyl iodide (17 g) in 40 ml of dry ether was added dropwise so that gentle reflux was maintained. At the completion of this addition, the reaction mixture was refluxed for 30 min more. Dry cyclohexane (80 ml) was added dropwise, while the ether was distilled off. When the temperature of the distilling solution reached 80°, and little or no ether was distilling over, 5.6 g of methyl 4-camphylcarboxylate (prepared from 4-camphylcarboxylic acid[40] using diazomethane) in 40 ml of dry cyclohexane was added dropwise.

At the completion of this addition, gentle refluxing was maintained for 14 hr. The mixture was then cooled and saturated ammonium chloride solution was added dropwise until a clear separation of the precipitate occurred. The organic layer was decanted off and combined with the ethereal washings of the residue. The solution was washed with 10% sodium bicarbonate, clarified over charcoal, and dried over anhydrous magnesium sulfate. Evaporation of the solvent gave 7 g of a dark liquid residue. This was chromatographed on alumina using petroleum ether–ether as the eluent. The initial fraction consisted of a small amount of hydrocarbon. The middle fraction was predominantly recovered ester, while the terminal fraction was the desired alcohol. This amounted to 2.2 g of a colorless oil, mp *ca.* 15°. The infrared spectrum was consistent with the structure being closely similar to that of 2,3,3-trimethyl-2-butanol. The characteristic hydroxyl bands were found at 3600 and 3460 cm^{-1}. The alcohol was used in the next step without further purification.

Preparation of Hydroperoxides. *t*-**Butyl Hydroperoxide.** Lucidol *t*-butyl hydroperoxide was distilled and material having bp 44–45° (28 mm) was used.

t-**Amyl hydroperoxide** was prepared by the method of Milas and Surgenor[41] or by the method given below for 2,3-dimethyl-2-butyl hydropxoeride. Material having bp 34–35° (7 mm), $n^{25}\text{D}$ 1.4120 [lit.[42] bp 32–33° (4.3 mm), $n^{25}\text{D}$ 1.4132], was used.

2,3-Dimethyl-2-butyl Hydroperoxide. To a mixture of 10 g of 2,3-dimethyl-2-butanol, 7.8 g of 50% hydrogen peroxide, and 40 ml of reagent grade chloroform, 3.2 g of 70% sulfuric acid was added. The reaction mixture was refluxed for 20 min with stirring, and then it was rapidly cooled. The organic layer was separated, and the aqueous layer was extracted with chloroform. The combined organic layer and extracts were washed with water, dried over magnesium sulfate, and concentrated. The residue was distilled at reduced pressure to give 2 g of the hydroperoxide, bp 56–57° (10 mm), $n^{25}\text{D}$ 1.4226 [lit.[4] bp 51–59° (12 mm)].

2,3,3-Trimethyl-2-butyl Hydroperoxide. A stirring solution of 40 g of 90% Lucidol hydrogen peroxide and 0.05 ml of concentrated sulfuric acid was cooled down to 5°. In small quantities, 8 g of 2,3,3-trimethyl-2-butanol hemihydrate was added. It was later found that the use of acid was not required, while the use of the relatively large quantity of acid prescribed by Criegee[3] gave little or no hydroperoxide. The mixture was allowed to stir for 6 hr. Then 50 ml of distilled water was added, and the aqueous solution was decanted from the precipitated white solid. The white solid was dissolved in pentane, and the solution was washed with water and dried over magnesium sulfate. Concentration and cooling gave 5 g of a colorless crystalline solid with a strong hydroperoxide odor, mp 112–113° (lit.[3] mp 114°). The hydroperoxide was stable and volatile enough to be sublimed *in vacuo* without decomposition at around 50°.

1-Phenyl-2-methyl-2-propyl Hydroperoxide. Dimethylbenzylcarbinol (6 g) was combined with 30 ml of 90% hydrogen peroxide at 5° and acidified with 12 drops of concentrated sulfuric acid. The reaction was allowed to continue for 31 hr with stirring. Distilled water (30 ml) was then added, and the mixture was extracted with pentane. The pentane layer was washed with distilled water, dried over anhydrous magnesium sulfate, and concentrated to give 6.1 g of a white crystalline solid, mp 38–41° (lit.[43] mp 41°). The hydroperoxide gave a strong test for active oxygen and had an infrared spectrum consistent with the structure.

1-(4-Methoxyphenyl)-2-methyl-2-propyl Hydroperoxide. The 1-(4-methoxyphenyl)-2-methyl-2-propanol (1 g) was combined with 5 ml of 90% hydrogen peroxide acidified with one drop of 50% sulfuric acid. The reaction mixture was stirred for 8 hr. Work-up as above yielded 8 g of slightly colored oil having characteristic hydroperoxy absorption in the infrared and a strongly positive test for active oxygen.

1-(3-Methoxyphenyl)-2-methyl-2-propyl Hydroperoxide. The preparation from the alcohol was carried out as above with a close to quantitative yield of hydroperoxide being obtained as an oil.

α,α'-Dimethyl-β-phenylethyl Hydroperoxide. The preparation from the alcohol was carried out as above with about an 80% yield of crude hydroperoxide being obtained as an oil.

2-(4-Camphyl)-2-propyl Hydroperoxide. The alcohol (0.3 g) was added to 2 ml of stirring, ice-cold 90% hydrogen peroxide. The reaction mixture was let stand for 24 hr. At the end of this period, a white precipitate formed. Distilled water (2 ml) was added, and the precipitate was filtered off. The colorless, crystalline solid was washed with water and then dried at room temperature *in vacuo* for 3 hr. The yield of product was 0.3 g, mp 37–39°. The hydroperoxide gave a strong test for active oxygen.

Preparation of Peresters. The *p*-nitroperbenzoates were prepared by combining the hydroperoxide and recrystallized *p*-nitrobenzoyl chloride at low temperatures (−20–0°) and letting the reaction mixture stand overnight. The lower reaction temperature was used for the more reactive peresters (IId and i). Work-up was carried out by either pouring the reaction mixture into a slush of concentrated hydrochloric acid and ice or in one case by pouring into ether. Crude peresters were generally recrystallized from cold mixtures of ether–pentane. Their properties are summarized in Table VII. In general all of the *p*-nitroperbenzoates had 100 ± 10% active oxygen content by the transesterification analytical method described below. Two typical preparations follow.

t-**Amyl *p*-Nitroperbenzoate.** Recrystallized *p*-nitrobenzoyl chloride (8.35 g) was dissolved in 31.3 ml of dry pyridine. The mixture was cooled down to 0° and 4.6 g of *t*-amyl hydroperoxide was added. The reaction mixture was kept overnight in the refrigerator. The

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Table VII

R	Mp, °C[a]	Calcd, % C	Calcd, % H	Found, % C	Found, % H	$\gamma_{C=O}$, cm^{-1} [b]
CH_3	77–78[c]	...	...	...	...	1760
CH_3CH_2	49.5–50.0[d]	...	...	...	...	1762
$(CH_3)_2CH$	56.5–57.5	58.43	6.37	58.61	6.18	1762
$(CH_3)_3C$	88 dec	59.77	6.77	59.97	6.46	1765
$C_6H_5CH_2$	68–69	64.75	5.43	64.50	5.35	1750
p-$CH_3OC_6H_4$-CH_2	68–69	62.60	5.50	62.39	5.40	1750[e]
m-$CH_3OC_6H_4$-CH_2	83.5–85.5	62.60	5.50	62.57	5.54	1748[e]
$C_6H_5CH_2CH_2$	88–90	65.70	5.83	65.13	5.83	1748[e]
	115 dec	66.41	7.53	66.06	7.57	1748

[a] Uncorrected. [b] Position of characteristic perester carbonyl band. Spectra were generally obtained in dilute chloroform solution unless noted. [c] Lit.[14] mp 78°. [d] Lit.[42] mp 48–49.5°. [e] Spectra obtained in potassium bromide pellets.

resulting mixture of yellow solution and white precipitate was poured into 32 ml of concentrated hydrochloric acid in *ca.* 75 g of ice with stirring. A white-yellow precipitate was separated and partially dissolved in pentane–ether. The insoluble portion was discarded. The pentane-ether solution was washed with 10% hydrochloric acid and 10% sodium hydroxide and dried over magnesium sulfate. The solution was concentrated and cooled to give 7.2 g of the yellow crystalline perester, mp 49.5–50.0° (lit.[42] mp 48–49.5°). The active oxygen content was 95% by the usual method and 110% by the transesterification method described below. The infrared spectrum contained the characteristic perester carbonyl band at 1762 cm^{-1}.

2-(4-Camphyl)-2-propyl *p*-Nitroperbenzoate. The solid hydroperoxide (0.180 g) was added to a solution of 0.17 g of recrystallized *p*-nitrobenzoyl chloride in 3 ml of dry pyridine at −20°. The mixture was allowed to stand for 24 hr at −20°, and the reaction mixture was poured into *ca.* 100 ml of ether. The ether solution was stirred well and then filtered to remove the precipitated pyridinium salt. The solution was washed with cold, 10% hydrochloric acid, 10% sodium bicarbonate solution, and finally with water. After drying over anhydrous magnesium sulfate, the solution was concentrated to give about 0.250 g of a yellow crystalline solid. This was recrystallized carefully from ether-pentane to give the pure perester, mp 115–116° dec. About 10% of the crude product was found to be *p*-nitrobenzoyl peroxide by infrared, melting point, and C, H analysis.

Anal. Calcd for $C_{20}H_{27}NO_5$: C, 66.41; H, 7.53. Found: C, 66.06; H, 7.57.

The perester had the characteristic perester carbonyl band in the infrared at 1748 cm^{-1}.

***t*-Butyl *p*-Pertoluenesulfonate.** The crude perester was obtained by the method of Bartlett and co-workers[4e] and recrystallized from ether-pentane at Dry Ice-acetone temperatures. The analytical sample, mp 36–39° dec (lit.[4e] mp 36.5–37.0° dec), was obtained after two recrystallizations.

Anal. Calcd for $C_{11}H_{16}SO_4$: C, 54.08; H, 6.60. Found: C, 53.81; H, 6.77.

The pertosylate decomposed violently on standing at room temperature for about 10 min to give a red tar as noted by previous workers.[4e] It was stored over Dry Ice and was quite stable at this temperature.

Product Analysis. Analysis for Methyl *p*-Nitrobenzoate from the Decomposition of *t*-Butyl *p*-Nitroperbenzoate (Ia) in Methanol. *t*-Butyl *p*-nitroperbenzoate (0.33 g) was dissolved in 16.5 ml of dry methanol and decomposed at 75° for *ca.* 15 half-lives. After decomposition the solvent and volatile products were stripped off *in vacuo* and the residue was dissolved in ether. The ethereal solution was washed with 10% sodium carbonate solution, 10% hydrochloric acid, and water. After drying over anhydrous potassium carbonate, the ethereal solution was concentrated to give a yellow crystalline solid, mp 92° (23%). The infrared spectrum of this material corresponded exactly to that of pure methyl *p*-nitrobenzoate and the mixture melting point was not depressed.

The aqueous basic extract was acidified with hydrochloric acid and the resulting precipitate was separated. After drying, the melting point of this material was 239°. No depression occurred for a mixture melting point with pure *p*-nitrobenzoic acid. Titration for evolved acid after ten half-lives (infinity titer in rate measurements) indicated that the yield of acid was 65%.

Analysis for Acetone and Formaldehyde from the Decomposition of *t*-Butyl *p*-Nitroperbenzoate (Ia) in Methanol. *t*-Butyl *p*-nitroperbenzoate (0.67 g) was dissolved in 33.5 ml of dry methanol and decomposed at 75° for *ca.* ten half-lives. The resulting solution (10 ml) was added to 2,4-DNP reagent prepared by dissolving 0.4 g of Eastman White Label 2,4-DNP in 3 ml of concentrated sulfuric acid and then slowly adding 13 ml of water. An immediate precipitate formed in the product analysis mixture. It was let stand for 4 hr, after which the precipitate was separated on a sintered glass funnel. The orange precipitate was washed with *ca.* 70 ml of 10% sulfuric acid and 100 ml of water. It was then dried at 100° for 30 min. The 2,4-DNP derivative yielded 0.136 g and melted at 136–150°. Recrystallization from absolute ethanol gave a larger fraction of yellow crystals melting at 161–165°, and a smaller fraction melting at 115–128°. The former did not depress the melting point of pure formaldehyde 2,4-DNP, while the latter depressed the melting point of pure acetone 2,4-DNP by a few degrees.

Both formaldehyde and acetone alternatively were detected by gas chromatography on a glycerol column (see below).

Gravimetric Analysis for Acetone from the Decomposition of IIb, c, and d in Methanol. Approximately 0.08 g of the perester was dissolved in 6 ml of dry methanol, and the solution was sealed in a rate tube. The perester solution was then decomposed for ten half-lives at a convenient temperature. After removal from the thermostated bath, the tube was cooled and broken. The contents were washed quickly into 50 ml of a saturated solution of 2,4-DNP reagent in 2 *N* hydrochloric acid with methanol. The mixture was allowed to stand at 0° for about 5 hr. The precipitate was filtered using a tared, glass-sintered funnel, and then washed with 70 ml of 2 *N* hydrochloric acid, 10–15 ml of 5% sodium bicarbonate solution, and 100 ml of distilled water. It was evacuated for 6 hr at room temperature and 1-mm pressure. The tared funnel, with the precipitate, was weighed, and the melting point of the derivative obtained. Controls were run with methanol solutions containing acetone and *p*-nitrobenzoic acid The melting point of the derivative obtained from the product analysis experiments corresponded to that from the control experiment (mp 124–126°).

Gas Chromatographic Analysis. In general, kinetic concentrations (about 0.03 *M*) of a solution of the perester were made up in the appropriate solvent and sealed in a rate tube. The tube was placed in a thermostated bath for at least ten half-lives. After opening the tube, the internal standard was added at a known concentration and this solution was injected into the gas chromatograph. Hydrolysis of the dimethyl ketal of acetone in the product solution was accomplished by adding a one-fourth volume of distilled water.

The analysis generally was carried out with an Aerograph Model A-90 gas chromatograph. Peak areas were measured by cutting out the peaks and weighing them on a semimicro balance. Tracings were used to preserve the original chromatograms. Retention times and thermal responses relative to the particular internal standard were obtained from known solutions. The analytical conditions for each column and corresponding internal standards are summarized in Table VIII. Column 1 was used for the analysis of ketal, alcohol, and ethers from perester decompositions in methanol and for the product analysis for the decomposition of *t*-butyl *p*-nitroperbenzoate in acetic acid. Column 2 was used for the analysis of olefins (propene and isobutylene). Column 3 was used for the analysis of the products from *t*-amyl *p*-nitroperbenzoate in acetic acid. Finally, column 4 was used for the analysis of benzyl alcohol from the decomposition of 2-benzyl-2-methyl-2-propyl *p*-nitroperbenzoate.

Kinetic Techniques. Approximately a 0.03 *M* solution of the perester was made up in the kinetic solvent. Immediately after solution of the perester, rate tubes were filled to approximately the 6-ml level and sealed. The rate tubes had been washed in hot detergent, rinsed six times with distilled water, and dried at 110° for 6 hr. The tubes were placed in the thermostated rate bath simultaneously. The first point was taken after 5–10 min. For rates at 50–100°, the tubes were quenched in ice water and then warmed to 25° before analysis. For rates at 25°, the tubes were removed from the bath and broken, and an aliquot taken. Rates at 25° were alternatively run by placing the rate solution in a thermostated glass-stoppered flask and extracting aliquots. This method was also used for rates at temperatures below 25°. The t_0 and

Table VIII. Gas Chromatography Columns[a]

Column	Length, m	Packing	Internal stand.	Oven temp, °C	Injection temp, °C
1	4	25% glycerol on 60–80 Firebrick	*p*-Dichlorobenzene	75	150–160
2	2	25% thiodipropionitrile on 60–80 Firebrick	*n*-Butyl ether	75	150–160
3	2	20% dimethylsulfolane on Celite	Air	35	40
4	2	Perkin-Elmer column A (diisodecyl phthalate)	*p*-Dichlorobenzene	166	~200

[a] Flow rate was generally 50–60 cc/min. Detector current was 280 ma.

subsequent *t*'s were taken at the time the tubes were quenched in ice water or the time at which the aliquot was drained into the analysis mixture for the kinetic temperature of 25°. In the latter case, the period of time between removal of the tube from the bath and the draining of the aliquot was kept reasonably constant for each point (*ca.* 60 sec).

For rates of decrease of active oxygen in acetic acid the following analytical method was used. A 0.001% solution (25 ml) of ferric chloride[44] in glacial acetic acid was pipetted into a glass-stoppered, 125-ml erlenmeyer flask. A small piece of Dry Ice was added, and the mixture was magnetically stirred for 1 min. A fresh solution of 4 g of reagent grade potassium iodide in 4 ml of distilled water was then poured into the flask. Stirring was continued for 1 min more. The glass stopper was adjusted periodically to release the carbon dioxide gas pressure. An aliquot then was pipetted into the analysis mixture. The analysis mixture was let stand for 12–15 min and then 35 ml of distilled water was added. The evolved iodine was titrated with standard thiosulfate solution. A blank was run on the reagents. This method gave reliable results only with *t*-butyl *p*-nitroperbenzoate (Ia).

The following analytical method was used for rates of decrease of active oxygen in methanol. An aliquot was quenched in 5 ml of 0.03 *M* sodium methoxide in methanol contained in a glass-stoppered 125-ml erlenmeyer flask. A small piece of Dry Ice was added. After all the carbon dioxide had been evolved, 25 ml of 0.001% ferric chloride in glacial acetic acid was added along with a fresh solution of 4 g of potassium iodide in 4 ml of distilled water. The analysis mixture was allowed to stand in the dark for 10 min. Then 35 ml of distilled water was added, and the evolved iodine was titrated with standard thiosulfate. A blank was run on the reagents.

The above analytical method for active oxygen, which is a modification of that used by Traylor,[9] is based on the very fast transesterification of these peresters with base. This procedure gave 112% of the theoretical active oxygen for pure 2,3,3-trimethyl-2-butyl *p*-nitroperbenzoate. With the other peresters, this method gave 98–111% of the theoretical active oxygen. The pure peresters were analyzed by dropping a tared microbeaker containing the perester into the solution of sodium methoxide.

The acidimetric rates in methanol were determined by draining an aliquot into 25 ml of cold ether containing five drops of *p*-hydroxyazobenzene indicator. The quenched aliquots were titrated with standard sodium methoxide.

Because of the small quantity of 2-(4-camphyl)-2-propyl *p*-nitroperbenzoate (IIi) available, the following kinetic method was used. About 20 mg of perester was added to 5 ml of dry ethanol in a jacketed reaction flask which had been thermostated at 25.00° for at least 1 hr. Five drops of *p*-hydroxyazobenzene indicator solution was added and the titrant, standard sodium ethoxide in ethanol, was first added when solution occurred. Special care was taken so that the kinetic solution was never made basic by the addition of excess titrant. The t_0 and subsequent *t*'s were taken when the indicator changed color.

The rates of decomposition of *t*-butyl pertosylate in acetic acid were determined by quenching aliquots with 25 ml of cold dioxane containing seven drops of brom phenol blue in acetic acid and titrating with standard sodium acetate.

Sample kinetic data are given in Tables IX–XI.

Table IX. Kinetics for the Decomposition of 1-Phenyl-2-methyl-2-propyl *p*-Nitroperbenzoate in Dry Methanol at 50.00°[a]

$10^3\Delta t$, sec	Titrant, ml	10^4k, sec^{-1}
0	0.249	. . .
0.65	0.520	1.38
1.99	0.790	(0.94)
4.29	1.630	1.34
5.58	1.948	1.38
6.96	2.182	1.36
8.50	2.410	1.36
∞	3.390	. . .
∞	3.416	. . .
		Av k = 1.36 ± 0.01

[a] Initial perester concentration, 0.00943 *M* aliquot, 5.003 ml; titrant, 0.0140 *M* sodium methoxide; indicator, *p*-hydroxyazobenzene; theoretical infinity, 3.42 ml.

Table X. Kinetics for the Decomposition of *t*-Butyl *p*-Nitroperbenzoate (Ia) in Acetic Acid at 75.00°[a]

$10^4\Delta t$, sec	Titrant, ml	10^6k, sec^{-1}
0	3.83	. . .
0	3.81	. . .
7.33	3.03	3.14
14.93	2.39	3.15
17.40	2.21	3.16
25.55	1.64	3.31
28.60	1.52	3.23
43.24	0.89	3.37
		Av k = 3.23 ± 0.08

[a] Initial perester concentration, 0.02709 *M;* titrant, 0.07009 *M* sodium thiosulfate; aliquot, 4.991 ml.

Table XI. Kinetics for the Decomposition of 2,3,3-Trimethyl-2-butyl *p*-Nitroperbenzoate (Id) in Dry Methanol at 25.00°[a]

Δt, sec	Titrant, ml	10^4k, sec^{-1}
0	0.579	. . .
217	0.951	(5.42)
554	1.400	7.99
882	1.730	7.85
1337	2.091	7.96
1817	2.337	7.97
2332	2.520	7.95
∞	2.880	. . .
∞	2.882	. . .
		Av k = 7.94 ± 0.04

[a] Initial perester concentration, 0.0187 *M;* aliquot, 5.043 ml; titrant, 0.03199 *M* sodium methoxide; indicator, *p*-hydroxyazobenzene; theoretical infinity, 2.92 ml.

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