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Substituent and Solvent Effects on the Rate of Perester Decomposition. The Case for Polar Contributions to the Transition State

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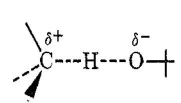
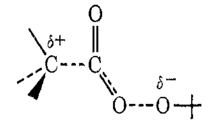
Substituent effects on the rate of decomposition of para-substituted *tert*-butylperoxy α-phenylisobutyrates were measured in three solvents. The rate constants correlated best with σ^+ to give a ρ value of -0.77 (dodecane), -0.75 (benzene), and -0.91 (acetonitrile). Correlation of the rate constants in alkanes, benzene, and acetonitrile with Brownstein's S values give R values of 2.1–2.6. By choosing suitable reference reactions it is shown that the correlation of the rate constants with substituent and solvent parameters both indicate the formation of a polar transition state.

Partial charge formation in free-radical reactions was first used to explain the alternating effect in copolymerization reactions.[2] Since then a number of radical reactions have been investigated and the results interpreted in terms of a polar effect on the transition state.[3] Many of these reactions were abstraction reactions, principally hydrogen abstraction, occurring in chain reactions.

Substituent effects on *tert*-butylperoxy phenylacetate decomposition have also been interpreted in terms of a polar effect on the transition state.[4] This interpretation was based on the improved correlation of the results for hydrogen-abstraction reactions.[5] Many examples of the effect of polar substituents on perester decomposition have subsequently been presented.[6]

Recently the interpretation of substituent effects on hydrogen abstraction reactions has been challenged and polar effects were termed "inconsistent with experimental observations."[7] Since the interpretation of polar effects in perester decompositions was originally based in part on analogy with hydrogen-abstraction reactions, one may also question the importance of polar effects on perester decompositions. The mechanism for electron transfer in perester transition states is very similar to that for hydrogen abstraction reactions.





The products, the effect of solvent, and the effect of substituents are of primary importance in determining whether a reaction is heterolytic or homolytic. For a reaction that gives typical radical products, substituent effects have generally been the principal criterion for partial charge formation in the transition state. Although the effect of solvent on radical reactions is well known, solvent effects are generally small and are usually considered to have as large an effect on the starting materials as on the transition state.

In this paper we will attempt to show that decompositions of ring-substituted *tert*-butylperoxy α-phenylisobutyrates respond to both substituents and solvent in a manner consistent with partial charge formation in the transition state.

With the exception of *tert*-butylperoxy *p*-nitrophenylacetate, the previously reported rate constants fit the Hammett equation using $\sigma_p{}^+$ values.[4] The rate constant for the *p*-nitro perester is larger than would be expected on the basis of the Hammett plot. Three tentative explanations have been offered for the faster rate.[4,8,9] We will show that the deviation of the *tert*-butylperoxy *p*-nitrophenylacetate from the Hammett plot is best interpreted by a shift of the mechanism to one-bond homolysis.

Results and Discussion

The rate constants for decomposition of several *tert*-butylperoxy α-phenylisobutyrates were determined

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[1] NDEA Fellow, 1969–1972; Tennessee Eastman Fellow, 1972–1973.

[2] F. R. Mayo and C. Walling, *Chem. Rev.*, **46**, 191 (1950).

[3] R. S. Davidson, *Quart. Rev., Chem. Soc.*, 249 (1967); R. Breslow, "Organic Reaction Mechanisms," Vol. 7, W. A. Benjamin, New York, N. Y., 1967; R. F. Bridger and T. A. Russell, *J. Amer. Chem. Soc.*, **85**, 3754 (1963); J. A. Howard and K. U. Ingold, *Can. J. Chem.*, **41**, 1744 (1963).

[4] P. D. Bartlett and C. Ruchardt, *J. Amer. Chem. Soc.*, **82**, 1756 (1960).

[5] G. A. Russell, *J. Amer. Chem. Soc.*, **78**, 1047 (1956); *J. Org. Chem.*, **23**, 1407 (1958). C. Walling and B. Miller, *J. Amer. Chem. Soc.*, **79**, 4181 (1957).

[6] C. Ruchardt, *Fortschr. Chem. Forsch.*, **6**, 251 (1966); *Angew. Chem., Int. Ed. Engl.*, **9**, 830 (1970).

[7] A. A. Zavitsas and J. A. Pinto, *J. Amer. Chem. Soc.*, **94**, 7390 (1972); A. A. Zavitsas, *ibid.*, **94**, 2779 (1972).

[8] W. A. Pryor and K. Smith, *J. Amer. Chem. Soc.*, **92**, 5403 (1970).

[9] R. C. Neuman, Jr., and J. V. Behar, *J. Org. Chem.*, **36**, 654 (1971).

by the excess scavenger method.[10] For radical initiators giving only free radicals and cage products, the first-order rate constants for scavenger disappearance and initiator decomposition are equal.[10b] We investigated two scavengers, galvinoxyl[11] and BDPA.[12] Comparison of the rate constants determined using these two scavengers is given in Table I. BDPA was thermally more stable than galvinoxyl and generally gave less fading in blank cells. However, at the concentrations used BDPA did not scavenge the radicals so efficiently as galvinoxyl; the fraction of radicals scavenged by BDPA was generally a few per cent less than the fraction scavenged by galvinoxyl. Galvinoxyl was used for all subsequent determinations.

TABLE I

RATE CONSTANTS AND CAGE EFFECTS AS A FUNCTION OF SCAVENGER AND THE SCAVENGER/PERESTER[a] RATIO

Scavenger	(Scavenger/perester)$_0$	k, sec$^{-1\,b}$ × 10^{-4}	Fraction cage effect[b]
Galvinoxyl	1.85	3.70 ± 0.03	0.54
Galvinoxyl	1.85	3.70 ± 0.06	0.53
BDPA	1.85	3.68 ± 0.03	0.59
BDPA	1.85	3.91 ± 0.03	0.59
BDPA	1.54[b]	3.61 ± 0.03	0.60
BDPA	1.96[b]	4.06 ± 0.05	0.60
BDPA	3.11[b]	4.01 ± 0.08	0.62
BDPA	3.94[b]	5.11 ± 0.12	0.55

[a] The perester was *tert*-butylperoxy α-phenylisobutyrate in dodecane at 60°. [b] Results for these experiments are the average of at least two runs; the kinetic sample were made up from the same stock solution and were run at the same time to minimize variations between the runs. The error limits reported are the standard errors. The 95% confidence limits can be obtained by multiplying the standard error by 2.36 (from a t Distribution Table with $\phi = 7$).

The reactions were followed in all cases for at least three half-lives, and infinity values were taken after ten half-lives. The absorbance values measured during a kinetic run were corrected for fading of the blank. The correction was made by one of two methods. The absorbance values were either corrected point by point, or the fading of the blank was assumed to be linear and a linear least-squares program was used to determine the correction. The results from both methods were the same within experimental error. Corrected absorbance readings were fit by computer to the Gauss Newton Exponential Function.[13] Values for the rate constant, absorbance at infinite time, and the absorbance change were determined in an iterative manner until the best fit of the absorbance *vs.* time curve was obtained (Table II). The activation parameters for the substituted *tert*-butylperoxy α-phenylisobutyrates are given in Table III.

To ascertain whether the decomposition of all the peresters was proceeding by two-bond homolysis, the rate constants were determined as a function of solvent viscosity. For radical initiators decomposing by one-bond homolysis Pryor and Smith have shown that the rate of decomposition decreases with increasing viscosity, whereas the rates for initiators decomposing by two-bond homolysis are independent of viscosity.[3] Our results clearly show that the rates of decomposition for all the peresters are viscosity independent and thus the peresters are decomposing by two-bond homolysis (Figure 1).

TABLE II

PERESTER RATE CONSTANTS AS A FUNCTION OF SUBSTITUENT, SOLVENT, AND TEMPERATURE[a]

Substituent	Solvent	Temp,[a] °C	k, sec$^{-1\,b}$ × 10^{-4}
H	Dodecane	67.0	7.13
H	Dodecane	60.0	3.00
H	Dodecane	50.00	0.877
H	Benzene	50.00	2.18
H	Acetonitrile	50.0	3.08
Cl	Octane	67.0	5.95
Cl	Octane	60.0	2.65
Cl	Octane	50.00	0.810
Cl	Dodecane	67.0	6.36
Cl	Dodecane	60.0	2.68
Cl	Dodecane	50.0	0.798
Cl	Hexadecane	67.0	5.96
Cl	Hexadecane	60.0	2.56
Cl	Hexadecane	50.0	0.800
Cl	Benzene	50.0	2.03
Cl	Acetonitrile	50.0	2.55
CH_3	Octane	60.0	5.43
CH_3	Dodecane	67.0	13.20
CH_3	Dodecane	60.0	5.58
CH_3	Dodecane	50.0	1.90
CH_3	Benzene	50.0	3.85
CH_3	Acetonitrile	50.0	6.00
CH_3O	Octane	50.0	4.18
CH_3O	Dodecane	57.0	10.28
CH_3O	Dodecane	50.0	4.21
CH_3O	Dodecane	40.0	1.49
CH_3O	Benzene	50.0	9.96
CH_3O	Acetonitrile	50.0	16.75
NO_2	Octane	67.0	1.98
NO_2	Dodecane	67.0	2.03
NO_2	Dodecane	60.0	0.927
NO_2	Dodecane	50.0	0.263
NO_2	Hexadecane	67.0	2.00
NO_2	Benzene	50.0	0.640
NO_2	Acetonitrile	50.0	0.750

[a] Temperature control was accurate to ±0.05° or better for all runs. [b] All rate constants are the average of at least three runs and generally the average of four.

TABLE III

ACTIVATION PARAMETERS FOR SUBSTITUTED *tert*-BUTYLPEROXY α-PHENYLISOBUTYRATES IN *n*-DODECANE

Registry no.	Substituent	ΔH^*,[a] kcal/mol	ΔS^*,[a] eu
40919-05-9	p-CH_3O	22.2 ± 0.6	−5.3 ± 1.0
40919-06-0	p-CH_3	24.0 ± 0.6	−1.6 ± 1.0
24161-29-3	H	26.1 ± 0.3	3.5 ± 0.5
40919-08-2	p-Cl	25.8 ± 0.3	2.5 ± 0.5
40919-09-3	p-NO_2	25.1 ± 0.3	−1.8 ± 0.5

[a] The error limits reported are the standard errors.

Generally the rates of radical formation reactions are correlated with either σ or $\sigma_p{}^+$.[3] Since recently the relative rates of hydrogen abstraction from substituted toluenes were correlated with $\sigma_p{}^-$, we have also attempted to correlate our data with this parameter.[7] The Hammett plot for our peresters *vs.* σ, $\sigma_p{}^+$, and $\sigma_p{}^-$ is given in Figure 2, and the results of least squares analysis are summarized in Table IV.

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[10] (a) R. C. Lamb and J. G. Pacifici, *J. Amer. Chem. Soc.*, **86**, 914 (1964); (b) R. C. Lamb and J. R. Sanderson, *ibid.*, **91**, 5034 (1969).

[11] P. D. Bartlett and T. Funahashi, *J. Amer. Chem. Soc.*, **84**, 2596 (1962).

[12] α,γ-Bis(diphenylene)-β-phenylallyl, also known as Koelsch's radical.

[13] Program was written by Dr. R. C. Johnson, Emory University.

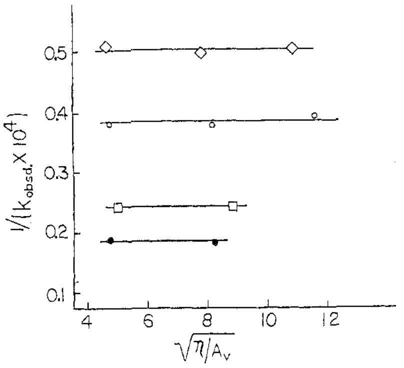

Figure 1.—The effect of viscosity on the rate of perester decomposition.

TABLE IV

TABLE OF RESULTS FROM HAMMETT PLOTS[a]

Solvent	$\rho + SE^b$	σ values used	Intercept	Correlation coefficient
Dodecane	-0.78 ± 0.04	Plus	0.06	-0.996
Dodecane	-1.02 ± 0.21	Normal	0.21	-0.94
Dodecane	-0.67 ± 0.20	Minus	0.24	-0.88
Benzene	-0.75 ± 0.03	Plus	0.04	-0.997
Acetonitrile	-0.91 ± 0.06	Plus	0.05	-0.994

[a] Rate data was taken at 50°. [b] The error limits reported are the standard errors. The 95% confidence limits can be obtained by multiplying the standard error by 2.10 (obtained from a Table for t Distribution with $\phi = 18$).

Hammett correlation of the rates with σ and σ_p^- is significantly poorer than for σ_p^+. It has been suggested that the correlation with σ_p^- is improved by not including points for substituents that are strongly electron donating, *e.g.*, the *p*-methoxy group.[7] The Hammett plot for perester decomposition *vs.* σ_p^- omitting the *p*-methoxy group does give an improved correlation, but one should question this procedure. It is not clear why *p*-methoxy groups should not be considered. The original σ_p^- values determined for phenols included these substituents.[14] Recent studies of the ionization of phenols indicate that the σ_p^- value for the *p*-methoxy group may be somewhat smaller than the σ value ($\sigma_p^- = -0.20$, $\sigma = -0.27$).[14] Nonetheless, a σ_p^- value for the *p*-methoxy group would appear to be reasonably well defined.

The improved correlation with σ_p^+ and the negative sign for ρ indicate a partial positive charge formation on the cumyl radical in the transition state. The absolute value of ρ (0.78) for substituted *tert*-butylperoxy α-phenylisobutyrates is smaller than that for substituted *tert*-butylperoxy phenylacetates ($\rho = -1.2$).[4] A smaller absolute value is expected for two reasons. First, the added two methyl groups should stabilize the partial positive charge in the transition state, leaving less charge to be stabilized by the substituents. Second, the two methyl groups may sterically accelerate the reaction, making the transition state occur earlier along the reaction coordinate and consequently less sensitive to substituents.[6] At the present time we know of no way of deciding between these two modes of action.

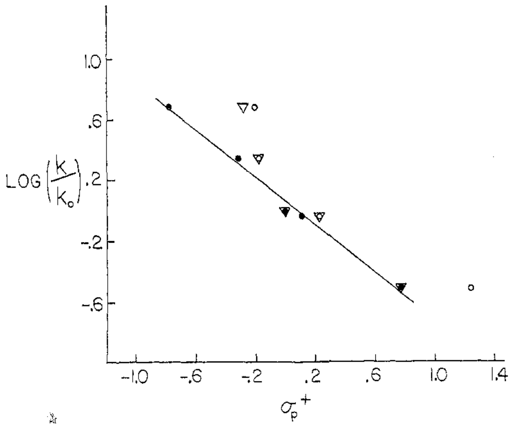

Figure 2.—Hammett plot for perester decomposition in dodecane at 50°: σ^+ values, ●; σ values, ▽; σ^- values, ○.

One can now ask what the value of ρ means in terms of how much partial charge is formed in the transition state for perester decomposition. The problem reduces to finding a suitable standard reaction. Solvolysis reactions would be an obvious first choice, but these reactions only occur in solvents capable of strongly stabilizing the ions. What is required is an ionization reaction that occurs in nonpolar solvents. A suitable choice is the gas-phase ionization of benzyl radicals.[15] For this reaction there is no solvent to stabilize the charge and no gegenion; all the stabilization must come from the substituent. The major problem with this choice of a standard reaction is that the substituents also may stabilize the radicals being ionized. Thus one must first be convinced that radical stabilization is of minor importance in determining the ionization potentials of the benzyl radicals. Three different arguments can be used to show that the effect of substituents on the stability of benzyl radicals is small relative to the effect of substituents on the stability of benzyl carbonium ions. First, electron spin resonance spectra of α-substituted ethyl radicals show that α substituents remove only a small fraction of the spin density from the radical site.[16] The α-methoxy group was the most effective of the substituents examined, and it removed only approximately 17% of the spin density from the radical site. Second, the decomposition of para-substituted azocumenes shows only small variation in the rate of decomposition with substituent.[17] Third, differences in bond dissociation energies for substituted toluenes are so small that the variation with substituent is within experimental error.[18] If radical stability contributes negligibly to the substituent effect in the gas-phase ionization of benzyl radicals, one finds that the decomposition of substituted *tert*-butylperoxy phenylisobutyrates is approximately 0.042 as sensitive to substituents as the gas-phase ionization of benzyl radicals.[19] Comparison of the decom-

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(14) R. W. Taft, Jr., *J. Amer. Chem. Soc.*, **79**, 1045 (1957); L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill, New York, N. Y., 1970, Chapter 11; H. H. Jaffe, *Chem. Rev.*, **53**, 191 (1963); R. W. Taft, Jr., and I. C. Lewis, *J. Amer. Chem. Soc.*, **80**, 2436 (1958).

(15) A. G. Harrison, P. Kenarle, and F. P. Lossing, *J. Amer. Chem. Soc.*, **83**, 777 (1961).

(16) H. Fischer, *Z. Naturforsch. A*, **20**, 428 (1965); R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **39**, 2147 (1963); H. Fischer, *Z. Naturforsch. A*, **19**, 866 (1964); W. T. Dixon and R. O. C. Norman, *J. Chem. Soc.*, 3119 (1963), 3635 (1964).

(17) J. R. Shelton, C. K. Liang, and P. Kovacic, *J. Amer. Chem. Soc.*, **90**, 354 (1968).

(18) M. Szwarc, *Chem. Rev.*, **47**, 75 (1950).

(19) $\rho_{\text{perester}}/\rho_{\text{ionization}} = -0.78/-19.2 = 0.042$.

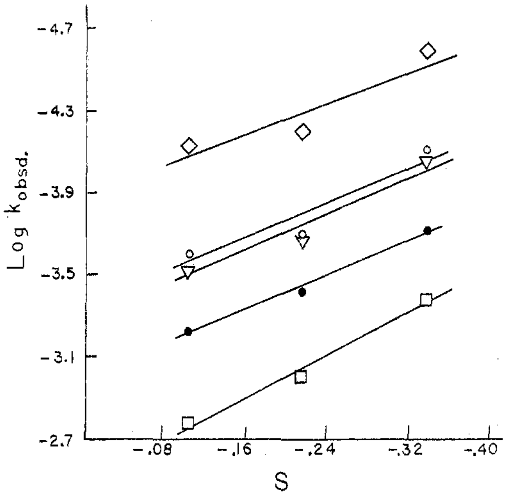

Figure 3.—Plot of log k_{obsd} *vs.* Brownstein's solvent polarity parameter *S:* ◇, *tert*-butylperoxy α-(*p*-nitrophenyl)isobutyrate; ○, *tert*-butylperoxy α-(*p*-chlorophenyl)isobutyrate; ▽, *tert*-butylperoxy α-phenylisobutyrate; ●, *tert*-butylperoxy α-(*p*-tolyl)isobutyrate; □, *tert*-butylperoxy α-(*p*-methoxyphenyl)-isobutyrate.

position of *tert*-butylperoxy phenylacetates to the ionization of benzyl radicals gives a relative sensitivity of 0.063. Thus the amount of partial charge formed in the transition state for perester decomposition is small.

To try to confirm that the ratio of ρ values for the perester decomposition and the ionization of benzyl radicals reflects partial charge formation in the transition state, a comparison was made between the sensitivity of a heterolysis reaction and perester decomposition to changes in solvent polarity. Several scales for measuring the sensitivity of a reaction to changes in solvent polarity are available.[20] However, most of these scales are limited to polar protic solvents and cannot be readily extended to nonpolar aprotic solvents. One system that allows correlation between very polar and nonpolar solvents is the Brownstein scale based on Kosower *Z* values.[21] Although this scale has been criticized because it cannot be related to an exact model process, it is nonetheless a scale that allows one to compare the sensitivity of solvolysis reactions in polar protic media and the sensitivity of perester decompositions in nonpolar aprotic media to changes in solvent polarity. The Brownstein plots for substituted *tert*-butylperoxy α-phenylisobutyrates are given in Figure 3. The *R* values for all the peresters are approximately the same, 2.1–2.6. The plots for the *p*-nitro, *p*-chloro, and unsubstituted peresters show a slight upward curvature; however, the plots for the *p*-methyl and the *p*-methoxy peresters are quite good straight lines. The slope, *R*, is a measure of the sensitivity of the reaction to changes in solvent polarity. *R* values range from 36 for the solvolysis of *tert*-butyl chloride to −3.5 for the keto–enol equilibrium of ethyl acetoacetate.[21] The solvolysis of 1-phenylethyl chloride has an *R* value of 29.4;[21] the decomposition of *tert*-butylperoxy α-phenylisobutyrates is about 2.3. The ratio of the two *R* values is 0.078.

A comparison of the sensitivity to substituents (0.042) with the sensitivity to solvent change (0.078) shows that both of these criteria for charge formation are in the same direction and of approximately the same magnitude. The fact that the ratios are not the same is undoubtedly due to the fact that the ideal standard reactions are not available for comparison. However, the major point remains that both criteria for partial charge formation are in agreement, adding confirmatory evidence that the response of perester decomposition to substituents is a response to partial charge formation in the transition state and not a response to changes in radical stability.

The effect of changing the solvent on the Hammett ρ value is just outside experimental error. The higher ρ in acetonitrile may indicate a more polar transition state upon which the substituents can exert a greater influence. This result is the opposite to the effect one would expect for an ionic reaction. For ionic reactions, as one increases the polarity of the solvent the ρ value generally decreases because the more polar solvent is better able to stabilize the charge. However, where only a partial charge develops in the transition state the increased solvent polarity may cause increased polar character in the transition state, making the reaction more sensitive to substituents.

Bartlett and Ruchardt in their study of the decomposition of substituted *tert*-butylperoxy phenylacetates found that the *p*-nitro perester decomposed faster than expected based on the Hammett plot.[4] Three tentative explanations have since been offered for the faster rate: decomposition of the perester partly by a Criegee rearrangement,[4] a shift in the mechanism to one-bond homolysis,[8] and an increase in the rate owing to increasing polar character and solvation of the transition state for peresters with strongly electron-donating substituents.[9]

The change of solvent to acetonitrile should greatly increase the rate of the Criegee rearrangement relative to homolysis.[22] Since the *tert*-butylperoxy α-(*p*-nitrophenyl)isobutyrate fits the Hammett plot in dodecane, benzene, and acetonitrile, Criegee rearrangement cannot be a significant pathway.

If increasing polar character and solvation of the transition state were significant factors, the peresters with strongly electron-donating substituents should be strongly accelerated, especially in acetonitrile, and give curved Hammett plots. Since *tert*-butylperoxy α-(*p*-methoxyphenyl)isobutyrate fits the Hammett plot, increased polar character and solvation of the transition state are not important.

Pryor and Smith have shown that the rate of decomposition of *tert*-butylperoxy (*p*-nitrophenyl)-acetate increases with decreasing solvent viscosity.[8] Two possible explanations were offered to explain the solvent dependence of the rate. First, the homolysis step in the perester decomposition was solvent dependent. Second, the change in viscosity of the solvent was changing the amount of return from the initial radical cage in which only the peroxide bond had been broken. Since the rate of decomposition of *tert*-butylperoxy α-(*p*-nitrophenyl)isobutyrate is independent of solvent (for *n*-alkanes), the homolysis

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(20) E. M. Kosower, "An Introduction to Physical Organic Chemistry," Wiley, New York, N. Y., 1968, Chapter 2.6.

(21) S. Brownstein, *Can. J. Chem.*, **38**, 1590 (1960).

(22) R. Criegee and R. Kaspar, *Justus Liebigs Ann. Chem.*, **560**, 127 (1948); H. L. Goering and A. L. Olson, *J. Amer. Chem. Soc.*, **75**, 5853 (1953).

step for this perester is not solvent dependent. One must conclude that the effect of changing solvents (n-alkanes) on the rate of decomposition of the *tert*-butylperoxy (p-nitrophenyl)acetate is a result of return from the cage from one-bond homolysis.

Experimental Section

Melting points were taken on a Thomas-Hoover melting point apparatus and are corrected. Infrared spectra were taken with a Perkin-Elmer Model 257 grating spectrophotometer. The nuclear magnetic resonance spectra were obtained with a Varian T-60, a Varian A-60, or a JEOL MH100 spectrophotometer using tetramethylsilane as an internal standard.

Benzene and the alkane solvents were purified by washing with concentrated sulfuric acid until the acid layer was clear, followed by washing with water, saturated sodium bicarbonate solution, and water until neutral, dried with magnesium sulfate, filtered, distilled from sodium, and finally redistilled from crude galvinoxyl. Vacuum distillation was used for the alkanes.

Galvinoxyl was prepared by the method of Coppinger[23] using the modification of Bartlett and Funahashi.[11] The crude material was recrystallized from pentane under nitrogen. Purity was checked by measuring the absorbance at 772 nm in benzene (ϵ 607).

tert-**Butyl hydroperoxide** (Lucidol) was purified by repeated vacuum distillation until the material had the literature value of the refractive index (n^{25}D 1.3986)[24] and showed no impurities in the nmr.

Sodium *tert*-**butylperoxide** was prepared by the method of Lorand and Bartlett.[25]

α-**Phenylisobutyric acid** was prepared by the method of Campaigne and Maulding,[26] crude yield 80%, mp 79–80° (lit.[27] mp 80–81°).

α-**Phenylisobutyryl chloride** was prepared by refluxing 5.0 g of the acid in 25 ml of thionyl chloride overnight followed by removal of the excess thionyl chloride by rotary evaporation and vacuum distillation of the crude product, yield 4.96 g (89%), bp 60–61° (0.7 mm) [lit.[28] bp 109° (13 mm)].

tert-**Butylperoxy** α-**phenylisobutyrate** was prepared by the method of Herkes, Friedman, and Bartlett.[29] The crude perester, obtained in 60% yield, was purified by dissolving the oil in 20 ml of pentane and passing the solution through a 1 × 10 cm water-cooled column of Woelm activity I alumina. The pentane was removed by rotary evaporation to yield a clear, colorless oil: ir (CCl_4) 1770 (C=O); nmr (CCl_4) δ 7.29 (m, 5), 1.60 (s, 6), and 1.12 (s, 9).

Anal. Calcd for $C_{14}H_{20}O_3$: C, 71.16; H, 8.53. Found: C, 71.33; H, 8.51.

α-(p-**Chlorophenyl**)**isobutyronitrile** was prepared by the procedure of Julia and Baillarge,[30] yield 62%, bp 80–84° (0.35 mm) [lit.[30] bp 142–145° (18 mm)].

α-(p-**Chlorophenyl**)**isobutyric acid** was prepared by hydrolyzing 10.7 g of the nitrile in 30 ml of concentrated sulfuric acid and 28 ml of water. The crude acid was recrystallized from a hexane–chloroform mixture (2:1) to give 7.9 g (68%) of white crystals, mp 125–126° (lit.[30] mp 124°).

α-(p-**Chlorophenyl**)**isobutyryl chloride** was prepared by refluxing 8.36 g (0.042 mol) of the acid in 50 ml of thionyl chloride for 7 hr, followed by removal of excess thionyl chloride by rotary evaporation and vacuum distillation of the crude product, bp 82° (0.25 mm), yield 8.58 g (94%).

tert-**Butylperoxy** α-(p-**chlorophenyl**)**isobutyrate** was prepared by adding dropwise 11.5 g (0.146 mol) of pyridine to 8.58 g (0.0395 mol) of the acid chloride and 10.16 g (0.114 mol) of *tert*-butyl hydroperoxide in 25 ml of anhydrous ether. The reaction mixture was kept at 0° and stirred with a magnetic stirrer. Stirring was continued for 30 min after addition was complete; the flask was then placed in a refrigerator for 4 days. The reaction mixture was then poured into 40 ml of pentane and 60 ml of ice water, and the layers were separated. The pentane layer was washed with ice-cold 10% H_2SO_4, water, ice-cold 10% KOH, and water until neutral and dried ($MgSO_4$), and the solvent was removed by rotary evaporation. The resulting oil, 8.9 g (83%), was chromatographed on a water-cooled 1 × 8 cm alumina column with pentane to remove carbonyl-containing impurities. Other minor impurities, visible in the nmr, were removed by low-temperature recrystallization from pentane: ir (neat) 1767 cm^{-1} (C=O); nmr (CCl_4) δ 7.34 (s, 4), 1.56 (s, 6), and 1.17 (s, 9).

Anal. Calcd for $C_{14}H_{19}ClO_3$: C, 62.10; H, 7.07; Cl, 13.10. Found: C, 62.08; H, 7.13; Cl, 13.16.

α-(p-**Nitrophenyl**)**isobutyric acid** was prepared by the method of Overberger and Gainer.[31] The crude product was recrystallized from toluene, mp 129–131° (lit.[31] mp 132–133°); the final yield was 39% after four recrystallizations.

α-(p-**Nitrophenyl**)**isobutyryl chloride** was prepared by dissolving 4.2 g of the acid in 50 ml of thionyl chloride and stirring overnight. The reaction mixture was then refluxed for 3 hr, and the excess thionyl chloride was removed by rotary evaporation. The crude acid chloride was recrystallized from petroleum ether (bp 30–60°) to give 3.1 g (68%) of white needles, mp 56–57° (lit.[32] mp 55–56°).

tert-**Butylperoxy** α-(p-**nitrophenyl**)**isobutyrate** was prepared by the same procedure as that for the unsubstituted perester, using 2.84 g (0.012 mol) of acid chloride, 3.24 g (0.036 mol) of *tert*-butyl hydroperoxide, and 3.65 g (0.046 mol) of pyridine. Work-up and purification were also the same, yielding a white solid: ir (CCl_4) 1764 cm^{-1} (C=O); nmr (CCl_4) δ 8.27–7.46 (m, 4), 1.65 (s, 6), and 1.18 (s, 9).

Anal. Calcd for $C_{14}H_{19}NO_5$: C, 59.77; H, 6.81; N, 4.98. Found: C, 59.63; H, 6.96; N, 5.00.

α-(p-**Methoxyphenyl**)**isobutyric acid** was prepared by the method of Hauser, Kenyon, and Kaiser.[33] The crude product was recrystallized from hexane and then from water, mp 88–89° (lit.[34] mp 89–90°).

α-(p-**Methoxyphenyl**)**isobutyryl chloride**[35] was prepared by dissolving 4.0 g (0.02 mol) of the acid in 50 ml of dry benzene and adding dropwise 13.1 g (0.10 mol) of oxalyl chloride dissolved in 20 ml of benzene. When the initial reaction subsided, the mixture was refluxed for 5 hr. The benzene and excess oxalyl chloride were removed by distillation, and the crude acid chloride was distilled to give 3.87 g (84%) of a clear liquid, bp 95–96° (0.5 mm).

tert-**Butylperoxy** α-(p-**Methoxyphenyl**)**isobutyrate**.—This perester has a half-life of about 30 min at 50°; hence it must be kept cold during synthesis, work-up, and purification to prevent its decomposition. To 1.5 g (0.0135 mol) of sodium *tert*-butylperoxide suspended in 50 ml of methylene chloride was added 1.15 g (0.0063 mol) of the acid chloride in 5 ml of methylene chloride. The reaction mixture was stirred with a magnetic stirrer and kept in a Dry Ice–carbon tetrachloride bath for 5 hr. The flask was then taken into a refrigerated room (approximately 4°) and worked up as follows. The reaction mixture was poured into 40 ml of pentane and 60 ml of ice water. The pentane layer was extracted five times with cold 10% KOH and five times with ice water and dried ($MgSO_4$). The solvent was removed by rotary evaporation, and the resulting oil was dissolved in 10 ml of pentane and passed through a 1 × 2 cm Florisil column. The pentane was removed by rotary evaporation to yield a clear, colorless oil: ir (neat) 1764 cm^{-1} (C=O); nmr (CCl_4) δ 7.52–6.83 (m, 4), 3.83 (s, 3), 1.60 (s, 6), and 1.18 (s, 9). This nmr was obtained on a Varian A-60 spectrophotometer at −5°.

Anal. Calcd for $C_{15}H_{22}O_4$: C, 67.64; H, 8.33. Found: C, 67.78; H, 8.37.

p-**Methylphenylacetonitrile**.—In a 3-l. three-neck round-bottom flask fitted with a mechanical stirrer and reflux condenser were placed 1600 ml of 50% ethanol, 116 g (1.78 mol) of potassium cyanide, and 250 g (1.78 mol) of p-methylbenzyl chloride. The

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mixture was stirred and refluxed overnight. The layers were separated, the water layer was saturated with sodium chloride and extracted with ether, and the ether was added to the organic layer. The solvent was removed by rotary evaporation, the crude product was taken up in fresh ether, dried ($MgSO_4$), and filtered, and the ether was removed by rotary evaporation. The crude product was distilled on a spinning band column to yield 99 g (42%) of *p*-methylphenylacetonitrile.

α-(*p*-Tolyl)isobutyronitrile.—In a three-neck, 1-l. round-bottom flask fitted with a reflux condenser and glass stoppers were placed 200 ml of benzene and 300 ml of *tert*-butyl alcohol, both dried by distillation from sodium. To this mixture was added 15.6 g (0.4 mol) of potassium metal piecewise, while stirring with a magnetic stirrer. When reaction was complete the solution was cooled to 10°.

In a separate three-neck, 1-l. round-bottom flask fitted with reflux condenser, nitrogen inlet, mecanical stirrer, and addition funnel were placed 26.1 g (0.2 mol) of the nitrile, 85.2 g (0.6 mol) of methyl iodide, and 50 ml of benzene. The alkoxide solution was added dropwise with stirring. The reaction mixture was kept cold for 5 hr, then allowed to warm to room temperature. Stirring was continued overnight, followed by refluxing for 3 hr. The reaction mixture was poured into water and the layers were separated. The water was saturated with sodium chloride and extracted with ether, and the ether was added to the organic layer. After the organic layer was dried ($MgSO_4$) the solvent was removed by rotary evaporation. The crude product was vacuum distilled to yield 26.9 g of material, bp 66–70° (0.25 mm). Analysis of the material by glpc and nmr showed that it was a 50:50 mixture of mono- and dimethylated nitriles. This product mixture was remethylated by the same procedure, using 7.8 g of potassium metal and 42.6 g of methyl iodide.

α-(*p*-Tolyl)isobutyric Acid.—In a 100-ml round-bottom flask were placed 12.0 g (0.075 mol) of α-(*p*-tolyl)isobutyronitrile, 12 ml of concentrated sulfuric acid, 12 ml of glacial acetic acid, and 12 ml of water. The mixture was refluxed for 6 hr, allowed to cool, and poured onto 100 g of ice–water. The product was collected by extraction with chloroform and dried ($MgSO_4$), and the chloroform was removed by rotary evaporation. The crude product was repeatedly recrystallized from hexane to give 4.3 g (32%) of white crystals, mp 81.5–82° (lit.[36] mp 82°).

α-(*p*-Tolyl)isobutyryl chloride was prepared by dissolving 4.0 g (0.022 mol) of the acid in 25 ml of thionyl chloride and refluxing for 6 hr. The excess thionyl chloride was removed by rotary evaporation and the crude product was vacuum distilled to give 3.77 g (86%) of clear liquid, bp 79–80° (0.65) mm.

***tert*-Butylperoxy α-(*p*-tolyl)isobutyrate** was prepared from 1.0 g of the acid chloride and 1.7 g of sodium *tert*-butylperoxide by the method previously described for the *p*-methoxy perester. Work-up and purification by the same method yielded a white solid (60%): ir (methylene chloride) 1761 cm^{-1} (C=O); nmr (CCl_4) δ 7.18 (m, 4), 2.34 (s, 3), 1.56 (s, 6), and 1.13 (s, 9).

Anal: Calcd for $C_{15}H_{22}O_3$: C, 71.97; H, 8.86. Found: C, 71.96; H, 8.91.

Procedure for Excess Scavenger Experiments.—A perester stock solution was prepared by weighing out approximately 20–30 mg of perester in a volumetric flask on a Mettler H20 balance. Kinetic samples were prepared by weighing out about 7 mg of galvinoxyl in a volumetric flask, adding the desired volume of perester stock solution, and diluting to the mark.

Cells used for the thermal decompositions were made from 1-cm-square Pyrex tubing, frosted on two opposite sides and polished on the other two. The cells were fitted with a male 10/30 joint for degassing and a constriction in the neck for sealing off.

The cells were filled with sample solutions using syringes with long hypodermic needles. The cells were degassed with at least five freeze–pump–thaw cycles with a final pressure less than 0.005 mm. Appropriate blanks were also prepared containing galvinoxyl but no perester.

The absorbance was read on a Cary 14 spectrophotometer at 764 nm (ϵ 540) for the alkane solvents, 769 nm (ϵ 607) in benzene, and 765 nm (ϵ 726) in acetonitrile. The cells were then wrapped in aluminum foil and placed in a thermostated oil bath. They were removed periodically and quenched in ice water, and the absorbance was recorded. This procedure was altered for some of the runs with the *p*-methoxy perester owing to its comparatively rapid decomposition. For these runs, the cell compartment of the spectrophotometer was thermostated at 50.0° ± 0.1°, and the absorbance was recorded continuously.

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Registry No.—Galvinoxyl, 2370-18-5; BDPA, 2152-02-5; *tert*-butyl hydroperoxide, 75-91-2; sodium *tert*-butylperoxide, 13250-54-9; α-(*p*-chlorophenyl)isobutyric acid, 6258-30-6; α-(*p*-chlorophenyl)isobutyryl chloride, 40919-11-7; α-(*p*-nitrophenyl)-isobutyryl chloride, 40919-12-8; α-(*p*-methoxyphenyl)isobutyric acid, 2955-46-6; α-(*p*-methoxyphenyl)isobutyryl chloride, 40919-14-0; *p*-methylphenylacetonitrile, 2947-61-7; α-(*p*-tolyl)isobutyronitrile, 40119-34-4; α-(*p*-tolyl)isobutyric acid, 20430-18-6; α-(*p*-tolyl)isobutyryl chloride, 40919-17-3.

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