Articles

Thermal Decomposition of *tert*-Butyl 1-Arylcycloalkanepercarboxylates

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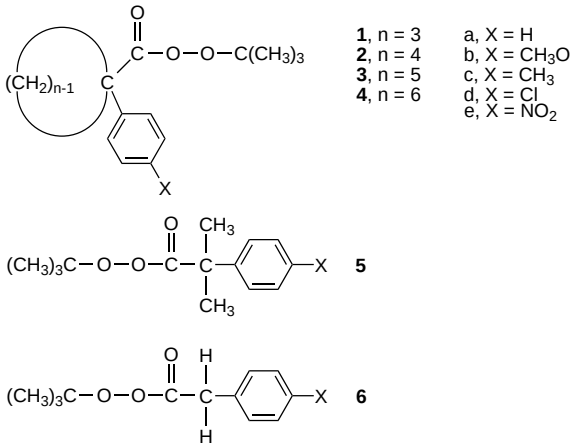
A series of *tert*-butyl 1-arylcycloalkyl peresters was prepared, and the rate constants for the peresters' thermal decomposition were measured at several temperatures. The decomposition rates and aryl-substituent effects on the decomposition rates for the three series of peresters are remarkably similar to each other and to the acyclic α,α-dimethylbenzyl analogue previously investigated. The magnitude of the activation parameters for the rates of thermolysis of the alicyclic peresters and the solvent viscosity effects on these rates suggest that the 1-arylcyclobutyl (**2**), -cyclopentyl (**3**), and -cyclohexyl (**4**) peresters undergo thermal decomposition primarily by the concerted, two-bond-cleavage mechanism and that the 1-arylcyclopropyl peresters (**1**) undergo thermolysis primarily by the stepwise mechanism.

Introduction

We are interested in the effects of ring size on the rates of formation and stability of alicyclic free radicals.[1,2] The radical-forming thermolyses of the 1-arylcycloalkyl peresters of this study (Chart 1) might allow a chance to investigate ring size effects on the relative electronic demands of the transition states of these reactions and (by inference) the relative stabilities of the resulting free radicals. In comparison to the substituent effects on the decomposition of the cumyl peresters (**5**)[3] and phenylacetyl peresters (**6**)[4] of these series, we would not a priori predict similar substituent effects or rates among the various cyclic and acyclic perester systems.

The present series of benzyl-radical producing reactions might be compared with similar benzyl-radical forming reactions, the thermal decomposition of phenyl-substituted symmetric bisalkyl diazenes,[5−8] and the solvolysis of 1-aryl cyclic and polycyclic chlorides.[9] We also want to compare the various tests of perester decomposition mechanism used for the 1-H cycloalkyl perester series reported in an earlier publication,[2] to see if subtle changes in mechanism with the size of the alicyclic rings for the 1-aryl alicyclic perester series might be detected.

Chart 1



Results and Discussion

The rate constants for the thermal decomposition of peresters **2**, **3**, and **4** in 2,2,4-trimethylpentane are given in Table 1. In Table 2 are given the rate constants of the same peresters in paraffin solvents more viscous than 2,2,4-trimethylpentane. The errors reported for the rate constants are the standard deviations ($n - 1$) from the average. Each rate constant is based on kinetic measurements of at least two different prepared batches of perester and two different batches of solvent. The initial concentrations of the peresters were all around 0.02 M. Styrene (0.10−0.20 M) was added to discourage any radical induced decomposition.[2] The first-order rate plots were linear in all cases over the entire measured course of the reaction (three to four half-lives). Each kinetic run consisted of 12−18 individual points. We attempted to

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Table 1. Rate Constants for Thermolysis of Peresters in 2,2,4-Trimethylpentane Solvent

	$k \times 10^4$ (s^{-1})[a]		
perester	61.6 °C	52.3 °C	43.5 °C
2a	2.46 ± 0.10	0.769 ± 0.027	
2b	11.99 ± 0.28	3.95 ± 0.08	
2c		3.58 ± 0.27	1.16 ± 0.02
2d	1.97 ± 0.01	0.614 ± 0.005	
2e[b]	0.627 ± 0.015	0.188 ± 0.004	
3a	3.51 ± 0.18	1.184 ± 0.055	
3b	16.11 ± 0.13	5.76 ± 0.09	
3c	7.02 ± 0.28	2.43 ± 0.07	
3d	3.20 ± 0.10	1.124 ± 0.025	
3e	0.972 ± 0.012	0.299 ± 0.002	
4a	12.18 ± 0.14	3.91 ± 0.02	1.27 ± 0.04
4c	25.6 ± 0.2	8.75 ± 0.21	2.89 ± 0.03
4d	10.75 ± 0.26	3.40 ± 0.01	1.22 ± 0.01
4e	4.07 ± 0.18	1.24 ± 0.03	0.436 ± 0.016

[a] Errors are standard deviations from the average. At least four kinetic runs for each perester under each condition were done. Initial concentrations of peresters were 0.01−0.02 M. Initial concentrations of styrene were 0.10−0.20 M. [b] $k = 2.02(\pm 0.02) \times 10^{-4}$ s^{-1} at 71.4 °C for perester **2e**.

Table 2. Rate Constants for Thermolysis of Peresters in Viscous Paraffin Solvents

perester	solvent[a]	temp, °C	$k \times 10^4$ (s^{-1})[b]
2a	C-12	52.3	0.789 ± 0.010
2a	C-16	52.3	0.880 ± 0.028
2e	C-16	71.4	2.11 ± 0.02
2e	C-16	61.6	0.645 ± 0.025
2e	C-16	52.3	0.188 ± 0.007
3e	C-16	52.3	1.020 ± 0.009
3e	C-16	43.5	0.324 ± 0.008
4e	C-16	61.6	3.97 ± 0.05
4e	C-16	52.3	1.42 ± 0.02

[a] For Tables 2, 4, 5 and 6, C-8 refers to 2,2,4-trimethylpentane, C-12 refers to dodecane and C-16 refers to hexadecane. [b] See footnote *a*, Table 1.

Table 3. Activation Parameters for Thermolysis of Peresters[a]

perester	$\Delta H^{\ddagger}$ [b,c]	$\Delta S^{\ddagger}$ [b,d]	perester	$\Delta H^{\ddagger}$ [b,c]	$\Delta S^{\ddagger}$ [b,d]
1a	32.8 ± 1.6	7.3 ± 4.0	**3a**	24.7 ± 2.3	1.2 ± 7.1
1b	31.9 ± 0.5	6.8 ± 1.3	**3b**	23.3 ± 0.6	0.1 ± 1.7
1c	32.4 ± 1.0	6.8 ± 2.7	**3c**	24.1 ± 1.6	0.7 ± 5.0
1d	32.0 ± 0.1	5.3 ± 0.2	**3d**	23.7 ± 1.2	−1.9 ± 3.9
1e	34.4 ± 2.6	11.0 ± 6.7	**3e**	26.8 ± 0.4	5.3 ± 1.4
2a	26.4 ± 1.8	3.7 ± 5.3	**3e**[e]	26.1 ± 0.8	3.1 ± 2.4
2b	25.2 ± 1.0	3.2 ± 3.1	**4a**	25.7 ± 0.5	4.6 ± 1.5
2c	25.6 ± 2.1	1.9 ± 6.4	**4c**	24.8 ± 0.2	3.3 ± 0.6
2d	26.4 ± 0.4	3.3 ± 1.0	**4d**	24.7 ± 0.4	1.3 ± 1.2
2e	27.0 ± 0.2	2.8 ± 0.5	**4e**	25.4 ± 0.9	1.4 ± 2.9
2e[e]	27.6 ± 0.3	4.3 ± 0.7	**4e**[e]	23.3 ± 0.6	−4.8 ± 1.9

[a] 2,2,4-Trimethylpentane solvent, unless otherwise indicated. [b] Errors are propagated from the standard errors of the average rate constants. [C] In kcal/mol. [d] In cal/deg mol. [e] Hexadecane solvent.

be consistent with the types of *p*-phenyl substituents for each perester series. However, the accelerated rates of decomposition of perester **3b** (one neat sample exploding at 30 °C) discouraged us from attempting the synthesis of perester **4b**.

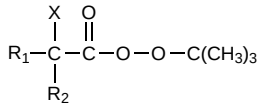
The activation parameters for the various cyclic peresters are given in Table 3. Included for comparison are the values for the thermolysis of the 1-arylcyclopropyl peresters reported earlier.[1] The errors for the activation parameters are propagated from the standard errors of the average rate constants.[9] A direct comparison of the rates of thermal decomposition of several peresters in isooctane versus more viscous solvents is made in Table 4. In column 4 of Table 4 are compared the absolute viscosities as calculated from an Arrhenius relationship.[4a]

Table 4. Solvent Viscosity Effects on Perester Thermolysis Rate Constants

perester	temp, °C	thick solvent[a]	η(th)/η(C-8)[b]	k(C-8)/k(th)[c]
1a	113.0	C-12	2.43	1.03 ± 0.01
1a	113.0	C-16	4.12	1.05 ± 0.01
1e	113.0	C-16	4.12	1.07 ± 0.04
2a	52.3	C-12	2.90	0.97 ± 0.05
2a	52.3	C-16	5.47	0.87 ± 0.06
2e	71.4	C-16	4.95	0.96 ± 0.02
2e	61.6	C-16	5.20	0.97 ± 0.06
2e	52.3	C-16	5.47	1.00 ± 0.06
3e	52.3	C-16	5.47	0.95 ± 0.02
3e	43.5	C-16	5.75	0.92 ± 0.03
4e	61.6	C-16	5.20	1.03 ± 0.06
4e	52.3	C-16	5.47	0.87 ± 0.03

[a] See footnote *a*, Table 2. [b] Calculated from $\eta = A_v \exp(E_v/RT)$ from values of A_v and E_v given in ref 4a. Values of absolute viscosity of isooctane at 113.0 °C are estimations, since this temperature is above the boiling point of isooctane. "th" refers to the solvents thicker than 2,2,4-trimethylpentane. [c] Errors are propagated from the standard deviation of the average rate constants.

Table 5. Effect of Substitution of Phenyl for Hydrogen on Rates of Decomposition of *tert*-Butyl Peracetates



		k(X=Ph)/k(X=H),[a]	
R_1	R_2	at 52.3 °C	solvent[b]
$-(CH_2)_2-$		(1.45)[c]	C-8
$-(CH_2)_3-$		3230	C-8
$-(CH_2)_4-$		4950	C-8
$-(CH_2)_5-$		1820	C-8
H	H	3190[d]	chlorobenzene
CH_3	CH_3	562[e]	C-8 (X = H) and C-12 (X = Ph)

[a] Rate constants for X = H extrapolated from higher temperatures, using activation parameters determined in ref 2. [b] See footnote *a*, Table 2. [c] Ratio at 113.0 °C. [d] References 4b and 10. [e] References 3 and 11.

The effects on the magnitudes of the rates of thermolysis of substituting phenyl for hydrogen at the α position of several *tert*-butyl peracetates are given in Table 5. The relative rates of decomposition at a common temperature and the activation parameters for thermolysis of the series of 1-phenyl-substituted acetyl peresters are given in Table 6.

Hammett σ/ρ correlations for peresters **1**−**6** are given in Table 7 (results of plots versus σ^+).[13] The standard errors of the slopes and the squares of the correlation coefficients of the plots are also given. All rate measurements were run in nonpolar, aliphatic solvents. The same para-substituents (CH_3O, CH_3, H, Cl and NO_2) were used for each series, except as noted.

Scheme 1 outlines the synthesis of some of the 1-aryl alicyclic carboxylic acids.

The peresters investigated in this study are the *tert*-butyl 1-arylcyclopropane percarboxylates [phenyl (**1a**), *p*-methoxyphenyl (**1b**), *p*-tolyl (**1c**), *p*-chlorophenyl (**1d**), and *p*-nitrophenyl (**1e**)]; the *tert*-butyl 1-arylcyclobutane-

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(11) Wolf, R. A. Unpublished results.
(12) Koenig, T.; Wolf, R. *J. Am. Chem. Soc.* **1969**, *91*, 2574.
(13) Hammett, L. P. op. cit., p 356.

Table 6. Comparison of Rates of Thermolysis of Benzyl-Type Peresters

perester	solvent[a]	k(rel)[b]	$\Delta H^{\ddagger}$ [c]	$\Delta S^{\ddagger}$ [d]
1a	C-8	2.1×10^{-4}	33.2	8.5
2a	C-8	0.65	26.4	3.7
3a	C-8	2.97	24.7	1.2
4a	C-8	3.31	25.7	4.6
$PhCH_2CO_3tBu$	PhCl[e]	0.029	27.9	2.0
$PhCH_2CO_3tBu$	C-8[f]	0.013	29.7	5.8
$PhCH(CH_3)CO_3tBu$	C-8[f]	0.199	26.8	2.4
$PhC(CH_3)_2CO_3tBu$	C-12[g]	(1)	26.1	3.5

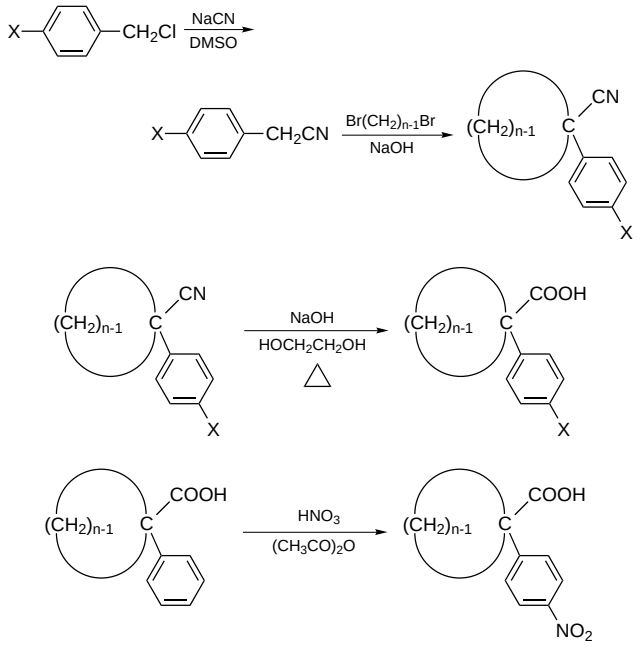
[a] See footnote *a*, Table 2. [b] Calculated at 52.3 °C from published activation parameters, for all peresters except **2a**, **3a** and **4a**. [c] In kcal/mol. [d] In cal/°C mol. [e] Reference 4b. [f] Reference 12. [g] Reference 3.

Table 7. Hammett Linear Free Energy Plots (vs σ^+) for Thermolysis of Peresters in 2,2,4-Trimethylpentane

perester	temp, °C	$\rho \pm$ SE[a]	r^2 [b]
1[c]	113.0	-0.31 ± 0.06	0.895
2	61.6	-0.80 ± 0.04	0.984
2	52.3	-0.83 ± 0.04	0.984
3	52.3	-0.78 ± 0.02	0.996
3	43.5	-0.82 ± 0.02	0.996
4	61.6[d]	-0.70 ± 0.03	0.978
4	52.3[d]	-0.74 ± 0.04	0.974
4	43.5[d]	-0.71 ± 0.04	0.970
5[e]	50.0	-0.78 ± 0.03	0.992
5[e]	60.0[d]	-0.70 ± 0.01	0.996
6[f]	77.5[g]	-1.03 ± 0.05	0.992

[a] Standard error of slope. [b] Square of correlation coefficient for Hammett plot. [c] Reference 1. [d] *p*-Methoxy substituent omitted. [e] Dodecane solvent, ref 3. [f] *n*-Octane solvent, ref 4a. [g] *p*-Chloro substituent omitted.

Scheme 1

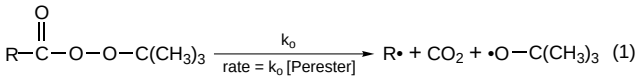


percarboxylates [phenyl (**2a**), *p*-methoxyphenyl (**2b**), *p*-tolyl (**2c**), *p*-chlorophenyl (**2d**), and *p*-nitrophenyl (**2e**)]; the *tert*-butyl 1-arylcyclopentanepercarboxylates [phenyl (**3a**), *p*-methoxyphenyl (**3b**), *p*-tolyl (**3c**), *p*-chlorophenyl (**3d**), and *p*-nitrophenyl (**3e**)], and the *tert*-butyl 1-arylcyclohexanepercarboxylates [phenyl (**4a**), *p*-tolyl (**4c**), *p*-chlorophenyl (**4d**), and *p*-nitrophenyl (**4e**)].

The two mechanisms usually cited for the thermal decomposition of *tert*-butyl peresters under nonpolar conditions are given in Scheme 2.[15] It is also possible that these represent two extremes of a mechanistic continuum.

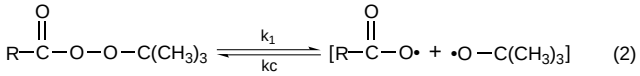
Scheme 2

Concerted:

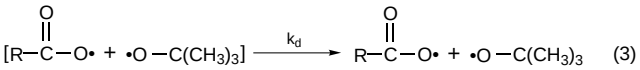


(1)

Stepwise



(2)



(3)

(4)

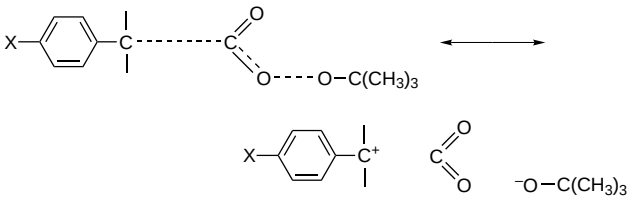
$$\text{rate} = \frac{k_1(k_d + k_2)}{k_c + k_d + k_2}\ [\text{Perester}] \quad (5)$$

Alternative mechanisms for the decomposition of these peresters can be ruled out. The lack of curvature in the first-order kinetic plots for peresters **1**−**4**, the low initial perester concentration used, and the presence of added radical scavenger (styrene) suggest that radical-induced decomposition is not operating in these systems.[2] Contribution from an ionic ("Criegee"-type[16]) decomposition can be ruled out on the basis of product studies on the unsubstituted 1-phenyl alicyclic peresters[17] and on the lack of significant rate acceleration for perester **5** upon changing to a more polar solvent.[3,18] A modest rate acceleration for aromatic solvents, as compared to aliphatic solvents, seems to be a consistent phenomenon in perester decomposition studies.[2] The thermolyses of peresters **2a**−**4a** proceed at 80% faster rates in ethylbenzene solvent[17] as compared to 2,2,4-trimethylpentane at the same temperature (this work). This rate acceleration could be caused by aromatic solvents interacting with the reacting peresters by polarization effects.[2]

The sign of the ρ values measured for peresters **1**−**6** is opposite to that predicted by the Criegee mechanism. The sign of the ρ values is in the predicted direction for a carboxy inversion type ionic rearrangement, analogous to known reaction pathways observed for diacyl peroxides under some conditions.[19] However, careful product determinations by others for many perester decompositions, done under reaction conditions similar to those of this work, have failed to detect any carbonate esters, which would have resulted from such rearrangements of peresters. For example, the decomposition products measured by Ruechardt from the thermolysis of **1a**−**4a** were entirely consistent with the concerted and stepwise mechanisms cited above.[17] These products are phenylcycloalkanes, bis-1,1′-diphenylcycloalkanes, 1-phenylcycloalkenes, 1-phenyl-1-*tert*-butoxycycloalkanes, *tert*-butyl alcohol, and acetone.

(14) Ruechardt, C. *Angew. Chem., Int. Ed. Engl.* **1970**, *9*, 830.
(15) Koenig, T. In Free Radicals; Kochi, J. K., Ed.; Wiley-Interscience: New York, 1973; Vol. 1, pp 120−136.
(16) Criegee, R. *Chem. Ber.* **1944**, *77*, 722.
(17) Bonnekessel, J.; Ruechardt, C. *Chem. Ber.* **1973**, *106*, 2890.
(18) Herkes, F. E.; Friedman, J.; Bartlett, P. D. *Inter. J. Chem. Kinet.* **1969**, *1*, 193.
(19) Reference 15, p 114.

Scheme 3



The effects of phenyl substitution at the α carbon on the stability of the transition state for the concerted perester thermolysis mechanism are expressed in Scheme 3. Analogous resonance forms (with perhaps less charge separation) could be written for the decarboxylation step (k_2) of the stepwise process.

The delocalization of unpaired electrons and separation of charges depicted in Scheme 3 rationalize the sign of the ρ values observed for the thermolysis of peresters **1**−**6** (see below) and the rate-accelerating effect of substituting phenyl for hydrogen at the α position (Table 5). Arguments can be made for considering the effect of the phenyl substituent groups on the relative energies of the reactants for these reactions.[20] An example of the reactant state substituent arguments would be the effects on the heats of formation of *tert*-butyl perbenzoates.[21]

Concerted versus Stepwise Mechanisms. We believe that the results of Tables 1−6 support the assertion that all members of perester groups **2**−**4** undergo thermal decomposition primarily by the concerted mechanism. The 1-phenyl alicyclic peresters (except for perester group **1**) decompose at rates many times faster than their 1-H alicyclic analogues (Table 5). Since the 1-H alicyclic peresters are thought to undergo decomposition primarily by the concerted mechanism for larger rings (e.g. cyclopentyl and larger[2]), this suggests the predominance of the concerted mechanism for the perester series **2**−**4**. The relatively low $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values for peresters **2**−**4**, as compared to those values for the 1-H alicyclic analogues and peresters thought to decompose by the stepwise mechanism (such as perester group **1**), may support the concerted mechanism for the thermal decomposition of peresters **2**−**4**.[10,22] The magnitude of the activation parameters, however, has been questioned as an a priori test of the decomposition mechanism.[23]

The magnitudes of the rate constants for thermolysis of peresters **2**−**4** in viscous, nonpolar solvents support the proposed concerted mechanism for the decomposition of these peresters (Tables 2 and 4). If the stepwise mechanism were making a significant contribution to the overall decomposition process, such a contribution should be most strongly felt by the slowest (*p*-nitro substituted) perester of each series.[4a] No such rate decreases for thermolyses in viscous solvents for peresters **2a**, **2e**, **3e**, and **4e** could be detected. A tendency toward slightly faster rates in more viscous solvents can be detected for most of the peresters of this study. We cannot explain this phenomenon at this time.

The situation is quite different for the solvent viscosity effects on peresters **1a** and **1e**. We believe, in analogy with the 1-H alicyclic peresters,[2] that the decrease in rates of thermolysis for peresters **1a** and **1e** with increased solvent viscosity suggests contribution from the stepwise mechanism for these peresters.

The results given in Tables 2 and 4 do not rule out the possibility of a stepwise mechanism, with the decarboxylation process occurring faster than radical diffusion and cage recombination ($k_2 \gg k_d$ and k_c in eq 6 of Scheme 2). The solvent viscosity test would fail to detect the presence of any intermediate carboxyl radical. The stepwise and concerted mechanism then become kinetically indistinguishable.[4a] Indeed, careful studies of perester decompositions by carbon-13 CIDNP,[24] oxygen-18 scrambling,[25] and photodecomposition[26] experiments support the idea of the intermediacy (however brief) of the alkylcarboxyl radical, even when the alkyl radical resulting from decarboxylation is resonance stabilized. However, the deuterium isotope effects measured for peresters which undergo thermolysis at rates slower to or comparable to the rates for peresters **2**−**4** (such as peresters **5a** and **6a** and *tert*-butyl per-2-phenylpropionate)[12,27] and volumes of activation studies on perester **6**[28] support the proposal that peresters **2**−**6** undergo thermal decomposition by a "true concerted", two-bond-cleavage mechanism.

One way to accommodate the apparently conflicting experimental results of this study and those of the cited references might be to allow for a nonsynchronous concerted mechanism, whereby the C−C and O−O bonds do not break to the same degree at the transition state. Another way to state this idea would be to propose that the stepwise and concerted mechanisms for perester decompositions are at the ends of a mechanistic continuum.

Ruechardt has presented evidence which suggests that the transition state for concerted perester thermolysis occurs so early on the reaction coordinate that the C(α)−C(carbonyl) bond of the transition state has not been significantly stretched.[14,29] Thus, there would be little free radical (and little partial charge) character at the α carbon at the transition state. One series of supportive experiments for this idea is the effect of aliphatic ring size on the rates of thermolysis of 1-phenylcycloalkane-peresters (**1a**−**4a**). Ruechardt found, as do we, that the rates of thermolysis follow the sequence (fastest to slowest) **4a** > **3a** > **2a** ≫ **1a**.

That this trend does not follow ring strain changes in going from reactants to transition states is suggested by the completely different behavior for the solvolysis of cyclic halides (**7**)[30] and the thermolysis of trans symmetric bisalkyldiazenes (**8**).[17,31]

For both cyclic chloride group **7** and diazene group **8** the rates of reaction follow the trend (fastest to slowest) $n = 5 > n = 4 > n = 6$ ($> n = 3$). The solvolysis of the cyclopropyl derivative was not studied. The trends for the reactions of compounds **7** and **8** can be explained by invoking relief of conformational strain (accelerating the cyclopentyl system) and increase of ring strain in going

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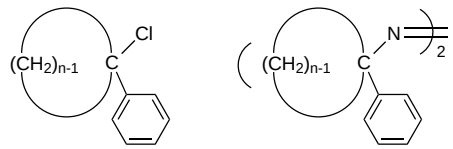

7 8

to transition states (slowing down the cyclobutyl and cyclohexyl systems).[32]

The relative rates of thermolysis of peresters **1a**−**4a** are explained by Ruechardt not by transition state effects but by a combination of polar and steric effects on the reactant state. However, linear free energy effects calculated by semiempirical molecular orbital methods suggest that the rates of decomposition of acyclic peresters could be driven by transition state effects (stabilization of radicals being formed) and not by steric effects.[33] The rates of radical forming decomposition of trans-symmetric bisalkyl diazenes and the rates of carbon−carbon homolysis of hydrocarbons seem to be driven by both transition state effects and reactant state steric effects.[33]

The results of Table 5 suggest that the α-substituted phenyl group interacts with the developing free radical at the α carbon at the transition state by resonance effects. These data, and the measured deuterium isotope effects for analogous acyclic perester systems cited earlier, might support the idea of a stretched C(α)−C(carbonyl) bond in the transition state, with some free radical character at the α carbon. The degree of stretching of this bond in the transition state for peresters would be less than the stretching of the analogous bonds for the trans-symmetric bisalkyl diazenes and homolysis of hydrocarbons because of the more highly exothermic nature of the perester thermolyses, as compared to the diazenes and hydrocarbons. The "stretched" transition states from hitherto designated concerted perester decompositions might lead to alkylcarboxyl radical intermediates with stretched C(α)−C(carbonyl) bonds, which would then very rapidly decarboxylate. This interpretation might account for the disparate experimental observations for "concerted" perester decompositions: Substituent effects, secondary deuterium isotope effects, stereochemical effects, viscosity dependences, and volumes of activation support the concerted mechanism, and carbon-13 CIDNP, oxygen-18 scrambling, and photolyses studies support the stepwise mechanism, for the same series of peresters.

The small increase in rate of thermolysis for perester **1a** as compared to *tert*-butyl percyclopropanecarboxylate (Table 5) could be explained in terms of inhibition of phenyl resonance stabilization at the transition state for perester **1a**. This inhibition might be due to hybridization effects of the cyclopropane ring (insufficient P character in the developing lone electron-containing atomic orbital at the α carbon). Thus, the mechanism of thermolysis of perester **1a** shifts to primarily stepwise.

The Hammett linear free energy correlations for the peresters of this study are given in Table 7. In Figure 1 is given the σ^+/ρ plot for the *tert*-butyl 1-arylcyclopentanepercarboxylates. The negative sign of the ρ values

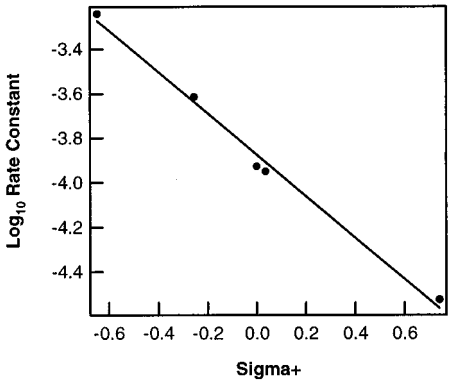

Figure 1. σ^+/ρ plot for the thermal decomposition of *tert*-butyl para-substituted 1-arylcyclopentanepercarboxylates in 2,2,4-trimethylpentane at 52.3 °C.

may suggest some partial positive charge character at the benzyl carbon in the transition states (Scheme 3) for the decomposition process.[4b,c] If all five substituent groups are included in the Hammett correlations, the linear fit with σ^+ values for peresters **1a**−**4a** is much better than with σ values. Other attempts at correlations (with σ^n, σ^o, σ^* and σ^-) give much worse linear correlations than with σ (upward curvature). The better fit with σ^+ for benzyl-type peresters was previously reported.[3,4] Although it is tempting to try to use these Hammett correlations as further support of some concerted character [C(α)−C(carbonyl) bond stretching] in the transition states for the decompositions of the peresters of this study, it is probably invalid to do so, since the σ^+ values were developed from a carbocation-forming reaction.

Summary and Conclusions

The *tert*-butyl 1-arylcycloalkanepercarboxylates **2**−**4** decompose primarily by a concerted pathway, like the acyclic analogue series **5**. The *tert*-butyl 1-arylcyclopropanepercarboxylates **1** decompose primarily by a stepwise mechanism. These conclusions are supported by the effects on the rates of decomposition of substituents (phenyl versus hydrogen), temperature, and solvent viscosities demonstrated by this study. The apparent conflicting results of other studies regarding the assignment of concerted versus stepwise mechanisms for perester decomposition may be resolved by invoking a continuum of mechanisms, with mostly stepwise at one end and mostly concerted at the other.

In the present study the crossover from mostly stepwise to mostly concerted mechanisms of decomposition for these 1-arylcycloalkylperesters occurs in changing the ring size from cyclopropyl to cyclobutyl. The *tert*-butyl 1-arylcyclobutanepercarboxylates (and larger cycloalkane series) might decompose via a mechanism leading to a stretched C(α)−C(carbonyl) bond in the transition state, allowing some resonance stabilization by the aryl group attached to the α carbon, but leading to a stretched alkylcarboxyl radical intermediate, which would very rapidly decarboxylate in the cases of the larger ring peresters, but slowly decarboxylate in the case of the cyclopropylcarboxyl radical.

Experimental Section

Melting points were taken on a Thomas-Hoover melting point apparatus and are uncorrected. IR spectra (for analytical purposes and for kinetics) were recorded on a Beckmann IR-

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33 or on a Beckmann Acculab spectrophotometer. NMR spectra were recorded on a Varian T-60 spectrophotometer (CCl_4 solvent, TMS internal standard), on a JEOL-JNM-MH-100 spectrophotometer ($CDCl_3$ solvent, TMS internal standard) or on a JEOL-JNM-FX-60 spectrophotometer ($CDCl_3$ solvent, TMS internal standard for ^{13}C NMR).

Kinetics. The kinetic procedures used in this study were described previously.[2] The same precautions and tests were used to determine the accuracy and precision of the first-order rate constants.

Materials and Solvents. All hydrocarbon solvents used for the reaction kinetics solutions were distilled prior to use, with the forerun being discarded. Reagent grade solvents (2,2,4-trimethylpentane, dodecane and hexadecane) were purchased from Aldrich Chemical and from Eastman Organic Chemicals.

tert-Butyl hydroperoxide (Aldrich Chemical) was distilled prior to use (30 °C at 30 Torr). A forerun and sizable amount of distillation pot residue were discarded. Thionyl chloride (Baker Chemical and Pfaltz and Bauer) was distilled immediately before use in the preparation of acid chlorides. The following solvents for syntheses were used as received: diethyl ether (Mallinckrodt reagent grade), DMSO (Baker Chemical), and diethylene glycol (Eastman Organic Chemicals). All starting compounds were distilled prior to use, with the exception of the purchased 1-arylcycloalkyl cyanides and 1-arylcycloalkyl carboxylic acids.

The precursor organic chemicals for synthesis of the peresters in this study were all purchased from Aldrich Chemical Co. These purchased compounds were all the para-substituted 1-phenylcyclopropanecarboxylic acids (except for the *p*-nitro compound), 1-(*p*-chlorophenyl)cyclobutanecarboxylic acid, 1-phenylcyclobutanecarboxylic acid, 1-phenylcyclopentanecarboxylic acid, 1-(*p*-chlorophenyl)cyclopentanecarboxylic acid, 1-(*p*-methoxyphenyl)cyclopentanecarboxylic acid, 1-(*p*-tolyl)cyclopentanecarboxylic acid, 1-(*p*-chlorophenyl)cyclohexanecarboxylic acid, 1-phenylcyclohexanecarboxylic acid, 1-phenylcyclobutanecarbonitrile, 1-*p*-tolylcyclohexanecarbonitrile, 1,3-dibromopropane, *p*-tolylacetonitrile, *p*-methoxyphenylacetonitrile, *p*-chlorophenylacetonitrile, and phenylacetonitrile.

Peresters. Peresters were synthesized by the method previously described.[12,34] Peresters were purified by column chromatography through silica gel or alumina and by recrystallization from isooctane or hexane. The peresters were pumped free of solvent by high vacuum pump. **Note: A neat sample of perester 3b (*p*-methoxy substituent) experienced a runaway exotherm, resulting in an explosion. All neat samples of the peresters of this study should be kept cold and should be handled with appropriate personal protective equipment and with caution!** Yields of peresters were typically 50−80% from the acid chlorides. The remaining material balance from the acid chlorides could be isolated as carboxylic acids.

Many of the peresters were liquids at room temperature. The following melting ranges were measured for the solid peresters: **1b** (43.3−44.4 °C), **1c** (77.9−79.3 °C), **1d** (63.7−64.2 °C), **1e** (106.8−107.8 °C), **2d** (33−35 °C), **2e** (68.0−70.0 °C), **3d** (64.5−66.3 °C), 3e (33−36 °C), **4d** (65.2−66.8 °C), and **4e** (68.0−69.8 °C).

The infrared spectra of peresters **1a**, **2a**, **3a** and **4a** matched those previously published.[17] Table 8 gives the proton NMR spectral characteristics of the peresters in series **1**−**4**.

Table 9 gives the ^{13}C NMR spectral characteristics (500−1000 scans). Spectra were recorded under broad band decoupling mode, using a pulse width of 3 ms (flip angle of 40°), pulse repetition rate of 2.8 s, and field width of 4 kHz. The instrument was locked onto the deuterium of $CDCl_3$ solvent. Relative carbon intensities are given in parentheses. Chemical shifts are relative to tetramethylsilane.

Table 10 lists carbon/hydrogen analyses for some of the peresters. Analyses were performed by Integral Microanalytical Laboratories, Inc., Raleigh, NC. Because of the thermal instabilities of these compounds, special precautions were taken to deliver the samples at temperatures below ambient.

Table 8. Proton NMR Spectral Data for 1−4

perester	δ values (ppm) (from TMS−CCl_4 solvent)
1a	1.10 and 1.60 (m, 13H), 7.21 (s, 5H)
1b	1.10 (m and s, 11H), 1.48 (m, 2H), 3.70 (s, 3H), 6.60−7.75 (AB q, J = 8.7 Hz, 4H)
1c	1.18 and 1.48 (s and m, 13H), 2.31 (s, 3H), 7.11 (m, 4H)
1d	1.23 and 1.59 (s and m, 13H), 7.25 (s, 4H)
1e	1.10 and 1.15 (s and m, 11H), 1.66 (m, 2H), 7.42−8.17 (AB q, J = 8.5, 4H)
2a	1.08 (s, 9H), 1.77−3.10 (m, 6H), 7.20 (s, 5H)
2b	1.13 (s, 9H), 1.73−2.97 (m, 6H), 3.67 (s, 3H), 6.55−7.07 (AB q, J = 8.5 Hz, 4H)
2c	1.10 (s, 9H), 1.57−2.93 (m), 2.30 (s) (7H) and 7.03 (m, 4H)
2d	1.10 (s, 9H), 1.78−3.08 (m, 6H), 7.20 (s, 4H)
2e	1.17 (s, 9G), 1.74−3.16 (m, 6H), 7.33−8.20 (AB q, J = 9.2 Hz, 4H)
3a	1.00 (s, 9H), 1.57−2.23 (m, 6H), 2.40−2.83 (m, 2H), 7.30 (m, 5H)
3b	1.10 (s, 9H), 1.57−2.20 (m, 6H), 2.43−2,87 (m, 2H), 3.77 (s, 3H),6.73−7.30 (AB q, J = 8.5 Hz, 4H)
3c	1.07 (s, 9H), 1.53−2.87 (m) and 2.33 (s) (11H), 7.13 (m, 4H)
3d	1.05 (s, 9H), 1.67−2.13 (m, 6H) 2.33−2.80 (m, 2H), 7.27 (s, 4H)
3e	1.15 (s, 9H), 1.67−2.90 (m, 8H), 7.43−8.17 (AB q, J = 8.7 Hz, 4H)
4a	1.07 (s, 9H), 1.33−2.67 (m, 10H), 7.20 (m, 5H)
4c	1.10 (s, 9H), 1.65 and 2.43 (m and s, 13H), 7.23 (s, 4H)
4d	1.19 (s, 9H), 1.70 and 2.45 (m, 10H), 4.38 (s, 4H)
4e	1.15 (s, 9H), 1.68 and 2.44 (m, 10H), 7.40−8.25 (AB q, J = 8.5 Hz, 4H)

The peresters are listed in decreasing order of analysis accuracy. The less stable the perester, the less accurate the carbon/hydrogen analysis. This suggests that some of the peresters underwent some decomposition en route to the elemental analyses.

Carboxylic Acid Chlorides. Carboxylic acid chlorides were prepared from their corresponding corresponding acids by adding 0.12 mol of freshly distilled thionyl chloride to 0.04 mol of carboxylic acid dissolved in 25 mL dry benzene. The solutions were heated to reflux for 3−5 h. Benzene and excess thionyl chloride were removed by distillation under reduced pressure. Most of the acid chlorides were purified by distillation under reduced pressure. The *p*-nitrophenyl alicyclic carbonyl chlorides were not distilled, however, due to decomposition at the distillation temperatures. The *p*-nitrophenyl alicyclic peresters were the most readily purified by recrystallization from hydrocarbon solvents. Yields of purified acid chlorides ranged from 50 to 80%. IR and NMR spectra for all the carboxylic acid chlorides prepared in this study were consistent with the assumed structures. No impurities could be detected in the IR and NMR spectra of the acid chlorides. IR carbonyl peaks for the acid chloride precursors to peresters **1a**, **2a**, **3a**, and **4a** matched published values.[17]

1-(*p*-Nitrophenyl)cycloalkanecarboxylic Acids. A modified method of Roberts[35] was used to nitrate the benzene ring of the 1-phenylcycloalkanecarboxylic acids. To a solution of 0.03 mol of 1-phenylcycloalkanecarboxylic acid in 35 mL of acetic anhydride at 10 °C, was slowly added a solution of 17 mL of concentrated (96%) sulfuric acid and 15 mL of concentrated nitric acid (prepared cold, in small scale). It was found that yields were generally higher if nitric acid from a freshly opened bottle was used. The resulting solution was allowed to stir for 2−3 h at 10 °C. To this solution 250 mL of distilled water was carefully added, and the yellowish solid precipitate was collected by suction filtration. The filtered solid was stirred with 100 mL of distilled water and collected again by

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Table 9. Carbon NMR Spectral Data for 1−4

perester	δ values (ppm) (from TMS−$CDCl_3$ solvent)
1a	16.63 (2C), 25.86 (3C), 27.94 (1C), 83.30 (1C), 127.54 (1C), 128.19 (2C), 130.47 (2C),137.87 (1C), 171.59 (1C)
1b	16.89 (2C), 25.92 (3C), 27.09 (1C), 55.16 (1C), 83.36 (1C), 113.57 (2C), 130.01 (1C), 131.51 (2C), 158.93 (1C), 172.05 (1C)
1c	16.76 (2C), 21.12 (1C), 25.86 (3C), 27.48 (1C), 83.36 (1C), 128.91 (2C), 130.34 (2C), 134.95 (1C), 137.10 (1C), 171.92 (1C)
1d	16.83 (2C), 25.92 (3C), 27.35 (1C), 83.56 (1C), 128.39 (2C), 131.77 (2C), 133.39 (1C), 136.51 (1C), 171.20 (1C)
1e	17.02 (2C), 25.99 (3C), 27.81 (1C), 83.88 (1C), 123.51 (2C), 131.44 (2C), 145.34 (1C), 147.29 (1C), 170.29 (1C)
2a	16.96 (1C), 25.87 (3C), 32.36 (2C), 51.39 (1C), 83.62 (1C), 126.11 (2C), 126.89 (1C), 128.32 (2C), 142.68 (1C), 172.76 (1C)
2d	16.89 (1C), 25.86 (3C), 32.42 (2C), 50.94 (1C), 83.69 (1C), 127.67 (2C), 128.52 (2C), 132.74 (1C), 141.25 (1C), 172.18 (1C)
2e	17.02 (1C), 25.92 (3C), 32.62 (2C), 51.59 (1C), 84.08 (1C), 123.64 (2C), 127.35 (2C), 146.90 (1C), 150.09 (1C), 171.46 (1C)
3a	23.52 (2C), 25.86 (3C), 36.13 (2C), 58.28 (1C), 83.69 (1C), 126.70 (1C), 126.83 (2C), 128.19 (2C), 142.23 (1C), 172.96 (1C)
3d	23.46 (2C), 25.99 (3C), 36.32 (2C), 57.89 (1C), 83.82 (1C), 128.32 (2C), 128.45 (2C), 133.00 (1C), 140.86 (1C), 172.44 (1C)
3e	23.59 (2C), 25.99 (3C), 36.51 (2C), 58.54 (1C), 84.08 (1C), 123.58 (2C), 128.00 (2C), 146.97 (1C), 149.70 (1C), 171.66 (1C)
4d	23.33 (2C), 25.34 (1C), 26.12 (3C), 34.50 (2C), 50.29 (1C), 83.69 (1C), 127.54 (2C), 128.65 (2C), 133.00 (1C), 141.32 (1C), 171.72 (1C)
4e	23.33 (2C), 25.21 (1C), 26.12 (3C), 34.57 (2C), 51.13 (1C), 84.10 (1C), 123.64 (2C), 127.22 (2C), 146.91 (1C), 150.09 (1C), 171.01 (1C)

Table 10. Analysis Data for Some Peresters

perester	% C found (calcd)	% H found (calcd)
1e	60.39 (60.21)	6.19 (6.14)
1d	62.72 (62.57)	6.71 (6.38)
1c	72.36 (72.55)	8.37 (8.12)
1b	68.08 (68.16)	8.11 (7.63)
2e	61.64 (61.42)	6.82 (6.53)
2d	61.71 (63.71)	6.62 (6.77)
3e	60.48 (62.53)	6.11 (6.89)
3d	62.76 (64.75)	6.90 (7.13)
4e	61.12 (63.54)	6.80 (7.21)
4d	60.30 (65.69)	6.52 (7.46)

suction filtration. The proton NMR spectra of the crude, yellow, air-dried crystals exhibited a complicated aromatic group of protons, suggesting a major amount of *p*-isomer (AB quartet), substantial minor amounts of *o*- and *m*-nitro isomers and some unreacted 1-phenylcycloalkanecarboxylic acid.

It was found that fractional recrystallization from carbon tetrachloride gave the *p*-nitro isomer, completely uncontaminated by the other isomers and starting material. Two to three recrystallizations were performed on each sample. The yields of the purified (yellow crystals) *p*-nitrophenyl alicyclic carboxylic acids were 50−60%.

1-(*p*-Nitrophenyl)cyclopropanecarboxylic Acid. This carboxylic acid was not easily purified by direct recrystallization from CCl_4. The methyl ester of the acid was prepared and was purified by repeated recrystallizations from CCl_4. The ester was then hydrolyzed by heating in aqueous ethanol and sodium hydroxide, and the free acid was collected by addition of HCl and filtration. mp: 192−194 °C (lit.[35] 192−193.5 °C). Proton NMR (acetone solvent) of aromatic region: δ 7.00−7.77 (ABq, J = 8.6 Hz, 4H), 9.53 (s, 1H).

1-(*p*-Nitrophenyl)cyclobutanecarboxylic Acid. mp: 155−157 °C. Proton NMR (acetone-d_6): δ 1.47−3.13 (m, 6H), 7.43−8.20 (ABq, J = 8.6 Hz, 4H), 9.80 (s, 1H).

1-(*p*-Nitrophenyl)cyclopentanecarboxylic Acid. mp: 180−181 °C (lit.[36] 181−182 °C). Proton NMR (acetone-d_6): δ 1.57−2.97 (m, 8H), 5.80 (s, 1H), 7.50−8.17 (ABq, J = 9.1 Hz, 4H).

1-(*p*-Nitrophenyl)cyclohexanecarboxylic Acid. mp: 138−142 °C (lit.[36] 175−177 °C). Proton NMR (acetone-d_6): δ 1.70 and 2.49 (m, 10H), 7.61−8.29 (ABq, J = 8.9 Hz, 4H), 9.20 (s, 1H).

1-Arylcycloalkanecarboxylic Acids from 1-Arylcycloalkanecarbonitriles. The 1-arylcycloalkanecarbonitriles used in this study were hydrolyzed to corresponding carboxylic acids by the method of Lyle.[37] Yields were 75−91%. The carboxylic acids were purified by crystallization or by sublimation. The following carboxylic acids were prepared by this method.

1-(*p*-Methoxyphenyl)cyclobutanecarboxylic Acid. mp: 105−107 °C (lit.[38] 106−107 °C). Proton NMR (CCl_4): δ 1.60−3.07 (m, 6H), 3.57 (s, 3H), 6.60−7.33 (ABq, J = 8.7 Hz, 4H), 9.53 (s, 1H).

1-*p*-Tolylcyclobutanecarboxylic Acid. mp 101−105 °C (lit.[38] 115−116 °C). Proton NMR (CCl_4): δ 1.57−3.10 (m), 2.33 (s) (9H), 7.10 (m, 4H), 8.63 (s, 1H).

1-*p*-Tolylcyclohexanecarboxylic Acid. mp (subl.): 168−171 °C (lit.[39] 172 °C). Proton NMR (CCl_4): δ 1.58 (m, 10H), 2.32 (s, 3H), 7.21 (m, 4H), 8.53 (s, 1H).

1-Arylcyclobutanecarbonitriles from Arylacetonitriles. The cyclization of arylacetonitriles with 1,3-dibromopropane to form 1-arylcyclobutanecarbonitriles was done by the method of Makosza and Serafin.[40] The nitriles were purified by distillation under reduced pressure. Yields of purified nitriles were 20−50%.

1-(*p*-Methoxyphenyl)cyclobutanecarbonitrile. bp 185−190 °C (15 Torr) [lit.[38] 117 °C (0.3 Torr)]. Proton NMR (CCl_4): δ 1.83−2.90 (m, 6H), 3.72 (s, 3H) and 6.67−7.33 (ABq, J = 8.9 Hz, 4H).

1-*p*-Tolylcyclobutanecarbonitrile. bp 188−192 °C [lit.[38] 93 °C (0.3 Torr)]. Proton NMR (CCl_4): δ 1.57−2.93 (m) and 2.30 (s) (9H) and 7.11 (m, 4H).

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