However, in view of the proposals made to explain the variable pressure results (*vide supra*), the Hammett relationship should not rigorously apply to any of these data. If this constraint is removed, the p-nitro point need not be interpreted as an abnormally fast rate for this substituted perester.[7b] Rather, the upward curvature in the plot of Bartlett's data *including the latter point* can be interpreted as a reflection of both the increasing polar character and solvation of the transition state with an increase in electron-donating ability of the substituent (*vide supra*).

Based on our limited high pressure data at 79.6° (cumene solvent) for the p-CH_3, H, p-Cl, and m-Cl peresters, the *apparent* ρ value is pressure insensitive (*ca.* -1.1). This is not surprising in view of the small variation in the rate constants with pressure and the narrow range of σ^+ covered by these substituents. However, this result does indicate that no *major* mechanism variations occurred at high pressure.[17]

A small inverse viscosity dependence of the decomposition rate for **1c** at atmospheric pressure had led to the suggestion that its decomposition mechanism involves both one-bond (O–O) and concerted two-bond (C–C and O–O, eq 2) scission processes.[18] The rates of decomposition of **1d** and **1e** were viscosity invariant.[18] However, observed activation volumes of +7 to +10 cc/mol for authentic one-bond scission peresters[19] indicate that those of the peresters **1** are too small to be consistent with such a mechanism.[3b] Additionally, the similarity in the plots for **1c** and **1d** (Figure 1) precludes the gross mechanistic variation implied by the comparative viscosity results. All other observations support the two-bond scission mechanisms.[20]

Experimental Section

Perester Syntheses.—The substituted *tert*-butyl phenylperacetates were synthesized from the corresponding phenylacetyl chlorides and *tert*-butyl hydroperoxide.[3b,7b] The acid chlorides and *tert*-butyl hydroperoxide were distilled prior to their use. All peresters showed a carbonyl absorption in the infrared at 1783 cm^{-1}.

Attempts at iodometric titration of the peresters gave widely varying results on portions of the same sample. Samples were rechromatographed until their infrared spectra were free of extraneous carbonyl bands as well as any OH absorption. In addition, infrared spectra of completely decomposed samples (infinite time samples) in cumene exhibited only solvent absorption bands in the carbonyl stretching frequency region, indicating the absence of any contaminating carbonyl containing species among the decomposition products. The peresters were crystalline solids and decomposition rate constants did not vary for different samples of the same perester. All peresters were stored at low temperature.

High Pressure Apparatus and Kinetic Studies.—A complete description of the apparatus and experimental techniques has been presented.[3b] Kinetic runs and the data analysis were carried out following the procedures reported for unsubstituted *tert*-butyl phenylperacetate.[3b] Each kinetic point represented a separate pressure experiment.[3b]

Registry No.—**1a**, 27396-17-4; **1b**, 27396-18-5; **1c**, 3377-89-7; **1d**, 27396-20-9; **1e**, 27396-21-0.

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[17] (a) The reaction products from decomposition of the substituted peresters are analogous to those formed from *tert*-butyl phenylperacetate,[3b] and their relative yields show the expected dependence on pressure.[17b] (b) R. C. Neuman, Jr., and J. V. Behar, *J. Org. Chem.*, **36**, 657 (1971), accompanying paper.

[18] (a) W. A. Pryor and K. Smith, *Intra-Sci. Chem. Rep.*, **3**, 255 (1969); (b) *J. Amer. Chem. Soc.*, **92**, 5403 (1970).

[19] (a) These data were obtained from a study of *tert*-butyl perbenzoate in cumene[3b] and from a study of the cis and trans isomers of *tert*-butyl 2-propyl-2-peroxypentenoate in cumene.[19b] (b) R. C. Neuman, Jr., and G. D. Holmes, unpublished results.

[20] (a) T. Koenig and R. Wolf, *J. Amer. Chem. Soc.*, **91**, 2574 (1969); (b) T. Koenig, J. Huntington, and R. Cruthoff, *ibid.*, **92**, 5413 (1970).

High Pressure Studies. VII. The Pressure Dependence of Cage Effects. Products from Substituted *tert*-Butyl Phenylperacetates[1,2]

ROBERT C. NEUMAN, JR.,* AND JOSEPH V. BEHAR

Department of Chemistry, University of California, Riverside, Riverside, California 92502

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Thermal decompositions of ring-substituted *tert*-butyl phenylperacetates in cumene (79.6°) give the corresponding *tert*-butyl benzyl ethers, toluenes, bibenzyls, benzylcumyls, bicumyl, and *tert*-butyl alcohol as reaction products. The pressure dependences of the ether/*tert*-butyl alcohol ratios give the pressure dependence of the cage effect (combination *vs.* diffusion) for the initially generated geminate benzyl and *tert*-butoxy radicals. The cage effects increase with pressure but not so rapidly as might be expected. An analysis of the trends involving the potential role of the intervening carbon dioxide molecule is outlined. The remaining products reflect the distribution of diffused benzyl radicals, and the pressure dependences of yields indicate that a major source of the toluenes involves hydrogen abstraction by the benzyl radicals from the solvent cumene.

We have been investigating the effects of pressure on the rates of free-radical reactions in solution. Studies of homolytic scission reactions have shown that care must be used in interpreting the significance of the observed activation volume (ΔV^*_{obsd}) for decomposition of radical initiators.[1a,3] If the initially formed geminate radicals (eq 1) can return to starting material

$$\text{A–B} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \overline{\text{A}\cdot\text{B}\cdot} \xrightarrow{k} \qquad (1)$$

(k_{-1}), ΔV^*_{obsd} is not simply related to the activation volume for homolytic scission (ΔV^*_1) but depends as well on the competition between recombination (k_{-1}) and other processes (k) available to the caged pair (eq 2).

$$\Delta V^*_{\text{obsd}} = \Delta V^*_1 + RT\partial \ln (1 + k_{-1}/k)/\partial P \qquad (2)$$

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[1] (a) Part VI: R. C. Neuman, Jr., and J. V. Behar, *J. Org. Chem.*, **36**, 654 (1971), accompanying paper. (b) Support by the National Science Foundation through Grants GP-4287, 7349, and 8670 is gratefully acknowledged.

[2] Taken from the Ph.D. Dissertation of J. V. Behar, University of California, Riverside, 1969.

[3] R. C. Neuman, Jr., and J. V. Behar, *J. Amer. Chem. Soc.*, **91**, 6024 (1969).

TABLE I

PRODUCT RATIOS FOR SUBSTITUTED *tert*-BUTYL PHENYLPERACETATES (1) IN CUMENE (79.6°)[a]

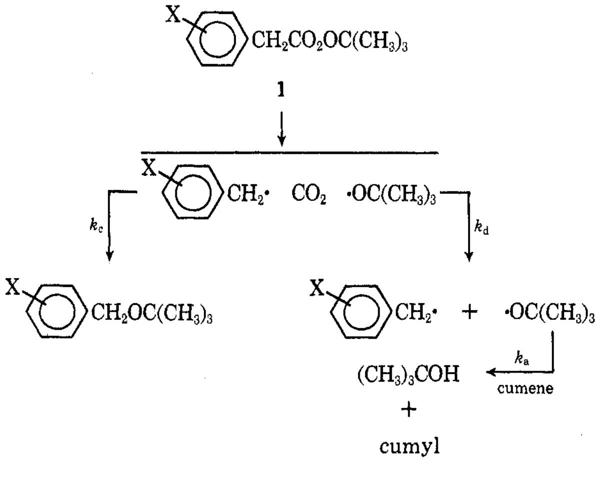
X	*P* (atm)	% ND[b]	Ether[c]	Toluene	Bibenzyl	Benzyl-cumyl[d]	Bicumyl
m-Cl	1		0.26	0.19	0.15	(0.28)	0.21
	2000		0.57	0.29	0.14	(0.31)	0.16
	4000	5	0.82 (0.86)	0.32	0.22	(0.30)	0.16
	6000	13	1.04 (1.24)	0.43	0.20	(0.22)	
p-Cl	1		0.26	0.15	(0.4)[e]		
	2000	4	0.69 (0.72)	0.30	(0.4)[e]		
	4000	5	0.79 (0.83)	0.31	(0.3)[e]		
	6000	12	1.15 (1.38)	0.39	(0.3)[e]		
H	1		0.37	0.17	0.19	(0.29)	0.27
	2000		0.78	0.30	0.15	(0.25)	0.30
	4000	4	1.01 (1.05)	0.41	0.11	(0.27)	0.25
	6000	13	1.26 (1.49)	0.49	0.09	(0.37)	0.16
p-CH_3	1		0.33	0.11	(0.5)[e]		0.26
	2000	7	0.64 (0.67)	0.22	(0.3)[e]		0.20
	4000	19	0.84 (1.02)	0.26	(0.3)[e]		0.17
	6000	37	1.18 (2.50)	0.29	(0.4)[e]		0.21
p-OMe	1		0.33[g]	0.04	0.18	(0.24)	0.16
	1[f]		0.38[g]	0.04	0.16	(0.26)	0.15
	2000[f]	11	0.98[g]	0.12	0.13	(0.17)	0.12
	4000[f]	28	1.29[g]	0.18	0.17	(0.31)	0.27
	6000[f]		1.25[g]	0.20	0.13	(0.21)	0.17

[a] Determined by glpc; moles of product divided by moles of *tert*-butyl alcohol. [b] Per cent decomposition under nonequilibrium conditions (see text). [c] Numbers in parentheses are corrected for decomposition during nonequilibrium conditions (see text). [d] Authentic samples were not available; the correction factor used for relative thermal conductivity comparison was the average of those for the bibenzyl and bicumyl; see Experimental Section. [e] Only peak for bibenzyl detected; peak for benzylcumyl assumed to overlap; see Experimental Section. [f] 60.0°. [g] Authentic sample not available; thermal conductivity correction used was average of those for other ethers in this table.

In the simplest case described by eq 1, the rate constant k is that for separative diffusion (k_d). Information about the pressure dependence of such combination–diffusion competitions would thus be helpful in interpretations of values of ΔV^*_{obsd} for systems described by eq 1.

We recently completed a study of the pressure dependence of the decomposition rates and products from ring-substituted *tert*-butyl phenylperacetates (1). These compounds decompose as shown in Scheme I.[4]

SCHEME I



The rate data have been reported and demonstrate variations in ΔV^*_1 when polar effects are important in free-radical reactions.[1a] The product data provide information about the pressure dependence of combination–diffusion competitions as well as about the pathways leading to the formation of the various reaction products subsequent to separative diffusion of the initial geminate radicals.

Results and Discussion

Cumene solutions (*ca.* 0.1 *M*) of the unsubstituted, and *m*-Cl-, *p*-Cl-, *p*-CH_3-, and *p*-OCH_3-substituted *tert*-butyl phenylperacetates (1) were completely decomposed at a thermostated bath temperature of 79.6° at various pressures. The products were analyzed by glpc and the mole ratios of each product relative to *tert*-butyl alcohol are reported in Table I. In these systems, *tert*-butyl alcohol is formed by reaction of diffused *tert*-butoxy radicals with cumene, and the virtual absence of acetone indicates that the reaction is quantitative. Thus, the ether/*tert*-butyl alcohol ratio is a direct measure of the cage effect (Scheme I) and the other ratios (except that for bicumyl) represent the partitioning of the diffused benzyl radicals among the various reaction products.[5]

During the initial phase of each high-pressure decomposition reaction, the sample was subjected to nonequilibrium pressure and temperature conditions. During pressurization of samples, heat is generated in the hydraulic fluid surrounding the reaction vessel due to com-

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

(5) Absolute yields were not determined in these studies; however, they appeared to be essentially quantitative in a previous study of unsubstituted *tert*-butyl phenylperacetate.[3] No extraneous peaks were observed in the glpc traces.

pression of the fluid. Temperature equilibration is usually achieved within about 12 min after a run has been started by dissipation of the heat into the walls of the high pressure bomb. This annoying problem can be eliminated in kinetic studies by the choice of an appropriate zero time after equilibration and careful reproduction of the procedures used during pressurization for each subsequent sample.[3] However, it could not be avoided in the product analyses, since products were analyzed by glpc and samples containing unreacted perester could not be accurately analyzed. Thus, the product ratios are composite quantities including the product distributions during both the equilibrium and nonequilibrium portions of each decomposition.

The amount of decomposition of the samples during the nonequilibrium period was estimated by comparing the intensities of the perester carbonyl infrared absorbtions in the master solutions with those of samples withdrawn from the high pressure apparatus after 15 min from initial insertion. The available data are included in Table I and indicate that the product ratios for all systems at 6000 atm, those at 4000 atm for the p-CH_3 and p-CH_3O perester, and those at 2000 atm for the p-CH_3O system may contain significant contributions from nonequilibrium decomposition.

Cage Effect.—The ether/*tert*-butyl alcohol ratios, which represent the competition between combination and separative diffusion of the initial geminate radical pair (Scheme I), increase for each perester with increasing pressure. During the nonequilibrium portion of each run, the mean pressure was lower than that at equilibrium and the temperature was higher (*vide supra*). Since cage effects generally decrease with increasing temperature[6] (compare the data for the p-CH_3O perester at 60 and 79.6°), both features of the nonequilibrium period would tend to lower the cage effect. We have estimated a maximum correction by assuming that the decomposition during the nonequilibrium period of the pressure runs was characterized by an ether/*tert*-butyl alcohol ratio equal to that for the corresponding perester at 1 atm. This leads to the corrected values of ether/*tert*-butyl alcohol shown in Table I.

The values of log (ether/*tert*-butyl alcohol) are plotted as a function of pressure in Figure 1. Both the observed and corrected values at each pressure are included and they are connected by the bars. If the ether/*tert*-butyl alcohol ratios are equal to k_c/k_d (Scheme I), the slopes of the various curves for each perester are directly related to the difference in the activation volumes for diffusion and combination ($\Delta V^*_d - \Delta V^*_c$).[3,7] These differences appear to be pressure dependent and the approximate values are given in Table II.

We have previously reported the effect of pressure on the competition between coupling and diffusion of two geminate *tert*-butoxy radicals generated from di-*tert*-butyl hyponitrite in n-octane (45°) (Scheme II).[7] The pressure dependence of the rate constant ratio k_c/k_d (2 × di-*tert*-butyl peroxide/*tert*-butyl alcohol) is qualitatively similar to the perester data, and the values of $\Delta V^*_d - \Delta V^*_c$ decrease with increasing pressure (Table III). The low pressure values of $\Delta V^*_d - \Delta V^*_c$ are significantly larger in the di-*tert*-butyl hyponitrite system; however, it is interesting to note that the low-pressure cage effect is simultaneously much smaller than for the perester systems. When the cage effect for *tert*-butoxy radical combination becomes approximately equal to those at atmospheric pressure for the peresters, the values of $\Delta V^*_d - \Delta V^*_c$ are rather comparable for the two systems (see Table III).

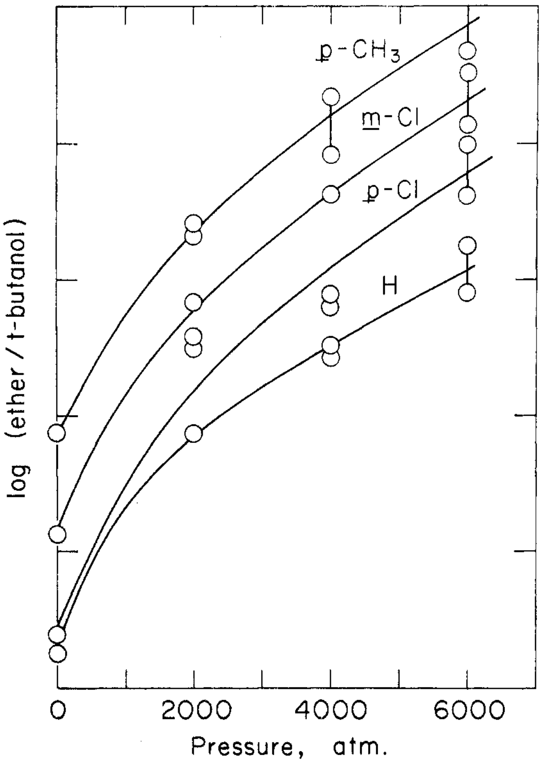


Figure 1.—Pressure dependence of the ether/*tert*-butyl alcohol product ratios. Each division on the vertical axis corresponds to 0.2 log units and the placement of the curves was arbitrary (see Table I).

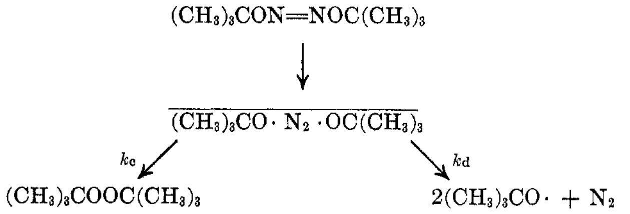
TABLE II

PRESSURE DEPENDENCE OF VALUES OF $\Delta V^*_d - \Delta V^*_c$ FOR DECOMPOSITION OF *tert*-BUTYL PHENYLPERACETATES IN CUMENE (79.6°)

Pressure range, atm × 10^{-3}	$\Delta V^*_d - \Delta V^*_c$, cc/mol[a]			
	m-Cl	p-Cl	H	p-CH_3
0–1	+14	+14	+14	+12
1–2	+8	+9	+7	+8
2–3	+6	+7	+5	+6
3–4	+5	+6	+4	+5
4–5	+5	+5	+4	+5
5–6	+4	+5	+4	+4

[a] Calculated from the slopes of chords connecting points on the plots (Figure 1) at the extremes of the pressure ranges indicated in the first column.

SCHEME II



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[6] S. F. Nelsen and P. D. Bartlett, *J. Amer. Chem. Soc.*, **88**, 143 (1966).

[7] R. C. Neuman, Jr., and R. J. Bussey, *ibid.*, **92**, 2440 (1970).

TABLE III

COMPARISON OF THE PRESSURE DEPENDENCES OF THE CAGE EFFECTS AND VALUES OF $\Delta V^*_{\mathrm{d}} - \Delta V^*_{\mathrm{c}}$ FOR DI-*tert*-BUTYL HYPONITRITE AND *tert*-BUTYL *m*-CHLOROPHENYLPERACETATE

	Hyponitrite[a]		Perester[b]	
P,[c] atm	$k_{\mathrm{c}}/k_{\mathrm{d}}$	$\Delta V^*_{\mathrm{d}} - \Delta V^*_{\mathrm{c}}$, cc/mol	$k_{\mathrm{c}}/k_{\mathrm{d}}$	$\Delta V^*_{\mathrm{d}} - \Delta V^*_{\mathrm{c}}$, cc/mol
1	0.10		0.26	
1000	0.27	+26	(0.42)[d]	+14
2000	0.46	+15	0.57	+8
3000	(0.71)[d]	+11	(0.68)[d]	+6
4000	0.88	+8	0.82	+5

[a] Taken from the data given in ref 7; *n*-octane, 45°. [b] From Tables I and II; cumene, 79.6°. [c] Values of $k_{\mathrm{c}}/k_{\mathrm{d}}$ are those observed, or calculated from the plots, at each pressure; values of $\Delta V^*_{\mathrm{d}} - \Delta V^*_{\mathrm{c}}$ for each pressure P were calculated from the slopes of chords connecting points on the plots at P and $P + 1000$ atm. [d] Calculated from the plots; see *c*.

Limited data indicate that values of ΔV^*_{d} are positive;[8] diffusion processes are retarded by increasing pressure. It is well documented that pressure increases the viscosity of most liquids[9] and diffusion constants decrease with increasing viscosity at atmospheric pressure.[10] Since homolytic scission reactions are pressure retarded,[1a,3,7] one would anticipate that their reverse, radical combination during an encounter, would be pressure accelerated;[11] values of ΔV^*_{c} should be negative. *A priori* the observed values of $\Delta V^*_{\mathrm{d}} - \Delta V^*_{\mathrm{c}}$ (Tables II and III) do not disagree with these predictions; however, it should be noted that these activation volume differences become rather small in the perester systems above 3000 atm. For a value of $\Delta V^*_{\mathrm{d}} - \Delta V^*_{\mathrm{c}}$ equal to +5 cc/mol, approximate extreme cases conforming to the predictions above would be ΔV^*_{d} and ΔV^*_{c} equal to +4 and −1 cc/mol, respectively, or equal to +1 and −4 cc/mol, respectively. We have previously estimated a value of −5 cc/mol for *tert*-butoxy radical combination, and this might suggest that the latter case was applicable. However, the requisite value of ΔV^*_{d} seems small.[12]

In our previous discussions of ΔV^*_{c} we have ignored the possible presence of an inert molecule (nitrogen or carbon dioxide) between the geminate radicals in the primary cage.[13] While recombination of two nearest neighbor radicals would seem in most cases to require a negative activation volume, it seems equally true that radicals in the primary cage could not recombine without first becoming nearest neighbors. Such a reorganization could be formally represented as shown in eq 3

$$\overline{\mathrm{A\cdot\ X\ \cdot B}} \xrightarrow{k_{\mathrm{r}}} \overline{\mathrm{A\cdot\ B\cdot\ X}} \xrightarrow{k_{\mathrm{c}}} \mathrm{AB + X} \qquad (3)$$

(k_{r}), and since it should be akin to diffusion it seems quite possible that its rate would decrease with increasing pressure ($\Delta V^*_{\mathrm{r}} > 0$). This could lead to the small positive values observed for $\Delta V^*_{\mathrm{d}} - \Delta V^*_{\mathrm{c}}$ since the *apparent* activation volume for combination might be actually positive at all pressures or become so as pressure increased. There seems to be ample precedent for assuming that the rate of the reorganization process is comparable to those for combination and separative diffusion.[14]

This analysis indicates that the pressure dependence of cage effects for systems initially containing an inert molecule interposed between the radical pair may not be good models for the pressure dependence of the quantity k_{-1}/k (eq 2) even when k is simply equal to k_{d}. It seems probable that this ratio might increase more rapidly with pressure in the absence of an intervening inert molecule and perhaps be characterized by a slope with a significantly smaller pressure dependence.

Pressure Dependence of Products Formed Subsequent to Diffusion.—The net result of separative diffusion is the formation of equivalent amounts of solvent-separated benzyl and cumyl radicals (Scheme I). We have previously indicated[3] that eq 4–9 represent the reactions available to these radicals and the more extensive product data now available (Table I) do not disagree with this. However, contrary to our previous suggestion,[3] these data indicate that reaction 5 (hydrogen abstraction from cumene) must be a major source of the toluenes.

$$\text{benzyl} + \text{benzyl} \xrightarrow{k_{\mathrm{B,B}}} \text{bibenzyl} \qquad (4)$$

$$\text{benzyl} + \text{cumene} \xrightarrow{k_{\mathrm{B,CH}}} \text{toluene} + \text{cumyl} \qquad (5)$$

$$\text{benzyl} + \text{cumyl} \xrightarrow{k_{\mathrm{B,C}}} \text{toluene} + \alpha\text{-Ms} \qquad (6)$$

$$\xrightarrow{k'_{\mathrm{B,C}}} \text{benzylcumyl} \qquad (7)$$

$$\text{cumyl} + \text{cumyl} \xrightarrow{k_{\mathrm{c,c}}} \text{cumene} + \alpha\text{-Ms} \qquad (8)$$

$$\xrightarrow{k'_{\mathrm{c,c}}} \text{bicumyl} \qquad (9)$$

Toluenes can be formed from benzyl radicals by hydrogen abstraction either from cumene (eq 5) or cumyl radicals (eq 6). The latter bimolecular reaction must be competitive with coupling to yield the benzylcumyls (eq 7). Data obtained in a study of the pressure dependence for competition between coupling and disproportionation of a cyclohexyl radical–*tert*-butoxy radical pair suggest that these two processes have very similar activation volumes.[3] Since the yields of the benzylcumyls remain relatively constant as pressure is increased (see data for H-, *m*-Cl-, and *p*-MeO-substituted peresters) while those for the toluenes increase significantly, the major source of the toluenes must not be *via* reaction 6. Reaction 5 is the only one among the competitive group of reactions 4–9 which is monomolecular in radicals. Since the efficiency of radical production decreases with pressure, all of those processes which involve bimolecular radical interactions should become decreasingly competitive with reaction 5, and this is borne out in the product data.

Scatter in the product data and overlap of the peaks for the bibenzyl and benzylcumyl products from the *p*-

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[8] (a) D. W. McCall, D. C. Douglass, and E. W. Anderson, *J. Chem. Phys.*, **31**, 1555 (1959); (b) W. A. Steele and W. Webb in "High Pressure Physics and Chemistry," Vol. 1, R. S. Bradley, Ed., Academic Press, New York, N. Y., 1963, pp 163–176.

[9] See, for example, P. W. Bridgeman, "Collected Experimental Papers," Vol. IV, Harvard University Press, Cambridge, Mass., 1964, p 2043.

[10] See, for example, G. Houghton, *J. Chem. Phys.*, **40**, 1628 (1964).

[11] Previous attempts to determine combination activation volumes have required rather severe approximations and the results are ambiguous. See ref 20 and 21 in our previous report.[7]

[12] There is some indication that values of ΔV^*_{d} decrease with increasing pressure.[8a] However, it is hard to imagine that they would become almost zero.

[13] We wish to thank Professor T. Koenig for helpful comments which prompted us to begin worrying about this feature of certain primary cages.

[14] (a) H. Kiefer and T. Traylor, *J. Amer. Chem. Soc.*, **89**, 6667 (1967); (b) T. Koenig, *ibid.*, **91**, 2558 (1969); (c) F. D. Greene, M. A. Berwick, and J. C. Stowell, *ibid.*, **92**, 867 (1970); (d) K. R. Kopecky and T. Gillan, *Can. J. Chem.*, **47**, 2371 (1969).

Cl- and *p*-CH$_3$-substituted peresters preclude a detailed analysis of substituent effects on the product yields. However, it should be noted that, with the exception of the data for the unsubstituted perester, the toluene yields appear to follow a reactivity trend with σ^+ which parallels the expected stability of the benzyl radicals (Figure 2).

Experimental Section

Peresters.—The synthetic origins have been outlined.[1a,3,4]

Benzyl *tert*-Butyl Ethers.—The ethers were prepared by the dropwise addition of the corresponding benzyl bromide or benzyl chloride to a refluxing solution prepared by the addition of *tert*-butyl alcohol to a suspension of sodium hydride in dry tetrahydrofuran.[15] The reaction mixtures were refluxed for several hours, washed with water, dried over anhydrous magnesium sulfate, and distilled under reduced pressure.

The nmr spectrum of each ether is consistent with structure (*vide infra*) and the glpc retention time of each ether corresponded to that of the product identified as ether in each reaction mixture. The ether retention times varied with structure in a manner analogous to those of the substituted toluenes and bibenzyls (see Table IV). (a) **Unsubstituted:** bp 84–87° (12 mm) [lit.[15] 98° (20 mm)]; nmr three singlets at 71, 259, and 430 Hz in the ratio 9:2:5, respectively. (b) *m*-**Chloro:** bp 56–59° (0.5 mm); nmr singlets at 74 and 264 Hz, multiplet at 436 Hz, in the ratio 9:2:4, respectively. (c) *p*-**Chloro:** mp 33.5–34.5°; nmr three singlets at 73, 260, and 431 Hz in the ratio 9:2:4, respectively. (d) *p*-**Methyl:** bp 49–50° (0.1 mm); nmr three singlets at 72, 136, and 267 Hz, multiplet at 432.5 Hz, in the ratio 9:3:2:4, respectively. (e) *p*-**Methoxy:** attempts to prepare the benzyl halide precursor were unsuccessful; this compound was not synthesized.

TABLE IV

GLPC RETENTION TIMES FOR TOLUENES, ETHERS, AND BIBENZYLS[a,b]

	Time, min		
Substituent	Toluene	Ether	Bibenzyl
H	5.4	15.7	21.1
p-CH$_3$	8.3	16.6	23.0
m-Cl	10.1	17.4	23.9
p-Cl	10.5	18.2	25.1
p-OCH$_3$	13.0	(18.7)[c]	24.5

[a] Samples in cumene solution. [b] Analyzed using conditions outlined in the section describing product analyses. [c] Authentic sample not available; retention time of supposed ether peak in glpc traces of reaction mixtures.

Substituted Toluenes.—All of the variously substituted toluenes were reagent grade chemicals obtained from Matheson Coleman and Bell.

Substituted Bibenzyls.—Bibenzyl was furnished to us by Dr. Kenji Kawoka. The **3,3′-dichloro-**, **4,4′-dichloro-**, and **4,4′-dimethylbibenzyl** were prepared from the corresponding benzyl bromides using the procedure of Boekelheide, *et al.*[16] The **4,4′-dimethoxybibenzyl** was prepared by reaction of *p*-methylanisole with *tert*-butyl peroxide. The physical properties of all of the bibenzyls corresponded to those previously available in the literature,[16-18] and the nmr spectra were consistent with structure.

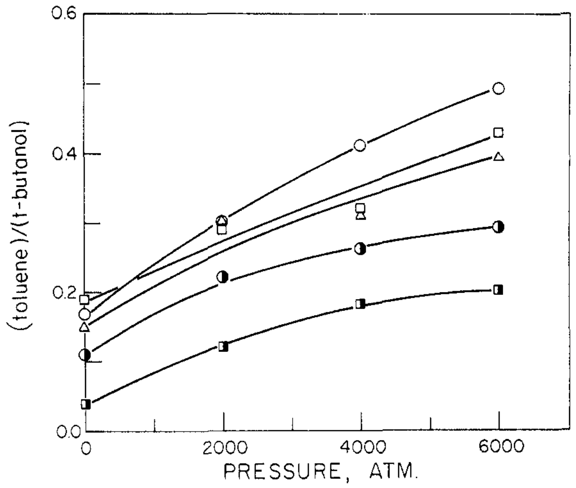

Figure 2.—Pressure dependence of the toluene/*tert*-butyl alcohol product ratio from decomposition of the *m*-Cl- (□), *p*-Cl- (Δ), H- (O), *p*-CH$_3$- (◑), and *p*-MeO- (◨) substituted *tert*-butyl phenylperacetates.

High Pressure Apparatus.—A complete description of the apparatus and experimental techniques has been presented.[3]

Product Analyses.—The products were determined by glpc analyses of completely reacted samples of the peresters in cumene using an F & M Model 700 gas chromatography instrument with WX filaments equipped with an F & M Model 240 power proportioning temperature programmer. The instrument contained a matched pair of 6 ft × 1/8 in. columns packed with 10% SE-30 on 80–100 AWDMCS-700; helium was the carrier gas. For all analyses the columns were held at 65° for 4 min after sample injection and then programmed to 220° at a rate of 10°/min.

Products (Table I) were identified by comparison with authentic samples and quantitatively determined by comparison with standard solutions containing authentic samples, with the exception of the benzylcumyls and *p*-methoxybenzyl *tert*-butyl ether.

A sample containing unsubstituted benzylcumyl along with bibenzyl and bicumyl was prepared by decomposition of *tert*-butyl peroxide in a mixture of toluene and cumene. This permitted assignment of the benzylcumyl retention time for studies of *tert*-butyl phenylperacetate but precluded quantitative yield measurements. The quantitative data presented for benzylcumyl were calculated using an average of the area ratio–molar ratio proportionality factors for bibenzyl and bicumyl. The latter procedure was also used for the substituted benzylcumyls, and their assignments were based on an elimination process. Separate peaks for the benzylcumyls in the *p*-Cl and *p*-CH$_3$ systems were not observed. They are assumed to overlap the corresponding bibenzyl peaks because of the large apparent areas for the latter (see Table I).

Registry No.—1 (X = *m*-Cl), 27396-17-4; 1 (X = *p*-Cl, 27396-18-5; 1 (X = H), 3377-89-7; 1 (*X* = *p*-CH$_3$), 27396-20-9; 1 (X = *p*-OMe), 27396-21-0.

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