# Mechanisms of Induced Decomposition. I. Reactivity of Di-*tert*-butylperoxy Homoterephthalate[1]

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Di-*tert*-butylperoxy homoterephthalate (6) reacts in toluene at 85° to give the perester products derived from the *p*-*tert*-butylpercarboxybenzyl radical 5. Calculations show that radical 5 has an average steady-state lifetime of $6 \times 10^{-3}$ sec at 50% reaction, without undergoing observable intramolecular, induced decomposition. The rate constant of reaction of 6 in cumene at 79.6° is $2.38 \times 10^{-5}$ $sec^{-1}$, which by comparison with the rates of reaction of other substituted phenylperacetates leads to a $\sigma^+$ value of 0.51 for the *p*-carbo-*tert*-butylperoxy substituent.

Induced decomposition is a pervasive phenomenon in the reactions of free radical precursors, and is most commonly considered[3] as the reaction of radicals derived from the radical source with the source itself, thereby accelerating the consumption of the precursor. The classic case of this process is the thermolysis of benzoyl peroxide in a solvent such as diethyl ether which possesses abstractable hydrogens (eq 1–3).[4] This example has been shown by kinetic studies,[4a-c] product isolation,[4d] and isotope labeling[4e] to occur by

$$PhC(=O^*)OOC(=O^*)Ph \xrightarrow{\Delta} 2PhC\overset{*}{O}_2\cdot \quad (1)$$

$$PhC\overset{*}{O}_2\cdot + CH_3CH_2OEt \longrightarrow PhC\overset{*}{O}_2H + CH_3\dot{C}HOEt \quad (2)$$

$$CH_3\dot{C}HOEt + PhC(=O^*)OOC(=O^*)Ph \longrightarrow PhC(=O^*)OCH(CH_3)OEt + PhC\overset{*}{O}_2\cdot \quad (3)$$

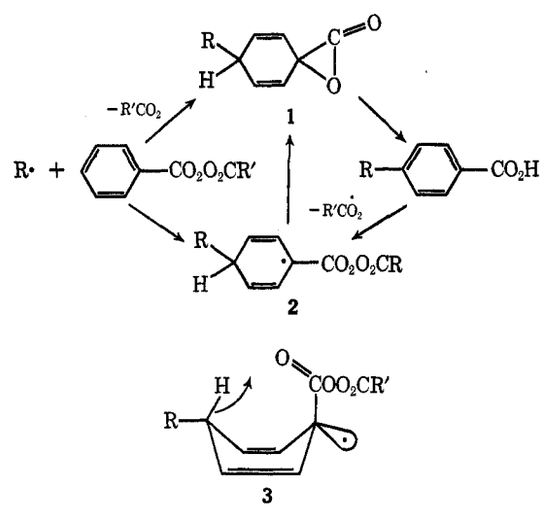
initial thermal cleavage of the benzoyl peroxide to form benzoyloxy radicals, which abstract hydrogen from the solvent to give $\alpha$-ethoxyethyl radicals, which displace at peroxidic oxygen to form an ester and another benzoyloxy radical. This induced decomposition constitutes an $S_H2$ displacement at peroxidic oxygen,[5] and numerous cases of such intermolecular reactions have been reported for diacyl peroxides, peresters, dialkyl peroxides, and perhaps other initiators.[5]

Another type of intermolecular, radical-induced decomposition involves bimolecular hydrogen atom transfer, for example to di-*tert*-butyl peroxide (eq 4).[5,6] A related process is the direct reaction between two nonradicals to give radical products ("molecule-induced homolysis").[7]

$$R_2\dot{C}OH + \textit{tert}\text{-BuOO-}\textit{tert}\text{-Bu} \longrightarrow R_2C{=}O + \textit{tert}\text{-BuOH} + \textit{tert}\text{-Bu}\dot{O} \quad (4)$$

Radical additions to benzoyl peroxides lead to induced decomposition,[8] and this is considered (Scheme I) to occur either *via* a concerted process giving an

SCHEME I




$\alpha$-lactone 1 directly,[8a-c] or by an initial addition and subsequent reaction of the intermediate $\alpha$-percarboxy radical 2.[8d,e] The latter process itself could occur by formation of the $\alpha$-lactone or by transannular hydrogen transfer as shown in structure 3.[8d] The case for the concerted addition–cleavage reaction rests most strongly on the lack of meta substitution in the reaction, suggesting acceleration of para attack.[8a,b] However, if meta attack were reversible, whereas ortho and para substitution led to formation of substitution products, the reaction could be nonconcerted, and reversible addition of benzoyloxy radicals to benzene is known.[9]

(1) Presented at the 160th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1970, Abstracts, ORGN 160. For part II, see ref 2. Supported by the U. S. Army Research Office, Durham, N. C.

(2) D. L. Cable, J. A. Ernst, and T. T. Tidwell, 162nd National Meeting of the American Chemical Society, Washington, D. C., Sept. 1971, Abstracts, ORGN 137; manuscript in preparation.

(3) (a) W. A. Pryor, "Free Radicals," McGraw-Hill, New York, N. Y., 1966, p 82; (b) C. Walling, "Free Radicals in Solution," Wiley, New York, N. Y., 1957, pp 475–480; (c) E. S. Huyser, "Free-Radical Chain Reactions," Wiley, New York, N. Y., 1970, Chapter 10.

(4) (a) K. Nozaki and P. D. Bartlett, *J. Amer. Chem. Soc.*, **68**, 1686 (1946); (b) W. E. Cass, *ibid.*, **68**, 1976 (1946); (c) P. D. Bartlett and K. Nozaki, *ibid.*, **69**, 2299 (1947); (d) W. E. Cass, *ibid.*, **69**, 500 (1947); (e) D. B. Denny and G. Feig, *ibid.*, **81**, 5322 (1959).

(5) K. U. Ingold and B. P. Roberts, "Free-Radical Substitution Reactions," Wiley, New York, N. Y., 1971.

(6) (a) E. S. Huyser and C. J. Bredeweg, *J. Amer. Chem. Soc.*, **86**, 2401 (1964); (b) E. S. Huyser and A. A. Kahl, *J. Org. Chem.*, **35**, 3742 (1970); (c) W. F. Smith, Jr., and B. W. Rossiter, *Tetrahedron*, **25**, 2059 (1969); (d) D. F. De Tar, *J. Amer. Chem. Soc.*, **89**, 4058 (1967).

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(8) (a) C. Walling and E. S. Savas, *J. Amer. Chem. Soc.*, **82**, 1738 (1960); (b) C. Walling and Ž. Čekovič, *ibid.*, **89**, 6681 (1967); (c) J. E. Leffler and R. G. Zepp, *ibid.*, **92**, 3713 (1970); (d) J. I. G. Cadogan, D. H. Hey, and P. G. Hibbert, *J. Chem. Soc.*, 3939 (1965); (e) D. F. De Tar and C. Weis, *J. Amer. Chem. Soc.*, **78**, 4296 (1957).

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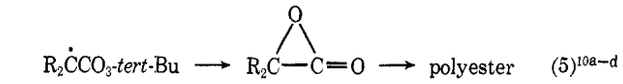
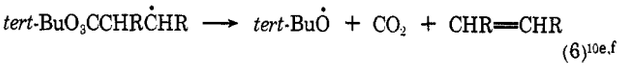
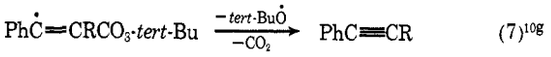
Intramolecular, induced decompositions between radical sites and acylperoxy functions have also been recorded (eq 5–9).[10] In these cases the radical was produced by atom abstraction, radical addition, or homolysis at another position one to four atoms removed in the molecule. For $\alpha$-acylperoxy radicals lactone formation is the characteristic reaction (eq 5),



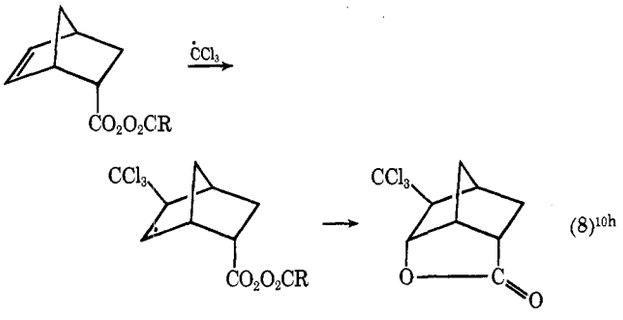
(5)[10a–d]



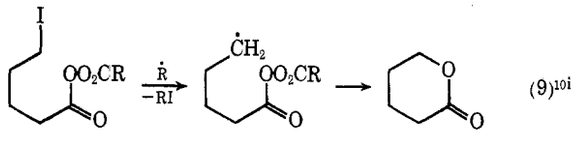
(6)[10e,f]



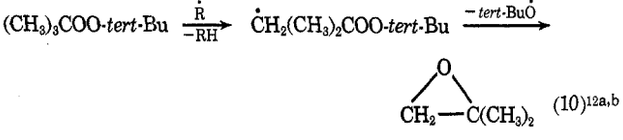
(7)[10g]



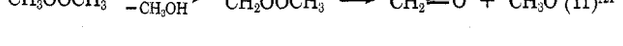
(8)[10h]



(9)[10i]



(10)[12a,b]



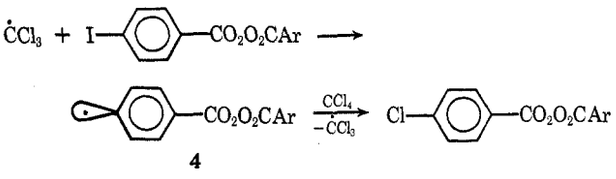
(11)[12f]

as was found in the case of additions to aromatic rings.[8] Radicals in $\beta$ positions lead to decarboxylative elimination (eq 6–7) whereas $\gamma$ and $\delta$ radicals lead to the formation of stable lactones (eq 8–9). In long-chain bisperesters, the peroxy groupings undergo reaction independently without induced decomposition if they are sufficiently removed from one another.[11] Dialkyl peroxides (eq 10, 11)[12] and hypochlorites[13] also give intramolecular induced decomposition where radicals are produced by abstraction.

Intramolecular analogies to "molecule-induced homolysis," in which substituents assist homolysis by anchimeric participation, exist in ortho-substituted *tert*-butylperoxy benzoates[14] and 5-aryl-4-pentenoyl peroxides.[15]

Azo compounds have also been observed to undergo radical-induced homolysis by a variety of mechanisms.[16]

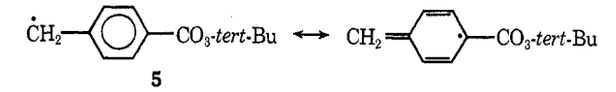
A notable case of a free radical substituted with a percarboxylate function which does not undergo induced decomposition is the radical **4** generated from



**4**

iodine atom abstraction from *p*-iodobenzoyl peroxide.[17] This radical survives for a sufficiently long period to abstract a chlorine atom from the solvent.

The prevalence of radical-induced decomposition, and its importance in the understanding of the properties of initiators, led us to initiate a study of the scope of this reaction. The present investigation, and that reported in part II,[2] deal with peresters.[18,19] Specifically, we chose to examine the reactivity of the *p*-*tert*-butylpercarboxybenzyl radical (**5**), which can interact through its $\pi$ system to place electron spin density at the $\alpha$ position to the peracyl function, analogous to the structure which results from addition to the para position of benzoyl peroxides leading to induced decomposition (Scheme I). In the case of **5**



**5**

it was of interest to determine if the driving force for induced decomposition was sufficient to overcome the resonance stabilization of the benzyl radical.

## Results

As a precursor to radical **5** we prepared di-*tert*-butylperoxy homoterephthalate (**6**) by reaction of the acid chloride **7** of homoterephthalic acid (**8**)[20] with *tert*-

(10) (a) P. D. Bartlett and L. B. Gortler, *ibid.*, **85**, 1864 (1963); (b) P. D. Bartlett and J. M. McBride, *ibid.*, **87**, 1727 (1965); (c) L. B. Gortler and M. D. Saltzman, *J. Org. Chem.*, **31**, 3821 (1966); (d) C. Rüchardt and H. Schwarzer, *Chem. Ber.*, **99**, 1861 (1966); (e) L. M. Bobroff, L. B. Gortler, D. J. Sahn, and H. Wiland, *J. Org. Chem.*, **31**, 2678 (1966); (f) E. N. Cain, R. Vukov, and S. Masamune, *J. Chem. Soc. D*, 98 (1969); (g) N. Muramoto, T. Ochiai, O. Simamura, and M. Yoshida, *ibid.*, 717 (1968); (h) H. Hart and F. J. Chloupek, *J. Amer. Chem. Soc.*, **85**, 1155 (1963); (i) R. G. Woolford and R. N. Gedye, *Can. J. Chem.*, **45**, 291 (1967).

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(15) R. C. Lamb, L. P. Spadafino, R. G. Webb, E. B. Smith, W. E. McNew, and J. G. Pacifici, *ibid.*, **31**, 147 (1966).

(16) (a) D. S. Malament and J. M. McBride, *J. Amer. Chem. Soc.*, **92**, 4586 (1970); (b) C. J. Michejda and W. P. Hoss, *ibid.*, **92**, 6298 (1970); (c) W. P. Neuman and H. Lind., *Chem. Ber.*, **101**, 2837 (1968); (d) W. P. Neuman, H. Lind, and G. Alester, *ibid.*, **101**, 2845 (1968); (e) D.-R. Chang and O. K. Rice, *Int. J. Chem. Kinet.*, **1**, 171 (1969); (f) D. H. Slater, S. S. Collier, and J. G. Calvert, *J. Amer. Chem. Soc.*, **90**, 268 (1968); (g) H. van Zwet, J. Reiding, E. C. Kooyman, *Recl. Trav. Chim. Pays-Bas*, **90**, 21 (1971).

(17) (a) M. M. Schwartz and J. E. Leffler, *J. Amer. Chem. Soc.*, **90**, 1368 (1968); (b) *ibid.*, **93**, 919 (1971).

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SCHEME II

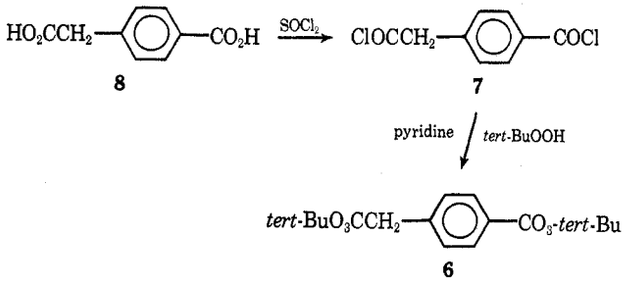
PRODUCT ANALYSIS FROM DI-*tert*-BUTYLPEROXY HOMOTEREPHTHALATE (6)

$$6 \xrightarrow[\text{toluene}]{85^\circ} CO_2 + \textit{tert}\text{-BuOH} + CH_4 + \text{acetone} + \text{bibenzyl} + \textbf{9–12}$$

$$\text{bibenzyl} + \textbf{9–12} \xrightarrow{H_2,\ \text{Pd–C}} \text{bibenzyl} + \text{soluble acids} + \textbf{13}\ (\text{precipitate})$$

$$\textbf{13}\ (\text{trace}) + \text{bibenzyl} + \text{soluble acids} \xrightarrow{CH_2N_2} \textbf{14} + \textbf{15} + \text{methyl toluate} + \text{bibenzyl} + \textbf{27}$$

$$\text{bibenzyl} + \textbf{9–12} \xrightarrow{LiAlH_4} \textbf{16} + \textbf{17} + p\text{-MePhCH}_2\text{OH} + \text{bibenzyl}\ (\textbf{18}\ \text{lost})$$




butyl hydroperoxide and pyridine. New compounds **6** and **7** were characterized by spectral properties, elemental analyses, and conversion to known compounds (*vide infra*). Hammering, scratching, and heating of **6** produced no explosive behavior.

The rates of thermal decomposition of **6** were measured in toluene and cumene solvents by following the decrease of the peracetate carbonyl in the infrared. The peracetate and perbenzoate carbonyl bands were well resolved and at the temperatures used the peracetate band completely disappeared with good first-order kinetics, whereas no decrease was observed in the perbenzoate band. The observed rate constants and derived activation parameters are summarized in Table I, along with suitable data for comparison.

TABLE I

RATES OF THERMAL DECOMPOSITION OF PERESTERS

| Perester | Temp, °C | Solvent | $k_1$, sec$^{-1}$ × 10$^6$ [a] | $\Delta H^*$, kcal/mol | $\Delta S^*$, eu |
|---|---|---|---|---|---|
| **6** | 100.5 | Toluene | 30.9 | 29.2[b] | 3.1[b] |
| **6** | 80.3 | Toluene | 2.80 | | |
| **6** | 70.6 | Toluene | 0.944 | | |
| **6** | 79.6 | Cumene | 2.38 | | |
| PhCH$_2$CO$_3$-*tert*-Bu | 79.6 | Cumene | 7.21 | | |
| PhCH$_2$CO$_3$-*tert*-Bu[c] | 79.6 | Cumene | 6.77[c] | 27.9[d] | 2.0[d] |

[a] Average of two runs at each temperature, maximum deviation ±2.5%. [b] In toluene. Standard deviations of $\Delta H^*$ and $\Delta S^*$ are 0.03 kcal/mol and 0.07 eu, respectively. [c] Reference 23b. [d] Reference 23a, activation parameters from reaction in chlorobenzene.

Products were determined for the reaction of **6** at 85° in toluene and are given in Table II. A schematic diagram of the product separation is given in Scheme II. Gaseous products were analyzed by absorption of $CO_2$ on Ascarite and identification of the residual gas as methane by mass spectrometry. The only volatile products, *tert*-butyl alcohol and acetone, were analyzed by vpc. A small quantity of acids was detected in the nonvolatile residue by ir and by bicarbonate extraction, and constituted no more than 3% of the total. The acidic product was esterified by diazomethane, but no methyl toluate could be detected by vpc. The residual product consisted of a mixture of bibenzyl, *tert*-butylperoxy *p*-toluate (**9**), *p*-carbo-*tert*-butylperoxybibenzyl (**10**), and *tert*-butylperoxy *p*-(*tert*-butoxymethyl)benzoate (**11**).[21] This mixture was converted to the corresponding acids by hydrogenolysis with Pd/C catalyst. *p,p'*-Dicarboxybibenzyl (**13**) precipitated and was weighed to give the yield of the corresponding bisperester **12**, and the remaining acids were treated with diazomethane to give the methyl esters, which were analyzed by vpc to give the yields of **9–11**. Control experiments on authentic samples of **9** showed that this reaction proceeded in at least 90% yield, although the authentic sample of **11** was partially converted to toluic acid under these conditions. To confirm the source of the 5.2% of *p*-methyl toluate from the hydrogenolysis, a mixture of **9–12** from a separate reaction of **6** was treated with $LiAlH_4$, which converted the perester groupings to benzyl alcohols, but as shown by a control experiment did not disturb the *tert*-butyl ether. The yields of benzyl alcohols (determined by vpc analysis) were consistently lower than those from the hydrogenolysis, but showed 2.5% benzyl alcohol, corresponding to the minimum yield of **9** from **6**. The lower net yields were presumably caused by loss of material in the gelatinous precipitate formed during work-up of the $LiAlH_4$ reaction. An nmr of the reaction mixture from **6** after removal of the volatile material showed only peaks assigned to bibenzyl and **9–12**.

TABLE II

PRODUCTS FROM THERMAL DECOMPOSITION OF DI-*tert*-BUTYLPEROXY HOMOTEREPHTHALATE AT 85° IN TOLUENE

| Product | Per cent, mol/mol **6** × 100 |
|---|---|
| $CO_2$ | 99.0 |
| $CH_4$ | 6.9[a] |
| Acetone | 6.9 |
| *tert*-BuOH | 86.6 |
| *p*-MePhCO$_3$-*tert*-Bu (**9**) | 5.2[b,c] |
| *p*-PhCH$_2$CH$_2$PhCO$_3$-*tert*-Bu (**10**) | 27.8[b,c] |
| Bibenzyl | *d* |
| *tert*-BuOCH$_2$PhCO$_3$-*tert*-Bu (**11**) | 17.1[b,c] |
| *p*-(CH$_2$PhCO$_3$-*tert*-Bu)$_2$ (**12**) | 16.9[c] |
| Acids | ~2–3 |

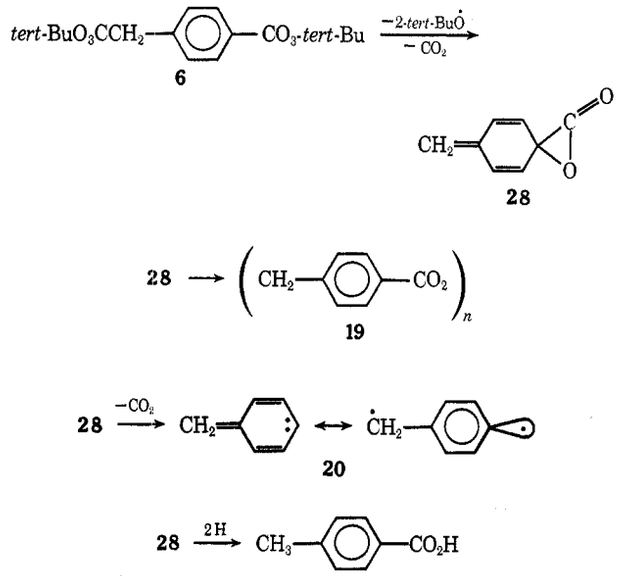
[a] Taken as equal to acetone. [b] Yields of **9**, **10**, and **11** from the work-up using $LiAlH_4$ were 2.5, 18.1, and 13.8%, respectively. [c] The sum of **9**, **10**, **11**, and 2 × **12** is 83.9, and equals the total residual perester. [d] The yield of bibenzyl corresponded to 17.1% (mol/mol) relative to **6**.

(21) These were identified in a separate experiment without prior base extraction. Due to the low solubility of several of the compounds present, it was advantageous to minimize handling of the solution.

## Discussion

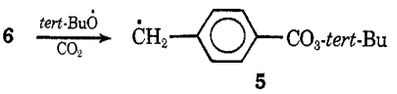
There are several reaction paths *a priori* open to **6**. One possibility would be concerted cleavage of both peroxide linkages to form the $\alpha$-lactone **28**, which might react in several ways (Scheme III), for example

SCHEME III



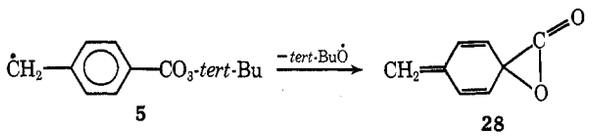

polymerizing to form poly(*p*-carboxybenzyl alcohol) (**19**), decarboxylation to form the diradical carbene **20**, or abstraction of two hydrogens to form toluic acid. However, the results exclude any significant contribution from this pathway. Thus, the reactivity of **6** is that expected for a normal phenylperacetate with an electron-withdrawing para substituent, with no evidence for an accelerated concerted reaction. None of the observed products was derived from reaction at the perbenzoate function. Polymer **19** was also prepared by an independent route and could not be detected in the product, although it is so insoluble that even a small amount would have been easily observed.

It may be concluded that **6** undergoes thermolysis



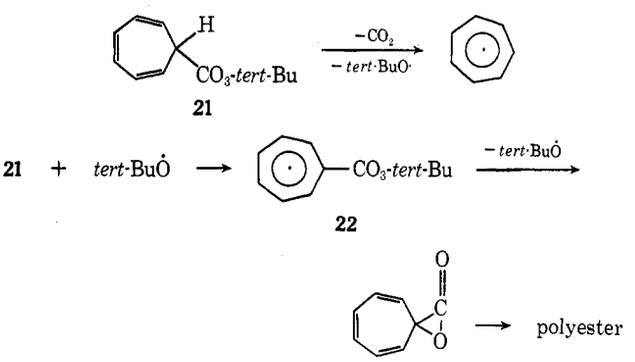

of the benzylic perester grouping to form **5**, presumably by an unimolecular two-bond scission.[22] Furthermore, **5** is sufficiently long-lived to undergo dimerization as well as coupling with solvent-derived benzyl radicals. A mechanism to account for the observed products is given in Scheme IV, where $k_1$ is the observed rate constant for disappearance of **6**, $f$ is the fraction of the original cage pair which dissociates to free radicals, and $k_2$ is the rate constant for dimerization of **5**.

The survival of **5** so that it could undergo dimerization is of interest, because of the potential route for induced decomposition available to this compound to



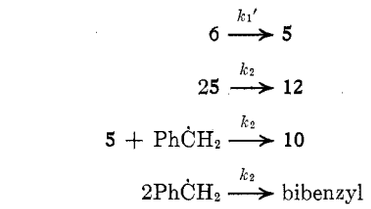

form the $\alpha$-lactone **28**. As discussed before, there is no evidence that any of the reaction proceeded through this intermediate, although $\alpha$-lactone formation is the principal reaction pathway for other $\alpha$-percarboxy radicals.[8,10a-d] The contribution of the resonance form of **5** which places the unpaired electron at the para position is certainly significant, as the esr spectrum of the benzyl radical reveals a hyperfine splitting of the para hydrogen of 6.3 G, and the observed hyperfine interactions are proportional to spin densities calculated by molecular orbital theory for this radical, with a calculated spin density at the para position of 0.231.[24]

It is interesting that **5** is isomeric to radical **22**, which




is formed by hydrogen abstraction from the cycloheptatrienyl perester **21** on thermal decomposition of the latter in chlorobenzene.[10d] However, **22** undergoes dimerization only to the extent of about one-fourth of the amount of polyester formed.[10d] The facile induced decomposition of **22** relative to **5** is striking, especially in view of the significant resonance stabilization of the cycloheptatrienyl radical (21 kcal/mol relative to cycloheptatriene).[25] The tropylium ion stabilization of the zwitterionic form of the $\alpha$-lactone may aid its formation from **22**.

The reactions of the radicals **5** which escape from the solvent cage can be represented as shown ($k_1' = fk_1$) if the rates of combination of **5** with **5**, **5** with benzyl




radicals, and benzyl radicals with benzyl radicals are the same. This is apparently true, because if equal numbers of **5** and benzyl radicals are formed the statistical distribution of **12**, **10**, and bibenzyl would be 1:2:1, and the actual yields are 1.00:1.65:1.02. It is possible to calculate the average steady-state lifetime for which the radical **5** survives without induced decomposition from the above scheme, using the relation-

(22) There is some controversy as to whether phenylperacetates with electron-withdrawing para substituents react by concerted two-bond[23a,b,c] scission or whether there is an appreciable contribution from one-bond scission, followed by decarboxylation.[23d] Either pathway would lead to **5**.

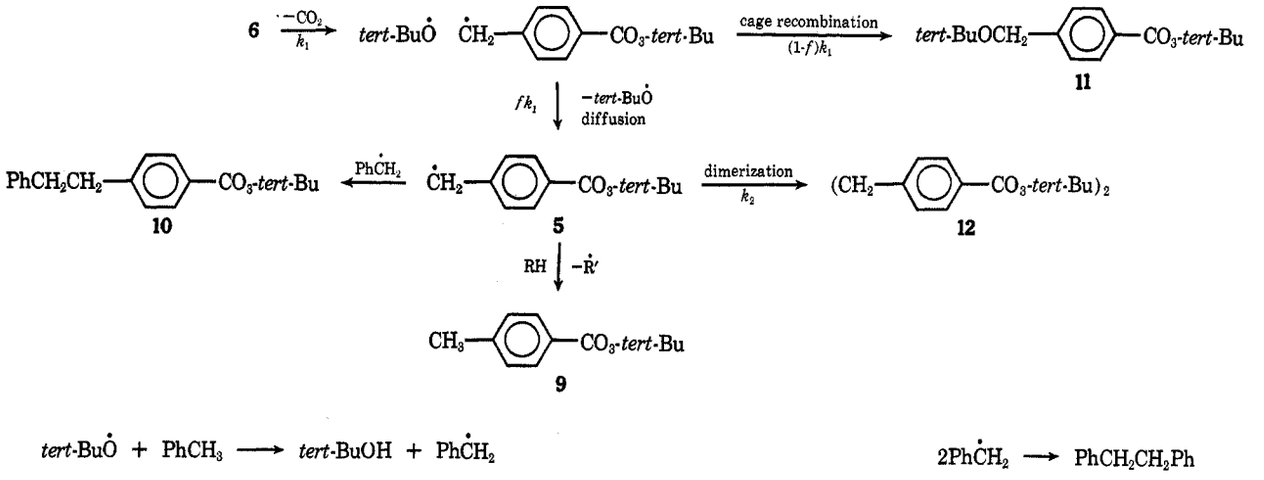
(23) (a) P. D. Bartlett and C. Rüchardt, *J. Amer. Chem. Soc.*, **82**, 1756 (1960); (b) R. C. Neuman, Jr., and J. V. Behar, *J. Org. Chem.*, **36**, 654 (1971); (c) T. Koenig, J. Huntington, and R. Cruthoff, *J. Amer. Chem. Soc.*, **92**, 5413(1970); (d) W. A. Pryor and K. Smith, *ibid.*, **92**, 5403 (1970).

(24) W. T. Dixon and R. O. C. Norman, *J. Chem. Soc.*, 4857 (1964).

(25) G. Vincow, H. J. Dauben, Jr., F. R. Hunter, and W. V. Volland, *J. Amer. Chem. Soc.*, **91**, 2823 (1969).

SCHEME IV

FORMATION AND REACTIONS OF *p*-*tert*-BUTYLPERCARBOXYBENZYL RADICAL (5)




$$tert\text{-}BuO\cdot + PhCH_3 \longrightarrow tert\text{-}BuOH + PhCH_2\cdot$$

$$2PhCH_2\cdot \longrightarrow PhCH_2CH_2Ph$$

ship (average lifetime) = (steady-state concentration of **5**)/(rate of disappearance of **5**). Thus, $[5] = (k_1'[6]/3k_2)^{1/2}$ and the average lifetime $\tau = (3k_1' \cdot k_2[6])^{-1/2}$.

The rate constant $k_2$ for combination of benzyl radicals in benzene at 25° has been reported[26] as $4.1 \times 10^9\ M^{-1}\ sec^{-1}$, less than a factor of two smaller than the calculated[26] diffusion-controlled rate constant ($7.2 \times 10^9\ M^{-1}\ sec^{-1}$). Equation 12 was used for

$$k = \frac{4\pi r D_{rel}(N/1000)}{1 + 4\pi r D_{rel}(N/1000k_c)} \qquad (12)$$

calculating the rate constant, where $D_{rel}$ is the diffusion coefficient of the benzyl radical. This diffusion coefficient was taken to be the same as that for toluene, and was estimated graphically from a plot of diffusion coefficient *vs.* the reciprocal of the solvent viscosity for a series of linear alkanes.[27a] Following this procedure and using the viscosity extrapolated for toluene at 85° (0.312 cP) from data at lower temperatures[27b] gives a diffusion coefficient of $4.36 \times 10^{-5}$ cm²/sec for the benzyl radical at 85°. If the only difference in $k_2$ for benzyl radicals in benzene at 25° and toluene at 85° arises from the difference in diffusion coefficients, eq 12 can be used to correct the reported value of $k_2$ given above to a value of $6.9 \times 10^9\ M^{-1}\ sec^{-1}$ for benzyl radicals at 85°, and the same value can be taken for the dimerization of **5**. At 85° the interpolated $k_1$ for **5** is $5.26 \times 10^{-5}\ sec^{-1}$; so $k_1'$ is 0.83 times this or $4.36 \times 10^{-5}\ sec^{-1}$. The average lifetimes of **5** under these conditions and at the initial concentration of **6** used (0.061 *M*) are $5 \times 10^{-3}$ sec at 25% reaction and $6 \times 10^{-3}$ sec at 50% reaction.

The failure of **5** to undergo induced decomposition during its lifetime of about $10^{-2}$ sec surely reflects at least in part the loss of resonance energy that would result from conversion of **5** to **28**. By contrast **22** undergoes induced decomposition due to its lower loss in resonance energy, and perhaps also to a slower rate of dimerization of **22**. At reduced concentrations the lifetime of **5** could be prolonged, unless side reactions with solvent intervened, and the formation of **28** might compete with the diffusion-controlled dimerization.

In an independent study[17b] radical **5** and some related radicals have been generated by NBS bromination of **9** and other peresters and diacyl peroxides. Benzyl bromides were formed, without decomposition of the peroxides, in harmony with the results of this investigation. The mechanism of NBS bromination is apparently now established as involving bromine atoms as the chain-carrying agent,[28] but, since the rate constants for the individual steps are not known, it is not now feasible to estimate the lifetime of **5** under these conditions. In a related study the decomposition of toluyl peroxide in bromotrichloromethane was proposed to involve formation of a radical peroxide similar to **5**, which abstracted a bromine atom from the solvent.[8d]

Using the measured rate constant for **6** in cumene at 79.6°, and the plot of log *k vs.* $\sigma^+$ for substituted phenylperacetates in cumene of Neuman and Behar,[23b] a $\sigma^+$ constant of 0.51 is derived for the *p*-carbo-*tert*-butylperoxy substituent. This compares to the value of 0.48 cited[29] for ester functions.

## Experimental Section

**General.**—Elemental analyses were performed by the Galbraith Laboratories, Knoxville, Tenn., and Mead Laboratories, Amherst, Mass. Qualitative infrared spectra wre determined using a Perkin-Elmer 337 spectrophotometer. Nmr spectra were measured using a Varian A-60 instrument with TMS as an internal standard. Melting points (open capillary) and boiling points are not corrected. Quantitative vapor phase chromatographic (vpc) analyses were carried out using a Varian-Aerograph 1800 temperature-programmed instrument and a Disc integrator mounted on a Sargent SRG recorder.

**Reagents.**—Cumene and toluene were purified by the procedure published for cumene.[30] Pyridine was distilled from BaO and stored over KOH. Pentane was distilled from calcium hydride and stored over sodium. Lucidol 90% *tert*-butyl hydroperoxide was purified by dissolving in pentane, extracting with saturated NaCl, drying over $MgSO_4$, and evaporating the solvent at aspirator pressure and 25°. The hydroperoxide was distilled twice through a 12-cm glass helix packed column and

(26) R. D. Burkhart, *J. Amer. Chem. Soc.*, **90**, 273 (1968).

(27) (a) P. Chang and C. R. Wilke, *J. Phys. Chem.*, **59**, 592 (1955); (b) "Handbook of Chemistry and Physics," 51st ed, Chemical Rubber Publishing Co., Cleveland, Ohio, p F-42.

(28) J. H. Incremona and J. C. Martin, *J. Amer. Chem. Soc.*, **92**, 627 (1970).

(29) C. D. Ritchie and W. F. Sager, *Progr. Phys. Org. Chem.*, **2**, 323 (1969).

(30) P. D. Bartlett, E. P. Benzing, and R. E. Pincock, *J. Amer. Chem. Soc.*, **82**, 1762 (1960).

the fraction boiling at 26–30° (13 Torr) was collected, $n^{23}D$ 1.4002. Iodometric titration[31] indicated a purity of 98.9%. Tetrahydrofuran was distilled from $LiAlH_4$ into the reaction vessels just prior to use.

**Homoterephthalic acid** (**8**) was prepared by the reported method in overall 25% yield, mp 238–240° (lit.[20] mp 239–241°). Later samples were prepared by custom synthesis at Columbia Organic Chemicals Co.

**Homoterephthalyl chloride** (**7**) was prepared by adding 138 ml (225 g, 1.9 mol) of thionyl chloride to 10 g (0.0056 mol) of **8**, stirring for 24 hr at 25°, and then refluxing for 4 hr. The thionyl chloride was removed under vacuum, leaving a red oil which gave 8.2 g (68%) of **7** as white crystals from pentane: mp 35–37°; ir ($CCl_4$) 1790 and 1815 $cm^{-1}$ (C=O); nmr $\delta$ 4.15 (s, 2, $ArCH_2$) and 7.66[32] (quartet, 4, $J$ = 8 Hz, $\Delta$ 0.72).

*Anal.* Calcd for $C_9H_6Cl_2O_2$ (217.05): C, 49.80; H, 2.66. Found: C, 49.53; H, 2.66.

**Di-*tert*-butylperoxy homoterephthalate** (**6**) was prepared by stirring 8.2 g (0.0038 mol) of **7** and 27.2 g (0.0302 mol) of *tert*-butyl hydroperoxide in 186 ml of 7.5:1 pentane–ether solution in a dry flask under $N_2$ at −5° for 10 hr. Then 23.8 g (0.0303 mol) of pyridine in 25 ml of pentane was added dropwise over 30 min with rapid stirring. A transient violet color was obtained on addition which faded to yellow. After stirring for 4 hr at −5° the solution was filtered and washed successively with water, cold 5% $H_2SO_4$, cold 5% NaOH, and water and then dried over $MgSO_4$ at 0°. The solvent was removed *in vacuo* to give a clear oil which was crystallized from ether–pentane at 0° to give 6.2 g (0.0019 mol, 51%) of **6**, mp 94–96°. This compound does not decompose on melting, scratching, or shock, but detonates without report on flash pyrolysis: ir ($CCl_4$) 1780 and 1770 $cm^{-1}$ (peracetate and perbenzoate C=O, respectively); nmr ($CCl_4$) $\delta$ 1.21 (s, 9, peracetate *tert*-Bu), 1.35 (s, 9, perbenzoate *tert*-Bu), 3.55 (s, 2, $ArCH_2$), and 7.52[32] (quartet, 4, $J$ = 8 Hz, $\Delta$ 0.52).

*Anal.* Calcd for $C_{17}H_{24}O_6$ (324.38): C, 62.95; H, 7.46. Found: C, 63.18; H, 7.58.

***tert*-Butyl *p*-(*tert*-butoxymethyl)benzoate** (**24**) was obtained by addition of 5.8 g (0.052 mol) of potassium *tert*-butoxide in 125 ml of anhydrous *tert*-butyl alcohol to 5.5 g (0.024 mol) of $\alpha$-bromotoluyl chloride[33] in 50 ml of *tert*-butyl alcohol at 75°. The mixture was refluxed for 8 hr, stirred for 12 hr at 25°, poured into 500 ml of water, extracted with ether, and dried over $MgSO_4$. After the ether was evaporated the residue was distilled, yielding 3.5 g (56%) of **24**: bp 113–116° (0.6 Torr); ir ($CCl_4$) 1725 $cm^{-1}$ (C=O); nmr ($CCl_4$) $\delta$ 1.35 (s, 9, $CH_2O$ *tert*-Bu), 1.66 (s, 9, $CO_2$ *tert*-Bu), 4.48 (s, 2, $ArCH_2$), and 7.57[32] (quartet, 4, $J$ = 8 Hz, $\Delta$ 0.58).

***p*-(*tert*-Butoxymethyl)benzoic acid** (**23**) was obtained by refluxing 3.5 g (0.00132 mol) of **24** with a solution of 2.1 g (0.0053 mol) of NaOH in 20% MeOH for 3 hr. After cooling the solution was acidified to yield 2.6 g of **23** as a white solid, mp 140–141° after recrystallization from aqueous ethanol. Treatment of 1.97 g of this material with excess diazomethane in ether at 0° and evaporation of the solvent gave 2 g of **methyl *p*-(*tert*)-butoxymethyl)benzoate** (**15**) which was recrystallized from hexane to give white plates: mp 135–137°; ir ($CCl_4$) 1735 $cm^{-1}$ (C=O); nmr ($CHCl_3$) $\delta$ 1.18 (s, 9, *tert*-Bu), 3.76 (s, 3, OMe), 4.35 (s, 2, $ArCH_2$), and 7.47[32] (quartet, 4, $J$ = 8 Hz, $\Delta$ 0.61).

***p*-(*tert*-Butoxymethyl)benzoyl chloride** (**25**) was prepared by addition of 1 equiv of aqueous NaOH to 3.85 g (0.00185 mol) of **23** in methanol. The methanol was removed under vacuum and benzene was added. After drying by distilling off part of the benzene, 30.2 g (0.0240 mol) of oxalyl chloride in 30 ml of dry benzene was added at 25°. After gas evolution ceased the mixture was refluxed for 30 min and the solvent was distilled away, leaving 4.1 g (98%) of crude **25**. Distillation gave a center fraction: bp 89–92° (0.25 Torr); ir ($CCl_4$) 1785 and 1765 $cm^{-1}$ (C=O); nmr ($CCl_4$) $\delta$ 1.25 (s, 9, *tert*-Bu), 4.43 (s, 2, $ArCH_2$), and 7.62[32] (quartet, 4, $J$ = 8 Hz, $\Delta$ = 0.60).

***tert*-Butylperoxy *p*-(*tert*-butoxymethyl)benzoate** (**11**) was obtained by dropwise addition of 3.1 g (0.0014 mol) of **25** in a solution of 5 ml of ether and 20 ml of pentane to a stirred mixture of 2.7 g (0.0030 mol) of 93% *tert*-butyl hydroperoxide and 2.4 g (0.0030 mol) of pyridine in 50 ml of pentane at 0°. After stirring for 4 hr at 0° the solution was filtered, washed with cold 10% KOH and then water, and dried, and the solvent was evaporated yielding a clear oil which was chromatographed on a 15-g Florisil with 5% ether–hexane. The first 100-ml eluent contained 1.1 g (0.004 mol, 29%) of **11** as a clear oil: ir ($CCl_4$) 1760 $cm^{-1}$ (C=O); nmr ($CCl_4$) $\delta$ 1.24 (s, 9, *tert*-$BuOCH_2$), 1.35 (s, 9, $CO_3$-*tert*-Bu), 4.40 (s, 2, $ArCH_2$), and 7.53[32] (quartet, 4, $J$ = 8 Hz, $\Delta$ 0.46).

*Anal.* Calcd for $C_{16}H_{24}O_4$ (280.37): C, 68.55; H, 8.63. Found: C, 68.62, H, 8.62.

***p*-(*tert*-Butoxymethyl)benzyl alcohol** (**17**) was obtained as the only product (vpc) from $LiAlH_4$ reduction of **24** in THF. Recrystallization from hexane gave white needles: mp 47–47.5°; nmr ($CCl_4$) $\delta$ 1.22 (s, 9, *tert*-Bu), 2.88 (broad s, 1, OH), 4.28 and 4.33 (each s, 2, $ArCH_2$), and 7.05 (s, 4, aromatic).

*Anal.* Calcd for $C_{12}H_{18}O_2$ (194.28): C, 74.19; H, 9.34. Found: C, 73.55; H, 9.02.

***p*-Carboxybibenzyl** (**26**) was prepared by the reported[34] procedure, mp 169–172° (lit.[34] mp 170–172°). Esterification with methanol and sulfuric acid gave the methyl ester **14**, bp 142° (0.6 Torr), which solidified on prolonged standing: mp 132–133°; nmr ($CCl_4$) $\delta$ 2.94 (s, 4, $CH_2CH_2$), 3.83 (s, 3, Me), 7.1 (m, 5, $C_6H_5$), and 7.37[32] (quartet, 4, $J$ = 8 Hz, $\Delta$ 0.73). Reduction of **14** by $LiAlH_4$ in THF gave ***p*-(hydroxymethyl)bibenzyl** (**16**) which after recrystallization from 3% benzene in hexane gave mp 67–68° (lit.[35] mp 57–58° *sic*); nmr ($CCl_4$) $\delta$ 1.76 (s, 1, OH), 2.90 (s, 4, $CH_2CH_2$), 4.52 (s, 2, $CH_2OH$), and 7.10 (br s, 9, aromatic).

*Anal.* Calcd for $C_{15}H_{16}O$ (212.29): C, 84.87; H, 7.60. Found: C, 85.00; H, 7.69

***p,p'*-Dicarboxybibenzyl** (**13**) was prepared by the reported[36] procedure as a white amorphous solid which did not melt below 320°. Treatment with diazomethane in ether at 5° gave the dimethyl ester **27**: mp 115–117° (lit.[37] mp 115–119°); nmr ($CCl_4$) $\delta$ 2.94 (s, 4, $CH_2CH_2$), 3.80 (s, 6, Me), and 7.43[32] (quartet, 4, $J$ = 8 Hz, $\Delta$ 0.74). Reduction of **27** with $LiAlH_4$ in refluxing THF gave ***p,p'*-di(hydroxymethyl)bibenzyl** (**18**), mp 151–154° (lit.[37] mp 157–159°).

***tert*-Butylperoxy *p*-toluate** (**9**) was prepared by the reported method.[38] ***p*-Methylbenzyl alcohol** was prepared by reduction of toluic acid with $LiAlH_4$, mp 57.5–58.5° (lit.[39] mp 61.0–62.1°).

**Poly(*p*-carboxybenzyl alcohol)** (**19**) was prepared by heating *p*-carboxybenzyl alcohol[40] in a sealed evacuated tube at 250° to give **19** as a brittle crystalline solid, mp 202–210° (lit.[41] mp 200–210°), insoluble in toluene, methylene chloride, and other common solvents and with an ir band (KBr) at 1725 $cm^{-1}$ (C=O).

**Kinetic Method.**—Rate runs were carried out by the infrared method.[42] Sample tubes were washed first with nitric acid, then ammonium hydroxide, and were thoroughly dried. In each tube was placed 0.5 ml of a 0.06 $M$ solution of perester and the tubes were sealed without degassing. Tubes were placed in the constant-temperature bath and after 15 min to equilibrate were removed at intervals. The transmittance of each sample between 1900 and 1650 $cm^{-1}$ was scanned using a Perkin-Elmer 621 spectrophotometer and 0.1-mm NaCl cells. Rate constants were calculated as the least-squares slope of 2.303 log $(A_t - A_\infty/A_0 - A_\infty)$ *vs.* time, where $A$ is the measured absorbance of the band at 1780 $cm^{-1}$. Reactions were followed for 60% reaction and gave no residual absorbance after 10 half-lives (taken as $A_\infty$).

**Product Studies.**—Gaseous, volatile, and nonvolatile products were determined in separate experiments. Gaseous and volatile product yields are the average of three separate determinations carried out using 0.8-g samples of **6** in 15 ml of degassed

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(32) The aromatic protons are a typical AA'XX' pair of perturbed doublets, and are reported as $\delta$ (midpoint of spectrum), $J$ (spacing of the doublets in Hz), and $\Delta$ (chemical shift difference between the midpoints of the two doublets in parts per million): L. M. Jackman and S. Sternhell, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," 2nd ed, Pergamon Press, New York, N. Y., 1969, pp. 134–137; D. H. Williams and I. Fleming, "Spectroscopic Methods in Organic Chemistry", McGraw-Hill, New York, N. Y., 1966, pp 120–122.

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(36) G. J. Sloan and L. R. Vaughan, *J. Org. Chem.*, **22**, 750 (1957).

(37) D. J. Cram and H. Steinburg, *J. Amer. Chem. Soc.*, **73**, 5691 (1951).

(38) A. T. Blomquist and I. A. Bernstein, *ibid.*, **73**, 5546 (1951).

(39) J. K. Kochi and G. S. Hammond, *ibid.*, **75**, 3443 (1953).

(40) W. S. Emerson and R. A. Heimsch, *ibid.*, **72**, 5152 (1950).

(41) J. G. Cook, J. T. Dickson, A. R. Lowe, and J. R. Whinfield, British Patent 604,985 (1948); *Chem. Abstr.*, **43**, P1223*g* (1949).

(42) P. D. Bartlett and P. R. Hiatt, *J. Amer. Chem. Soc.*, **80**, 1398 (1958).

toluene. The evacuated sample was sealed in a tube equipped with a break seal and placed in an 85° bath for 36 hr (10 half-lives); then the sample was opened on a vacuum line and the $CO_2$ was determined by absorption on Ascarite. Methane was identified by mass spectrometry. The products that were volatile at 25° and 0.05 Torr were collected in a Dry Ice cooled trap and made up to 25 ml with toluene. Cyclohexane was added as an internal standard and the vpc analysis (10 ft × $^3/_8$ in. 30% Carbowax 20M on Chromosorb W, 90°, 60 ml/min He) gave cyclohexane, acetone, *tert*-butyl alcohol, and toluene in that order. Identification was confirmed by isolation and spectral comparison with authentic samples.

In a separate experiment the product from 0.846 g (2.16 mmol) of **6** in 15 ml of toluene was treated as before, and 10 ml of toluene was removed by distillation. The residue was removed from the vacuum line and estimated to contain a 2.2% yield of acids (based on toluic acid) by comparison of the ir spectrum with those of authentic mixtures. This material was dissolved in 40 ml of ethanol and treated in the Brown[2] hydrogenator (1 atm of $H_2$, 5% Pd/C catalyst), 10 hr at 0°. The solution was filtered, the solvent was evaporated at room temperature, and the residue was dissolved in methylene chloride. An amorphous solid remained and after being rinsed several times with methylene chloride was identified as **13** (0.118 g, 0.44 mmol) by comparison with authentic material and conversion to the dimethyl ester **27**, also compared with authentic material. The methylene chloride solution was treated with excess diazomethane, made up to 25 ml, and dichlorobenzene was added as an internal standard. Vpc analysis (10 ft × $^3/_8$ in. 30% SE-30 on Chromosorb W, 75 ml/min He, programmed from 170 to 310°) gave the following peaks in order: dichlorobenzene (170°), *p*-methyl toluate (225°), bibenzyl (225°), **15** (225°), **14** (310°), and **27** (0.03 mmol) (310°).

In another experiment the product from 0.750 g (2.28 mmol) of **6** in 15 ml of toluene was concentrated under vacuum to 5 ml, and added very slowly to a solution of 1 g (0.03 mol) of powdered $LiAlH_4$ in 40 ml of dry THF at 0°. The solution was refluxed for 11 hr and cautiously hydrolyzed with water. The material was filtered through glass wool to remove the gelatinous precipitate, and the precipitate and glass wool were boiled with methylene chloride, which was filtered and combined with the previous extract. The solvent was evaporated, the residue was made up to 25 ml in $CH_2Cl_2$, and benzyl alcohol was added as an internal standard. Vpc analysis (10 ft × $^1/_8$ in. 5% Carbowax 20 M on Chromosorb G, 24 ml/min He, programmed from 175 to 245°) gave in order benzyl alcohol (175°), *p*-methylbenzyl alcohol (175°), bibenzyl (245°), and **17** (245°). Compound **18** was not detectably soluble in the solvents used, and *tert*-butyl benzyl ether was specifically shown to be absent.

The yields of products reported in Table II were determined from the integrations of the vpc curves. In all cases the integration was calibrated using weighed quantities of authentic materials with the internal standards.

**Registry No.**—**6**, 34201-98-4; **7**, 3965-62-6; **11**, 34202-00-1; **14**, 14518-67-3; **15**, 34224-28-7; **16**, 34224-29-8; **17**, 34224-30-1; **23**, 34224-31-2; **24**, 34224-32-3; **25**, 34224-33-4.

# Cyclobutyl Sulfonate Solvolysis. Leaving Group Study

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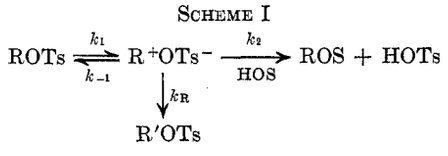
The solvolysis rates of a series of cyclobutyl para-substituted arenesulfonates have been determined in ethanol, acetic acid, and 2,2,2-trifluoroethanol. In addition, the solvolysis rates of cyclobutyl methanesulfonate have been determined in the same series of solvents. The data indicate that the partitioning of the carbonium ion among solvolysis and internal return isomerization routes is insensitive to anion solvation and charge dispersal effects but is sensitive to the steric bulk of the leaving group. The product distributions are also insensitive to the changes in the leaving group.

Recently, it was established[1] that cyclobutyl β-naphthalenesulfonate suffers solvolysis in a spectrum of solvents with little nucleophilic assistance by solvent but with considerable anchimeric assistance.

The nature of the cationic species responsible for the observed anchimeric assistance is interpreted[2] in terms of a rapidly equilibrating bicyclobutonium ion system which is common to solvolysis of cyclopropylcarbinyl and allylcarbinyl derivatives as well as cyclobutyl substrates.

The proposed cationic species have open three options: internal return ($k_{-1}$), internal return isomerization ($k_R$), and solvolysis ($k_2$), as illustrated in Scheme I.

SCHEME I




The internal return isomerization route is well documented for the cyclopropylcarbinyl system.[3,4]

The presence of internal return isomerization has also been observed in the solvolysis reactions of cyclobutyl derivatives.[1,5] In keeping with the common cationic species postulated for both the cyclopropylcarbinyl and cyclobutyl derivatives in acetolysis reactions, about 10% of both substrates isomerize by the $k_R$ route to allylcarbinyl derivatives.[1,4]

An examination of the literature suggests that the relative importance of the competing reactions, $k_2/k_R$, is sensitive to change in the nature of the leaving group. For example, the acetolysis of cyclobutyl chloride is accompanied by 40% internal return isomerization[5] while the acetolysis of cyclobutyl β-naphthalenesulfonate is accompanied by only 8% internal return isomerization.[1] Both cyclobutyl derivatives, however, exhibit the same solvent dependency behavior, *i.e.*, reduced internal return isomerization with increased solvent ionizing strength.[1,6]

These results contrast with the findings of related work. Thus Goering and coworkers,[7] using a combination of polarimetric and titrimetric kinetic techniques, demonstrated that the relative rates of com-

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(2) K. L. Servis and J. D. Roberts, *J. Amer. Chem. Soc.*, **86**, 3773 (1964).
(3) K. L. Servis and J. D. Roberts, *Tetrahedron Lett.*, 1369 (1967).
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