ing with a dialkyl phosphite anion is sketched in Scheme II.

Step 1 of the suggested mechanism is a photoactivated electron transfer from dialkyl phosphite anion to aryl iodide, and is the initiation step of an overall chain mechanism. An alternative possibility for initiation is photolysis of the C–I bond,[7] forming an aryl radical which enters the propagation sequence at step 3. Termination steps must also be involved, but are not shown.

Steps 2, 3, and 4 constitute a propagation cycle leading to product **5** in which the iodine atom has been replaced but substituent X survives. If intermediate radical anion **4** expels halide ion (in step 5) instead of transferring an electron (in step 4), steps 6 and 7 can then ensue, leading to disubstitution product **8**. Inasmuch as C–Br and C–I bonds are more readily broken than C–F and C–Cl bonds, it is not surprising that step 5 is favored when X is Br or I while step 4 predominates when X is F or Cl.

It is significant that photostimulated reaction of *m*-chloroiodobenzene with thiophenoxide ion gives mainly disubstitution[5,8] but with diethyl phosphite ion (run 10) principally monosubstitution. This contrasting behavior is probably to be attributed to greater stability for **4** (X = Cl) than for the corresponding intermediate in the reaction with thiophenoxide ion, namely, the *m*-chlorophenyl phenyl sulfide radical anion. Inasmuch as the $-PO(OEt)_2$ substituent is more strongly electron attracting than $-SC_6H_5$,[9] such an order of stability would be expected. Greater stability for **4** would enable it to survive long enough to transfer an electron in bimolecular step 4, and thereby form monosubstitution product **5**.

References and Notes

(1) Research supported in part by the National Science Foundation.

(2) G. M. Kosolapoff, *Org. React.*, **6**, 273 (1951); L. D. Freedman and G. O. Doak, *Chem. Rev.*, **57**, 479 (1957); E. F. Jason and E. K. Fields, *J. Org. Chem.*, **27**, 1402 (1962); P. Tavs, *Chem. Ber.*, **103**, 2428 (1970); A. G. Varvoglis, *Tetrahedron Lett.*, 31 (1972).

(3) J. B. Plumb and C. E. Griffin, *J. Org. Chem.*, **27**, 4711 (1962); J. B. Plumb, R. Obrycki, and C. E. Griffin, *ibid.*, **31**, 2455 (1966).

(4) J. K. Kim and J. F. Bunnett, *J. Amer. Chem. Soc.*, **92**, 7463 (1970).

(5) J. F. Bunnett and X. Creary, *J. Org. Chem.*, **39**, 3173, 3611 (1974).

(6) R. A. Rossi and J. F. Bunnett, *J. Org. Chem.*, **38**, 1407, 3020 (1973); J. F. Bunnett and B. F. Gloor, *ibid.*, **39**, 382 (1974).

(7) A. Levy, D. Meyerstein, and M. Ottolenghi, *J. Phys. Chem.*, **77**, 3044 (1973).

(8) *The photostimulated reaction of m-chloroiodobenzene with thiophenoxide ion affords predominantly the distribution product,* *m*-di(thiophenoxy)benzene.[5] There is evidence that *m*-chlorophenyl phenyl sulfide is not an intermediate on the main disubstitution reaction pathway. In the present case we have no proof that **5** is not an intermediate in formation of **8**, although that is implied by Scheme II and our discussion.

(9) L. D. Freedman and H. H. Jaffe, *J. Amer. Chem. Soc.*, **77**, 920 (1955); E. N. Tsvetkov, D. I. Lobanov, L. A. Izosenkova, and M. I. Kabachnik, *Zh. Obshch. Khim.*, **39**, 2177 (1969); H. H. Szmant and G. Suld, *J. Amer. Chem. Soc.*, **78**, 3400 (1956).

University of California
Santa Cruz, California 95064

J. F. Bunnett*
Xavier Creary

Received September 10, 1974

Steric Acceleration of Perester Decomposition Leading to Tertiary Alkyl Radicals

Summary. The rate accelerations observed in the formation of some tertiary radicals from crowded peresters are comparable to those in corresponding carbonium ion reactions.

Sir: The reactivity of organic peresters has been the subject of intense study, justified by the practical and theoretical importance of these compounds.[1] From these studies the mechanism that has emerged for peresters RCO_3-*t*-Bu, where R is a tertiary or similarly stabilized radical, involves concerted breaking of two bonds and formation of the R radical, carbon dioxide, and the *tert*-butoxy radical (eq 1).[1]

$$\mathrm{RCO_3{-}}t\text{-}\mathrm{Bu} \longrightarrow \underset{\textbf{1}}{[\mathrm{R{-}{-}{-}CO_2{-}{-}{-}O{-}}t\text{-}\mathrm{Bu}]^{\ddagger}} \xrightarrow{-\mathrm{CO_2}} \mathrm{R}\cdot + t\text{-}\mathrm{Bu}\dot{\mathrm{O}} \qquad (1)$$

Table I
Decomposition of Peresters in Cumene[a]

	T, °C	k_1, sec^{-1} [c]	k_{rel}	ΔH^*, kcal/mol	ΔS^*, eu
i-Pr_3CCO_3 *t*-Bu (**2**)	24.8	5.32×10^{-6}		26.6	6.7
	25.0[b]	5.67×10^{-6}	32		
	41.6	6.84×10^{-5}			
	55.2	3.78×10^{-4}			
	60.0[b]	7.08×10^{-4}	24		
$NpMe_2CCO_3$-*t*-Bu (**3**)	25.0[b]	6.13×10^{-7}	3.5	26.5	2.0
	40.8	6.15×10^{-6}			
	54.7	3.82×10^{-5}			
	60.0[b]	7.55×10^{-5}	2.6		
	70.7	2.73×10^{-4}			
t-$BuMe_2CCO_3$-*t*-Bu (**4**)	25.0[b]	7.18×10^{-7}	4.1	27.2	4.6
	42.2	8.76×10^{-6}			
	54.9	5.84×10^{-5}			
	60.0[b]	1.00×10^{-4}	3.4		
	70.3	3.36×10^{-4}			
t-$BuCO_3$-*t*-Bu	25.0[d]	1.75×10^{-7}	1.0	28.3	5.3
	60.0[d]	2.93×10^{-5}	1.0		
	70.3	1.11×10^{-4}			

[a] Np = neopentyl. [b] Calculated value. [c] Average of duplicate runs except as noted; maximum deviation ±5%. [d] Calculated from literature values at six temperatures plus one run reported here: J. P. Lorand, S. D. Chodroff, and R. W. Wallace, *J. Amer. Chem. Soc.*, **90**, 5266 (1968); R. C. Fort, Jr., and R. E. Franklin, *ibid.*, **90**, 5267 (1968).

Table II
Comparison of Rates of Formation of Radicals and Cations

	Radicals		Cations
R	RCO_3-*t*-Bu[a]	RN=NR[b]	RX
i-Pr_3C	32	206	49.0,[c] 109[d]
$NpMe_2C$	3.5	247	21,[e] 6.4[c]
t-$BuMe_2C$	4.1	5.3	4.4,[f] 2.5,[g] 1.2[h]
t-Bu	1.0	1.0	1.0

[a] This work, 25°. [b] In ethylbenzene at 180°, ref 3f. [c] Direct comparison of *p*-nitrobenzoates at 100° in 60% dioxane, ref 3f. [d] Direct comparison of *p*-nitrobenzoates at 100° in 70% acetone: C. F. Wilcox, Jr., and M. E. Mesirov, *J. Amer. Chem. Soc.*, 84, 2757 (1962). Extrapolation of data from other temperatures gives a calculated rate of 650 at 25° in 80% dioxane: P. D. Bartlett and T. T. Tidwell, *ibid.*, **90**, 4421 (1968); P. D. Bartlett and M. Stiles, *ibid.*, **77**, 2806 (1955). [e] Chlorides at 25°: H. C. Brown and H. L. Berneis, *ibid.*, **75**, 10 (1953). [f] *p*-Nitrobenzoates at 25°: H. C. Brown and E. N. Peters, *ibid.*, **95**, 2400 (1973). [g] Chlorides at 25°: P. D. Bartlett and M. S. Swain, *ibid.*, **77**, 2801 (1955). [h] Chlorides at 25°: H. C. Brown and R. S. Fletcher, *ibid.*, 71, 1845 (1949).

This report deals with the examination of the structure of the transition state **1** through study of the reactivity of peresters where R contains bulky alkyl groups. The influence of steric crowding on the rates of solvolysis reactions has been an important method for the study of carbonium ion reactions[2] but has been applied less frequently to reactions leading to the formation of free radicals.[3]

The substrates chosen for study were the *tert*-butyl peresters of aliphatic acids completely substituted at the 2 position with alkyl groups that were expected to lead directly to the corresponding tertiary radicals in one-step unimolecular decompositions. Ionizations leading to the corresponding carbonium ions were known to involve sizable rate accelerations attributable to steric effects. The peresters, their rates of decomposition, and the derived activation parameters are reported in Table I.[4] Rates for the corresponding carbonium ion reactions are presented in Table II for comparison, along with data for formation of radicals from azo compounds.[3f]

The rates for the peresters provide compelling confirmation of the mechanism in eq 1 for the reaction of peresters where the group R is a tertiary radical. The rapid rate of *tert*-butyl triisopropylperacetate relative to the less crowded peresters must be largely due to relief of steric strain on fragmentation of the molecule. The inductive effects may make a small contribution to the observed rate increases, but the nonlinear dependence of the rates on the degree of β substitution shows this is a minor factor. Models suggest negligible steric interaction between the developing alkyl radical and the departing *tert*-butoxy group. Therefore the possible sources of the steric acceleration are (a) rehybridization at the quaternary carbon to relieve "B" strain between the isopropyl groups, and (b) relief of "F" strain between the alkyl groups and the carboxy group by stretching the connecting bond. The latter effect is analogous to the steric repulsion of the leaving group which has been proposed to contribute to steric acceleration of carbonium ion formation.[2,5] It is not yet possible to define the specific contribution of these two effects to the observed rate increase, but it is clear the bond between R and the CO_2 group in 1 must be stretched for either effect to operate.

Comparison of the radical and carbonium ion forming reactions (Table II) shows that all are accelerated by bulky groups. The total effects are largest in the azo compounds, but these have two bulky groups present which each contribute to the observed acceleration.

Another conceivable contributing factor to these effects is a polar enhancement of reactivity due to rehybridization.[1d] As we have discussed for carbonium ion formation,[2] bulky groups may increase the p character in the carbon orbital bonded to the leaving group, and this rehybridization may enhance the formation of electron-deficient transition states. Since the generation of carbon free radicals is often assisted by the same electronic factors which favor carbonium ions,[1] strain-induced rehybridization would equally likely be a factor in perester decompositions as in ionization reactions.

Other effects which have been ascribed to steric factors in free radical formation include small increases in the rate of formation of secondary alkyl radicals from peresters[3a] and reactivity increases of 15–30 in hydrogen abstraction reactions where relief of back-strain is possible.[3b] Bulky ortho substituents also increase the rates of decomposition of *tert*-butyl perbenzoates.[3e] It is becoming clear that the atom rehybridizations and bond stretchings which lead to steric acceleration can make substantial net contributions to observed reactivities in formation of both radicals and carbonium ions from various types of precursors.

Acknowledgment. Professor M. S. Newman generously supplied our initial sample of triisopropylacetic acid. The research for this paper was supported by the Defence Research Board of Canada, Grant No. 9530-129. We also thank Professor C. Rüchardt for a preprint of ref 3f and helpful discussions.

References and Notes

(1) (a) T. Koenig in "Free Radicals," Vol. 1, J. K. Kochi, Ed., Wiley, New York, N. Y., 1973, p 113; (b) W. H. Richardson and H. E. O'Neal in "Comprehensive Chemical Kinetics," Vol. 5, C. H. Bamford and C. F. H. Tipper, Ed., Elsevier, New York, N. Y., 1972, Chapter 4; (c) L. A. Singer in "Organic Peroxides," Vol. 1, D. Swern, Ed., Wiley, New York, N. Y., 1970, Chapter 5; (d) C. Rüchardt, *Angew. Chem. Int. Ed. Engl.*, **9**, 830 (1970).

(2) For leading references, see T. T. Tidwell, *J. Org. Chem.*, in press, and ref 3.

(3) For recent examples, see (a) G. J. Abruscato and T. T. Tidwell, *J. Amer. Chem. Soc.*, **94,** 672 (1972); (b) S. J. Cristol and H. W. Mueller, *ibid.*, **95,** 8489 (1973); (c) J. W. Timberlake and M. L. Hodges, *ibid.*, **95,** 634 (1973); (d) W. Duismann and C. Rüchardt, *Chem. Ber.*, **106,** 1083 (1973); (e) S. Icli, K. A. Kandil, C. Thankachan, and T. T. Tidwell, to be submitted for publication; (f) W. Duismann and C. Rüchardt, *Tetrahedron Lett.*, in press.

(4) The peresters were all oils prepared from the known corresponding acids by conversion to the acid chlorides and reaction with sodium *tert*-butyl hydroperoxide in ether with purification by column chromatography. The new peresters gave the expected spectral parameters [**2:** ir (CCl_4) 1752 cm^{-1}; nmr (CCl_4) δ 1.03 (d, $J = 7$ Hz, 18, **Me_2**CH), 1.28 (s, 9, *t*-Bu), 2.40 (heptet, $J = 7$ Hz, 3, Me_2C**H**). **3:** ir (CCl_4) 1752 cm^{-1}; nmr (CCl_4) δ 0.95 (s, 9, *t*-$BuCH_2$), 1.23 (6, s, Me_2), 1.28 (s, 9, *t*-BuO), 1.60 (s, 2, CH_2). **4:** ir (CCl_4) 1765 cm^{-1}; nmr (CCl_4) δ 0.97 (s, 9, *t*-BuC), 1.14 (s, 6, Me_2), 1.28 (s, 9, *t*-BuO)]. Acceptable elemental analyses were obtained for **3** and **4,** but that for **2** (*Anal.* Calcd for $C_{15}H_{30}O_3$ (258.39): C, 69.73; H, 11.70. Found: C, 68.03; H, 11.40) deviated, apparently because of the thermal instability of this compound at room temperature. The products from the peresters are under investigation and will be reported as part of a general study of the reactivity of crowded radicals. The triisopropylemethyl radical from the corresponding perester has been observed by esr and is extremely long lived at room temperature: S. Icli, C. Thankachan, and T. T. Tidwell, *J. Chem. Soc., Chem. Commun.*, in press.

(5) J.-E. Dubois and J. S. Lomas, *Tetrahedron Lett.*, 1791 (1973); (b) J. Slutsky, R. C. Bingham, P. v. R. Schleyer, W. C. Dickason, and H. C. Brown, *J. Amer. Chem. Soc.*, **96,** 1969 (1974).

Department of Chemistry
University of Toronto
Scarborough College
West Hill, Ontario, Canada,
and
University of South Carolina
Columbia, South Carolina

John A. Ernst
Chacko Thankachan
Thomas T. Tidwell*

Received October 7, 1974

A New Polyketide Synthon

Summary: A phosphonium ylide derived from triacetic acid lactone has been prepared and used in the synthesis of tetraacetic acid lactone and other acetogenins.

Sir: Although Collie's hypothesis of the "multiple keten group" [1] lay fallow for decades in the literature, its resurrection as Birch's "Acetate hypothesis" [2] has proven of immense significance in fungal metabolism.[3] Of special interest are derivatives of 4-hydroxy-2-pyrone and, in particular, triacetic acid lactone 1[4,5] and tetraacetic acid lactone 2,[5] as these compounds represent the closest approximation of true "polyketides." A number of related pyrones have been biomimetically transformed into phenols of naturally occurring types.[6–9]

After repetition of reported syntheses of 2 from 1 *via* 3,[9] the 6-carboxy derivative of 4 *via* carboxylation of the 6-methyl anion,[8] and 5 from 3 *via* 6,[10] it became clear to us that none of these were readily adaptable to isotopic labeling studies, in addition to their other drawbacks.

This report deals with the preparation of a reagent which produces polyketide-related materials under relatively mild and selective conditions from carbonyl substrates