ring inversion with the size of the substituents at positions four and nine and the hybridization of these carbons is now in progress.

Acknowledgment. We wish to thank the National Science Foundation for support of this research.

---

[11] National Science Foundation Cooperative Fellow, 1965–1967; Stauffer Fellow, 1967–1968.

Bryan W. Roberts, John J. Vollmer,[11] Kenneth L. Servis
Department of Chemistry, University of Southern California
University Park, Los Angeles, California 90007

Received June 10, 1968

Formation of the Bridgehead Free Radical 1-Adamantyl by Perester Decomposition[1]

Sir:

The most favorable geometry of aliphatic free radicals remains an unsolved problem, since existing data are consistent with a geometry which is either pyramidal and rapidly inverting, or planar but easily deformed.[2–4] One approach to the problem is generation of the radical at a bridgehead of a bridged bicyclic system. For planar geometry, a stability order such as the following, well established for carbonium ions,[5] is predicted (the numbers are relative rates of alkyl bromide solvolysis): *t*-butyl > 1-adamantyl > 1-bicyclo[2.2.2]octyl ≫ 1-norbornyl, 1.0, 10^{-3}, 10^{-6}, and 10^{-14}, respectively. From their aldehyde decarbonylation study, however, Applequist and Kaplan concluded that 1-adamantyl and 1-bicyclo[2.2.2]octyl were appreciably more stable than *t*-butyl.[3] To reach this conclusion, they had to assume that the rates of capture of acyl radicals by CCl_4 were the same for all the alkyl groups studied.

We have attempted to assess the relative stabilities of 1-adamantyl and *t*-butyl radicals more directly by comparing the rates of thermal decomposition of the corresponding *t*-butyl peresters. We take advantage of the well-documented concerted two-bond scission (eq 1),

$$RCO_3\text{-}t\text{-Bu} \xrightarrow{\Delta} R\cdot + CO_2 + \cdot O\text{-}t\text{-Bu} \qquad (1)$$

I, R = 1-adamantyl
II, R = *t*-butyl

obtaining whenever the stability of R· is equal to or greater than that of isopropyl or *t*-butyl; $\Delta H^{\ddagger} \leqslant 32$ kcal/mol and $\Delta S^{\ddagger} \leqslant 11$ eu in such cases.[6] The rates of formation of the radicals should therefore be directly measurable. We now report our study of the decompositions of peresters I and II.[7–10]

Both peresters I and II were prepared by known methods, and were free of hydroxylic or carbonyl-containing impurities, as judged from their infrared spectra. I, prepared from the acid chloride (Aldrich Chemical Co., mp 52–54°, lit.[3] 48.5–52.0°) and anhydrous sodium *t*-butyl peroxide[11] in dichloromethane at 0°, was purified by column chromatography on silica gel. It was a clear oil freezing at 0°, showed λ_{max} 5.69 μ in the infrared, and evolved 85–90% CO_2 on thermal decomposition in degassed cumene solution at 85°.[12] By nmr analysis, ~5% dichloromethane was detected in a sample of I. II, which has been reported,[13,14] was prepared either from (a) acid chloride, *t*-butyl hydroperoxide, and pyridine or (b) anhydride and hydroperoxide, washed with dilute aqueous ammonia, and distilled, bp 30–35° (0.05 mm). It showed λ_{max} 5.65 μ in the infrared. Samples of II prepared using sodium *t*-butyl peroxide were apparently more difficult to purify than those prepared by methods a and b, since their decomposition rate constants tended to decrease with increasing initial perester concentration.

Kinetics of decomposition of I and II in undegassed cumene were followed at the temperatures indicated in Table I, perester concentration being monitored by infrared spectra at the carbonyl maximum. First-order plots were linear to at least three half-lives, and rate constants were independent of initial perester concentration (0.07–0.5 *M* for I; 0.2–1.0 *M* for II) within the stated limits. Activation parameters, calculated *via* the Eyring equation, are as follows: for I, $\Delta H^{\ddagger} = 27.9$ kcal/mol, $\Delta S^{\ddagger} = +4.9$ eu; for II, $\Delta H^{\ddagger} = 27.6$ kcal/mol, $\Delta S^{\ddagger} = +3.6$ eu.

Table I. Kinetics of Decomposition of Peresters I and II

	10^5k, sec^{-1} [a]		
Temp, °C	I	II	k_I/k_{II}
64.6	6.87 ± 0.10	5.81 ± 0.10	1.18
74.6	24.4 ± 1.0	18.7[b]	1.30
75.6		21.0 ± 0.7	
84.6	77.8 ± 1.5	59.4 ± 1.5	1.31

[a] Each value is the average of the least-squares *k*'s of four runs. [b] Extrapolated from 75.6°.

The products of decomposition of I, besides CO_2, included *t*-butyl alcohol (45%), adamantane (47%), *t*-butyl 1-adamantyl ether (15%), and dicumyl (73%). Carbonyl-containing products were absent. The products of decomposition of II in cumene included[15] CO_2 (98%), *t*-butyl alcohol (79%), isobutylene (40%), isobutane (30%), dicumyl (68%), and di-*t*-butyl ether (2%). Carbonyl-containing products were again absent.

Peresters I and II evidently decompose in cumene *via* spontaneous, concerted two-bond scission, without induced decomposition, as judged by the first-order kinetics, absence of carbonyl-containing products, and low activation parameters. The rate constants therefore reflect the radical stabilities, and it is clear from Table I that the 1-adamantyl and *t*-butyl radicals are

---

[1] Taken in part from the A.M. Thesis of S. D. C., 1968.

[2] W. A. Pryor, "Free Radicals," McGraw-Hill Book Co., Inc., New York, N. Y., 1966; *cf.* literature cited in ref 3.

[3] D. E. Applequist and L. Kaplan, *J. Am. Chem. Soc.*, **87**, 2194 (1965).

[4] A. D. Walsh, *J. Chem. Soc.*, 2296 (1953).

[5] R. C. Fort, Jr., and P. von R. Schleyer, *Chem. Rev.*, **64**, 277 (1964).

[6] (a) P. D. Bartlett and R. R. Hiatt, *J. Am. Chem Soc.*, **80**, 1398 (1958); (b) C. Rüchardt, *Fortschr. Chem. Forsch*, **6**, 251 (1966); (c) these activation parameters now appear to vary strongly with solvent; P. D. Bartlett and F. Herkes, private communication; (d) P. D. Bartlett and L. B. Gortler, *J. Am. Chem. Soc.*, **85**, 1864 (1963).

[7] We have also prepared the *t*-butyl perester precursor to 1-apocamphyl radical and found it to decompose *ca.* 500 times more slowly than I and II.

[8] R. C. Fort, Jr., and R. E. Franklin, *J. Am. Chem. Soc.*, **90**, 5267 (1968); Abstracts, 154th National Meeting of the American Chemical Society, Chicago, Ill., Sept 11-15, 1967, No. S-165.

[9] L. B. Humphrey, B. Hodgson, and R. E. Pincock, *Can. J. Chem.*, in press.

[10] I. Tabushi, J. Hamuro, and R. Oda, *J. Am. Chem. Soc.*, **89**, 7127 (1967).

[11] J. P. Lorand and P. D. Bartlett, *ibid.*, **88**, 3294 (1966).

[12] The vacuum line technique is described in ref 6a.

[13] P. D. Bartlett and D. M. Simons, *J. Am. Chem. Soc.*, **82**, 1753 (1960).

[14] T. Koenig and R. Wolf, *ibid.*, **89**, 2948 (1967).

[15] J. P. Lorand, Ph.D. Thesis, Harvard University, 1964.

of essentially identical stability. This result is in accord with those of Fort and Franklin[8] and Pincock, *et al.*,[9] but in conflict with the enigmatic statement about perester I by Tabushi, *et al.*[10] The discrepancy between our result and that of Applequist and Kaplan[3] is probably due to breakdown of the assumption referred to above.

The effect of geometry on the stability of bridgehead bicyclic radicals may be seen in the following series of "corrected" relative rate constants for perester decomposition, from the second and third of which an inductive effect has been factored out:[8,16] *t*-butyl > 1-adamantyl > 1-bicyclo[2.2.2]octyl > 1-norbornyl, 1.0, 0.3, 0.03, and 0.002, respectively. The extent of geometrical destabilization is considerable, and we conclude that alkyl radicals tend toward planar geometry. The lesser extent of destabilization, relative to that for the carbonium ions, might mean that radicals seek a flattened pyramidal state. It may also mean that they seek complete planarity, but possess low C–C–C bending force constants. This issue can evidently not be settled without spectroscopic information about alkyl radicals.

Acknowledgments. We are grateful to the Graduate School of Boston University for a grant in support of this work. We thank Professor Paul D. Bartlett and Dr. Frank Herkes for helpful discussions, and Professors Fort and Pincock for exchanging manuscripts prior to publication.

(16) No correction is made for 1-norbornyl, a case of one-bond scission, or for *t*-butyl, the standard of comparison, which lacks γ-carbons.

John P. Lorand, Susan D. Chodroff, Robert W. Wallace
Department of Chemistry, Boston University
Boston, Massachusetts 02215

Received June 3, 1968

The Thermolysis of Bridgehead *t*-Butyl Peresters

Sir:

The question of the relative influences of inductive, field, and geometrical effects upon the stability of carbon free radicals is of considerable interest.[1-3] An important attack on the problem was that of Applequist and Kaplan,[4] who studied the di-*t*-butyl peroxide induced decarbonylation of several bridgehead aldehydes. By measuring the relative amounts of decarbonylated and nondecarbonylated products, these workers reached the rather surprising conclusion that both the bicyclo[2.2.2]octyl and adamantyl bridgehead radicals were slightly *more* stable than the *t*-butyl radical. In light of these and other[5,6] observations, it was suggested[4-6] that there might be something "special" about the 1-adamantyl radical. No clear geometrical conclusions could, however, be based on the data obtained.

More recently, Tabushi, *et al.*,[7] reexamined the radical halogenation of adamantane and suggested that the bridgehead radical is *less* stable than the 2-adamantyl.[8]

We wish to report the initial[9] results of our study of the decomposition of *t*-butyl peresters of bridgehead carboxylic acids. The thermolysis of such peresters has been shown by Bartlett and coworkers[10] to occur by the concerted process of eq 1 in most cases when R is

$$\mathrm{RCO_3}\text{-}t\text{-}\mathrm{Bu} \xrightarrow{\Delta} \mathrm{R}\cdot + \mathrm{CO_2} + t\text{-}\mathrm{BuO}\cdot \qquad (1)$$

primary or tertiary. Thus the rate at which the peresters decompose should reflect, at least in a series of closely related compounds, the stability of the radicals formed.[10]

We have prepared[10,11] the peresters listed in Table I and measured[12] the rates of thermal decomposition in cumene solution by following the decrease of the perester carbonyl ir absorbance. Cumene was chosen as solvent to minimize induced decomposition[10] and simplify product analysis. Perester concentrations were varied over a five- to tenfold range; in no case was any variation in rate other than random experimental error observed. Addition of excess *n*-hexyl mercaptan does not change rates significantly.

Product analysis was carried out gas chromatographically using a 6-ft Carbowax on Chromosorb column. All systems except the 1-norbornyl gave high yields of the corresponding hydrocarbons, and no detectable acid, both in cumene alone and in cumene + *n*-hexyl mercaptan solutions. In the case of the 1-norbornyl perester small amounts of the carboxylic acid possibly produced by one-bond homolysis are found, but the constancy of the product analysis under both conditions suggests that the acyloxy radical is not an intermediate in the formation of decarboxylated product, and that the major reaction pathway is still the concerted decomposition.

The first point to be made is that the data of Table I suggest a significant inductive contribution to the rates (and therefore to the radical stabilities[13]). A correlation of the rates of the acyclic compounds with $\Sigma\sigma^*$ is excellent, yielding a ρ of -1.6 at 65°. This value is

---

(1) See J. P. Lorand, S. D. Chodroff, and R. W. Wallace, *J. Am. Chem. Soc.*, **90**, 5266 (1968); also L. B. Humphrey, B. Hodgson, and R. E. Pincock, *Can. J. Chem.*, in press.

(2) R. C. Fort, Jr., and P. von R. Schleyer, *Advan. Alicyclic Chem.*, **1**, 284 (1966).

(3) F. D. Greene and N. N. Lowry, *J. Org. Chem.*, **32**, 875, 882 (1967).

(4) D. E. Applequist and L. Kaplan, *J. Am. Chem. Soc.*, **87**, 2194 (1965).

(5) P. von R. Schleyer, R. C. Fort, Jr., W. E. Watts, M. B. Comisarow, and G. A. Olah, *ibid.*, **86**, 4195 (1964).

(6) R. C. Fort, Jr., and P. von R. Schleyer, *Chem. Rev.*, **64**, 277 (1964).

(7) I. Tabushi, J. Hamaro, and R. Oda, *J. Am. Chem. Soc.*, **89**, 7127 (1967).

(8) These workers report that preliminary rate measurements of the decomposition of the adamantane *t*-butyl perester indicated the reaction was not concerted, in contrast to our results (*vide infra*).

(9) Portions of this work were presented at the 154th National Meeting of the American Chemical Society, Chicago, Ill., Sept 11–15, 1967, Abstract S-165.

(10) (a) P. D. Bartlett, E. P. Benzing, and R. E. Pincock, *J. Am. Chem. Soc.*, **82**, 1762 (1960); (b) P. D. Bartlett, R. E. Pincock, J. H. Ralston, W. G. Schindel, and L. A. Singer, *ibid.*, **87**, 2590 (1965); (c) J. P. Lorand and P. D. Bartlett, *ibid.*, **88**, 3294 (1966); and other papers in this series.

(11) Because of their thermal instability, acceptable microanalyses could not be obtained on the esters. Their purity and structure were established *via* ir and nmr spectroscopy. Occasional trace amounts of *t*-butyl hydroperoxide were shown by control experiments not to affect rates measurably. Traces of acid or base caused drastic, erratic rate variations and were therefore carefully excluded.

(12) First-order rate constants were calculated on a Honeywell 2200 computer, employing a program kindly written for use by Dr. Lee Vescelius.

(13) One should note that observation of such a significant inductive contribution in radicals implies a much larger contribution to carbonium ion stabilities. Previous correlations of bridgehead carbonium ion stability with geometry[14-16] have not taken this into account.

(14) P. von R. Schleyer and R. D. Nicholas, *J. Am. Chem. Soc.*, **83**, 2700 (1961).

(15) R. C. Fort, Jr., and P. von. R. Schleyer, *ibid.*, **86**, 4194 (1964).

(16) G. J. Gleicher and P. von R. Schleyer, *ibid.*, **89**, 589 (1967).