

of essentially identical stability. This result is in accord with those of Fort and Franklin⁸ 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 Kaplan³ 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.

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(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.

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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 suggested⁴⁻⁶ that there might be something "special" about the 1-adamantyl radical. No clear geometrical conclusions could, however, be based on the data obtained.

(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).

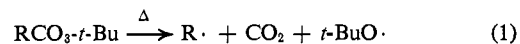
(4) D. E. Applequist and L. Kaplan, *J. Am. Chem. Soc.*, **87**, 2194 (1965).

(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).

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 initial⁹ 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 coworkers¹⁰ to occur by the concerted process of eq 1 in most cases when R is



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 measured¹² 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 decomposition¹⁰ 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 stabilities¹³). 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

(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 Vesceilius.

(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 geometry¹⁴⁻¹⁶ 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).

Table I. Thermal Decomposition of $\text{RCO}_2\text{-}t\text{-Bu}$

R	Temp, °C	$k \times 10^6, \text{sec}^{-1}$ ^a	$\Delta H^\ddagger,$ kcal/mol	$\Delta S^\ddagger,$ eu	Rel rate	Cor rel rate ^b
$(\text{CH}_3)_3\text{C}$	65	4.53	25.5	-2.9	1.0	1.0
	55	1.73				
	45	0.353				
$(\text{CH}_3\text{CH}_2)_3\text{C}$	65	14.6	24.7	-1.8	3.2	
	55	4.92				
	45	1.23				
$\text{CH}_3\text{CH}_2\text{CH}_2\text{C}(\text{CH}_3)_2$	65 ^c	7.76 ^c	25.2	-3.2	1.67	
	55	2.15				
	45	0.62				
1-Adamantyl	65	7.40	27.6	+3.7	1.63	0.36-0.47
	55	2.05				
	45	0.515				
1-Bicyclo[2.2.2]octyl	65	0.75	28.5	+2.2	0.16	~0.05
	75	2.82				
	85	8.47				
1-Bicyclo[2.2.1]heptyl	65 ^c	0.00574	37.1	17.5	1.26×10^{-3}	$\sim 0.4 \times 10^{-3}$
	85	0.116				
	100	1.02				
	110	3.76				

^a $\pm 5\%$. ^b See text for explanation. ^c Extrapolated.

rather higher than the average for radical reactions¹⁷ but is not out of line.^{18,19} Thus, in the absence of destabilization from other sources, *all* of the bridged radicals should be more stable than *t*-butyl, by virtue of the inductive effect of their "extra" carbons. Since we are dealing with saturated carbocyclic systems, the destabilizing factor can be identified reasonably as geometry.²

A crude correction for induction in the bridged molecules may be attempted, utilizing the linear free-energy relationship developed above. It is possible to sort out the skeleton of each bridged molecule (in several ways) into simple alkyl groups, and then use the linear free-energy plot to predict roughly the rate expected for a given compound were it not constrained geometrically. In this way, for example, we find that on an inductive basis adamantyl should be faster than *t*-butyl by a factor of the order of 3.5-4.6. Division of the observed relative rate by this quantity gives the corrected relative rate shown in the last column of Table I. The stability order obtained by similar treatment of the other bridged systems parallels the order for the corresponding carbonium ions.

A reasonable tentative conclusion at this point would be that carbon free radicals prefer a planar geometry, as do carbonium ions, but that the force constants for distortion of the radicals are, as expected,² much smaller than those for distortion of the cations. However, there is evidence that the transition state for the decomposition of some *t*-butyl peresters¹⁸⁻²⁰ (and for other radical reactions¹⁷) may have some polar character, at least when a stable carbonium ion (benzyl, tropylium) can be formed. In this event, of course, the corrected rate data would parallel carbonium ion data because some measure of positive charge is developing at the bridgehead in the transition state. Studies are under way to clarify this point.

(17) W. A. Pryor, "Free Radicals," McGraw-Hill Book Co., Inc., New York, N. Y., 1966.

(18) P. D. Bartlett and C. Ruchardt, *J. Am. Chem. Soc.*, **82**, 1756 (1960).

(19) R. E. Pearson and J. C. Martin, *ibid.*, **85**, 3142 (1963).

(20) C. Ruchardt and H. Schwartz, *Ber.*, **99**, 1861, 1878 (1966).

The stability obtained in this study for the 1-bicyclo[2.2.2]octyl radical is about a power of ten less than that found by Applequist and Kaplan⁴ and is more in line with the suggestion of Stock²¹ based on the Hunsdiecker reaction of the acid. Pyrolytic generation of the radical²² from bicyclooctylmethyl nitrite leads to ring-opened species, likewise indicating a surprising instability. (Recall that *no* ring-opened products were found in this work.) Further studies are being carried out on this system.

Finally, it would seem evident that there is nothing unusual about the 1-adamantyl radical; it is an ordinary tertiary radical with slight geometrical destabilization.

(21) F. W. Baker, H. D. Holtz, and L. M. Stock, *J. Org. Chem.*, **28**, 514 (1963).

(22) T. McAllister, Z. Dolesek, F. P. Lossing, R. Gleiter, and P. von R. Schleyer, *J. Am. Chem. Soc.*, **89**, 5982 (1967).

(23) Support of this work through a Kent State University faculty research fellowship is gratefully acknowledged.

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Unusually High *exo:endo* Rate Ratios in the Solvolysis of 2-*p*-Anisylcamphenyl and Related Compounds. Further Evidence for Steric Effects as a Major Factor in the *exo:endo* Rate Ratios of Tertiary Norbornyl Derivatives

Sir:

The *exo:endo* rate ratio in the solvolysis of 2-*p*-anisylcamphenyl *p*-nitrobenzoates is 44,000, as compared to a value of 284 observed in the parent system, 2-*p*-anisylnorbornyl.¹ Moreover, it remains sensibly constant as the 2-aryl substituent is made less and less electron supplying:² 2-phenyl, 49,000; 2-*p*-trifluoromethylphenyl, 24,000. A comparison of the rate data

(1) H. C. Brown and K. Takeuchi, *J. Am. Chem. Soc.*, **90**, 2691 (1968).

(2) K. Takeuchi and H. C. Brown, *ibid.*, **90**, 2693 (1968).