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Thermolysis of *tert*-Butyl Cubanepercarboxylate. The Cubyl Radical

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The rate and activation parameters for the thermal decomposition of *tert*-butyl cubanepercarboxylate have been measured in cumene. The cubyl radical is formed about 4600-fold less rapidly than the *tert*-butyl radical under the same conditions. The selectivity of the cubyl radical in halogen atom abstraction reactions has also been investigated. The competition constant, *r*, for the reactions of the radical with bromotrichloromethane and carbon tetrachloride is 80. This value is larger than the competition constants of other bridgehead radicals. These results may be rationalized on the basis of the novel hybridization of the carbon atoms of cubane.

The stereochemistry of tricoordinate carbon radicals has been actively investigated for some time.[1] Recent studies indicate that simple alkyl radicals are not strictly planar and that *tert*-butyl radicals are distinctly pyramidal.[2-5] However, the energy difference between the planar and pyramidal forms of the simple carbon free radicals is apparently quite small.[5]

Bridgehead radicals can neither undergo inversion nor become planar. The radicals of this class are readily formed and their chemistry has also been actively investigated. Two lines of investigation, the thermal decomposition of the peresters[6-9] and the selectivity of the radicals in halogen atom abstractions,[9-11] have received special attention. The rates of decomposition of the peresters depend on the structure of the radical importantly with norbornyl radical formed about 1000-fold less rapidly than the *tert*-butyl radical.[6-9] The selectivity of the bridgehead radicals in reactions with carbon tetrachloride and bromotrichloromethane at 80 °C decrease in the order: 3-homocubyl > 1-bicyclo[2.2.1]heptyl > 1-bicyclo[2.2.2]octyl > 1-adamantyl.[9-11] We have undertaken a complementary investigation of the related reactions of the more highly strained cubane derivatives.

Results and Discussion

Cubanecarboxylic acid was prepared by a well known procedure.[12,13] The acid was converted to the perester through reaction of the acid chloride with *tert*-butyl hydroperoxide. The *tert*-butyl perester of adamantane carboxylic acid was also prepared for study of the procedures used in this work.

Kinetic Observations. The rates of decomposition of the peresters of adamantane and cubane are presented in Table I.

First-order reactions were observed in all the kinetic experiments. The rate constant for the decomposition of adamantane is within experimental error of the constants reported in prior work.[6-9] The relative rates and activation parameters for the *tertiary* acyclic and bridgehead peresters are summarized in Table II.

Analyses of the data for the homolytic decomposition reactions of peresters indicate that such reactions occur by several different mechanisms which range from simple oxygen–oxygen bond homolysis to two-bond fragmentation reactions with varying degrees of polar character. Several experimental approaches have been used to distinguish between these two extremes. The entropy of activation has frequently been used as one of these criteria.[15] Generally, two-bond concerted decomposition reactions which proceed with rotational restriction exhibit more positive entropies of activation. From this viewpoint, the results presented in Table II suggest that the thermolysis of the bridgehead peresters may not all occur by the same mechanism. However, the experimental errors are relatively large and the reaction solvents differ. Further, Traylor and his students investigated the decomposition of 1-bicyclo[2.2.1]heptanecarboxy, cubanecarboxy, and 4-homocubanecarboxy radical in hydrocarbon solvents.[16] They report that even the relative rates of decarboxylation are immeasurably fast and that there is a quantitative evolution of carbon dioxide. These results do not require that the thermolysis reactions of the peresters proceed by two-bond fragmentation processes. However, these observations and

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Table I. Rates of Thermal Decomposition of *tert*-Butyl Peresters in Cumene

perester	registry no.	temp, °C	$k_1 \times 10^5$, s^{-1}
adamantyl[a]	66769-98-0	80	75.0 ± 0.3
cubyl[a]	21245-43-2	80	0.262 ± 0.019
		100	2.29 ± 0.10
		110	7.35 ± 0.26

[a] Concentration: 0.02 to 0.04 M.

Table II. Relative Rates and Activation Parameters for the Thermal Decomposition of *tert*-Butyl Peresters in Cumene

perester	rel rate, 80 °C	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, eu
tert-butyl[a,b]	1.0	25.5	−2.9, 3.6
1-adamantyl[a–c,f]	1.4	27.6	3.7
1-bicyclo[2.2.2]octyl[a,c]	0.1	28.7	2.2
1-bicyclo[3.2.1]octyl[d,e]	0.05	31.9	10
1-bicyclo[2.2.1]heptyl[a,c]	1.6×10^{-3}	35.9	14.8
9-triptycyl[d,e]	5.9×10^{-4}	34.6	10
3-homocubyl[d,e]	5.9×10^{-3}	35.6	17
cubyl[f]	4.6×10^{-3}	30.2 ± 1.5	1.0 ± 2.0

[a] Reference 7. [b] Reference 6. [c] Reference 8. [d] Reference 9. [e] In ethylbenzene. [f] This study.

the finding that the decomposition rates depend importantly on the structure of the alkyl group indicate that the reactions all proceed by mechanism in which carbon–carbon bond cleavage has a major influence on the energy requirements.

The relative rate data suggest that two factors, the hybridization of the exocyclic bonding orbital of the bridgehead carbon atom and the polar character of the endocyclic carbon–carbon bonding orbitals, are dominant. The compounds with high s character in the exocyclic bonding orbital, for example, the bicyclo[2.2.1]heptane, the homocubane, and the cubane, are all about 1000-fold less reactive than the adamantane or butane derivatives and the compound with the additional features of polar endocyclic carbon–carbon bonds, the triptycene, is the least reactive molecule of the series. We infer that the slow decomposition rates arise from the stronger carbon–carbon bonds in the molecules with greater s character and from the depressed opportunity for the development to polar character in the transition state in the reactions of such radicals. These experimental results do not require an interpretation based on the idea that bridgehead radicals are inherently unstable.

There are subtle variations in the rate data which suggest that other, probably less important factors also influence the reaction. Indeed, we recently proposed that rehybridization may influence the chemistry of cubane derivatives. Specifically, we suggested that the cubyl anion may undergo rehybridization to enhance s character of the exocyclic carbon orbital to bring the interorbital angles into better accord with the internuclear angles and thereby to relieve strain and stabilize the anion.[17] This idea can be extended to the radical to account for the greater rate of decomposition of the cubyl and homocubyl peresters compared to the bicyclo[2.2.1]heptyl perester.

Selectivity Measurements. The selectivity of the cubyl radical was determined by the study of the product distribution obtained in the Hunsdiecker reaction of the carboxylic acid in carbon tetrachloride[18] and in the decomposition of the *tert*-butyl perester in a solution of bromotrichloromethane and carbon tetrachloride.[9]

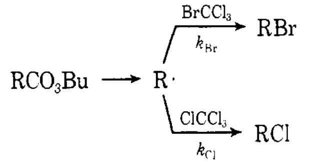
Table III. Bridgehead Radical Selectivity in Halogen Atom Abstraction Reactions

radical	Hunsdiecker reaction, 80 °C, [RBr]/[RCl]	perester dec, 80 °C, *r*
1-adamantyl	0.14[a,b]	29,[c] 30[a]
1-bicyclo[2.2.2]octyl	0.48[b,d]	59[c]
9-triptycyl		32[c]
1-bicyclo[3.2.1]octyl		56[c]
1-bicyclo[2.2.1]heptyl	0.50[b]	47[c]
3-homocubyl	1.00[b,e]	75[c]
cubyl	1.05[a]	80[a]

[a] This study. [b] Reference 11. [c] Reference 9. [d] Reference 10. [e] Reference 19.

$$\mathrm{RCO_2H} \xrightarrow[\mathrm{CCl_4,\ 78\ ^\circ C}]{\mathrm{HgO,Br_2}} \mathrm{RBr} + \mathrm{RCl}$$

In the Hunsdiecker reaction, the selectivity is measured by the cubyl bromide to cubyl chloride ratio. In the perester decomposition reaction, the selectivity is measured by the



competition constant, *r*, which depends on the initial concentration of the halocarbons as well as the product ratio.

$$r = \frac{k_{\mathrm{Br}}}{k_{\mathrm{Cl}}} = \frac{[\mathrm{RBr}][\mathrm{CCl_4}]_{\mathrm{i}}}{[\mathrm{RCl}][\mathrm{CBrCl_3}]_{\mathrm{i}}}$$

The experimental observations for several bridgehead radicals are presented in Table III.

The results obtained in the Hunsdiecker reaction parallel the data obtained in the perester decomposition reaction. The most remarkable feature of these data is the fact that the bridgehead radicals are much less selective in halogen atom abstraction reactions than other aliphatic radicals. Giese has recently shown that the *r* values for primary, secondary, and tertiary radicals are all about 2000 at about 60 °C.[20,21] It is not yet clear whether or not the bridgehead radicals exhibit an isoselective temperature as do the other alkyl and aryl radicals.[22] The *r* values for 1-adamantyl radical are 24, 29, and 25 at 90, 80, and 62 °C, respectively.[9] The *r* values for the 1-bicyclo[3.2.1]octyl radical are equally insensitive to temperature.[9] However, preliminary results for the 1-bicyclo[2.2.1]heptyl radical suggest that the *r* value for this radical is much more temperature dependent.[22] Thus, the *r* values for the bridgehead radicals may or may not converge to an isoselective temperature. In any event, the most striking feature of the results for cubane and the other bridgehead radicals is the large decrease in selectivity compared to other acyclic and monocyclic aliphatic radicals. Rüchardt and his students have commented on this aspect of the chemistry. They noted that the decreased steric requirement of the bridgehead radicals is one of the key factors in the lessened selectivity of these substances.[9] Giese also pointed out that the less sterically crowded radicals are generally less selective.[21] Hence, the finding that the bridgehead radicals are, as a group, unselective is not surprising. It is, however, somewhat surprising to find that the least hindered radicals of this group are the most selective. Such results, if not controverted by new data on radical selectivity at low temperature, suggest that the greater selectivity of the least hindered cubyl radical may originate in variations in the polar character of the transition state for the halogen with this character less developed in the halogen atom abstraction reaction of the cubane than for the adamantane.

Experimental Section[23]

***tert*-Butyl Cubanepercarboxylate.** Cubanecarboxylic acid[12,13] (200 mg, 1.35 mmol) and freshly purified thionyl chloride (5 mL) were refluxed for 1.5 h. The excess thionyl chloride was removed in vacuo to afford the acid chloride in satisfactory quality for the next reaction. It was dissolved in ether (10 mL) and cooled to 0 °C. Pyridine (0.5 mL) and *tert*-butyl hydroperoxide (500 mg, 5.56 mmol) were added in that order. Pyridine hydrochloride precipitated immediately. The cold bath was removed and the cloudy mixture was stirred for 2 h. The pyridine salt was collected. The filtrate was washed with three portions (10 mL each) of cold aqueous sulfuric acid (5%), three portions of aqueous sodium carbonate solution (5%), and finally with ice cold water. The organic phase was dried over sodium sulfate and then evaporated in vacuo to dryness. The white solid was taken up in petroleum ether (20 mL) and chromatographed on silica gel (5 g). The column was flushed with additional petroleum ether (20 mL). The total eluent was evaporated in vacuo. Crystallization of the colorless residue from hexane gave *tert*-butyl cubanepercarboxylate as light colorless feathers (260 mg, 87%, mp 62–63.5 °C). The NMR spectrum, δ 4.12 (m, 7 H), and 1.30 (s, 9 H), and the infrared spectrum, (CCl_4) 1760 and 1350 cm^{-1}, are in accord with the assigned structure. Anal. Calcd for $C_{13}H_{16}O_3$: C, 65.43; H, 7.28. Found: C, 65.37; H, 7.39.

***tert*-Butyl Adamantanepercarboxylate.** *tert*-Butyl adamantanepercarboxylate was prepared in the manner described above. Adamantane carboxylic acid (360 mg, 2 mmol) was transformed into *tert*-butyl adamantane percarboxylate (250 mg, 50%). The product was an oil which solidified in the refrigerator (4 °C) but liquified again at room temperature.[8]

General Procedure for the Study of the Thermal Decomposition of the Peresters in Cumene. A solution of the perester and cumene was transferred into six or eight ampules which were then degassed and thermostated. At intervals, the ampules were removed from the bath and the reaction was quenched by immersion of the ampules in a −10 °C bath. When all of the samples for one run had been obtained, they were warmed to room temperature and the concentration of the perester was measured by infrared spectroscopy. All determinations were made on a Beckman IR-7 infrared spectrophotometer using the perester carbonyl absorption near 1760 cm^{-1}. Preliminary study established that this absorption obeyed Beer's law over the concentration range used in this work. The concentration of the perester in the ampule withdrawn from the bath after 2 min was adopted as the zero value. All the rate constants were assessed from a plot of log (A_0/A_t) versus t in the usual way. Work with *tert*-butyl adamantylpercarboxylate verified the accuracy of this procedure. The results are summarized in Table I.

Selectivity Study. The Hunsdiecker Reactions. Equal molar quantities of mercuric oxide and the carboxylic acid were mixed in a 100-fold molar quantity of purified carbon tetrachloride. The suspension was heated to reflux (78 °C). An equivalent amount of bromine was added dropwise to the mixture and the mixture was refluxed for 1 h. The cooled solution was filtered to remove any solid residues. The filtrate was analyzed by gas chromatography. The products were identified by spectroscopic methods following their isolation by preparative VPC and comparison with authentic materials. A typical experiment for cubanecarboxylic acid is summarized.

Cubanecarboxylic acid (148 mg, 1 mmol) was mixed with red mercuric oxide (216 mg, 1 mmol) and carbon tetrachloride (15.4 g, 0.1 mol). The slurry was heated to reflux (78 °C). Bromine (160 mg, 1 mmol) was added dropwise to the mixture and the mixture was refluxed for 1 h. The cooled solution with filtered and the filtrate was analyzed as described above. Bromocubane (67 mg, 31%) was isolated; this product was identical in every respect with that prepared by other methods.[14] Chlorocubane (41 mg, 30%) was isolated as a colorless liquid which solidified below 4 °C, m/e 140.0201, 138.0233 (parent peaks), 103.0543 (base peak). Anal. Calcd for C_8H_7Cl: C, 69.40; H, 5.09; Cl, 25.51. Found: C, 69.28; H, 5.18; Cl, 25.41.

Selectivity Study. The Thermal Decomposition of *tert*-Butyl Peresters in Halocarbon Solvents. A solution of the *tert*-butyl perester and triphenylmethane in bromotrichloromethane and carbon tetrachloride was immersed in a constant temperature bath at 80 °C for several hours. The cooled solution was analyzed by VPC as described for the Hunsdiecker reaction. A typical experiment for the decomposition of *tert*-butyl cubanepercarboxylate is described.

tert-Butyl cubanepercarboxylate (118 mg, 0.5 mmol), bromotrichloromethane (510 mg, 2.5 mmol), and triphenylmethane (610 mg, 2.5 mmol) were dissolved in carbon tetrachloride (7.7 g, 0.05 mol). The reaction mixture was immersed in a thermostat at 80 °C for 100 h. Analysis of the cooled solution indicated that chlorocubane and bromocubane were produced in 13 and 50%, respectively, on the basis of the starting material consumed.

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Registry No.—Cubanecarboxylic acid, 53578-15-7; cubanecarbonyl chloride, 60462-14-8; 1-adamantane carboxylic acid, 828-51-3; chlorocubane, 23235-66-7.

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