double maxima at 319 and 398 mμ with shoulder at 386 mμ (end) occurring. This is probably indicative of isomers being present. These fractions on combination [spectroscopic yield of tridehydro-[30]annulene, 38 mg. (19%)], evaporation and crystallization from ether–pentane yielded 21 mg. (10.5%) of tridehydro-[30]annulene (XIII or an isomer) as a dark brown-violet crystalline powder which decomposed without melting on attempted melting point determination. The ultraviolet spectrum (Table I and Fig. 1) was unchanged on recrystallization from ether; $\lambda_{max}^{dioxane}$ 320 and 401 mμ (ε 51,000 and 113,000). The infrared spectrum (KBr) showed bands at 3.31(m), 4.64(w), 7.07(w), 7.75(m), 10.03(s), 10.32(m), 10.74(w), 11.88(w) and 13.28(m) μ. A benzene solution was dark red when concentrated and orange when dilute. No satisfactory elemental analysis could be obtained.

Anal. Calcd. for $C_{30}H_{24}$: C, 93.71; H, 6.29. Found: C, 88.91; H, 6.30.

Full hydrogenation of tridehydro-[30]annulene and subsequent crystallization from methanol–ethyl acetate yielded cyclotriacontane, m.p. 56–57°, undepressed on admixture with an authentic sample (m.p. 57–58°).[3c]

[20]Annulene (XI or an Isomer).—A solution of 31 mg. of bisdehydro-[20]annulene (*e.g.*, X) in 15 cc. of benzene was shaken in hydrogen over *ca.* 30 mg. of a Lindlar palladium catalyst[23] at room temperature and atmospheric pressure. In 15 minutes 3 molar equivalents of hydrogen had been absorbed and the reaction was stopped. The catalyst was filtered off and the filtrate, after concentration under reduced pressure to *ca.* 2 cc., was chromatographed on 50 g. of alumina; 25-cc. fractions were collected and the progress of the chromatogram was followed by determining the ultraviolet spectra of representative fractions.

Fractions 14–20 (light yellow solutions), eluted with pentane–ether (19:1), contained the [20]annulene; they all showed practically identical spectra, with maxima at *ca.* 267, 284, 297, 375 and 396 mμ, the first three being the most intense. Fractions 27-39 (light red-brown solutions), eluted with pentane–ether (9:1 to 4:1), contained unchanged starting material [11.4 mg. (37%), estimated spectroscopically], as shown by their ultraviolet spectra.

The above-mentioned fractions 14–20 on combination and evaporation yielded 7.8 mg. (25%) of [20]annulene as a yellow oil which could not be crystallized. The ultraviolet spectrum is given in Table II and Fig. 2. The infrared spectrum (chloroform) no longer showed the acetylene band at 4.64 μ present in the precursor. Rechromatography on 10 g. of alumina gave fractions with essentially identical ultraviolet properties.

Full hydrogenation of [20]annulene (material recovered from the rechromatography), followed by chromatography on alumina, elution with pentane, and crystallization from methanol–ethyl acetate, yielded cycloeicosane, m.p. 55–58°, undepressed on admixture with an authentic sample (m.p. 61–62°).[3c]

[30]Annulene (XIV or an Isomer).—A solution containing 12 mg. of tridehydro-[30]annulene (*e.g.*, XIII) in 10 cc. of benzene was shaken in hydrogen over *ca.* 20 mg. of a Lindlar palladium catalyst[23] at room temperature and atmospheric pressure. After *ca.* 2 hr. 4 molar equivalents of hydrogen had been taken up and the reaction was terminated. The catalyst was removed, the filtrate was evaporated almost to dryness under reduced pressure, and the residue was chromatographed on 30 g. of alumina. Elution with pentane–ether (1:1 to 1:3) yielded unchanged starting material, as evidenced by the ultraviolet spectra. [30]-Annulene was seen to move down the column as a more polar band, which was eluted with ether to ether–ethyl acetate (49:1) to give orange-colored fractions with maxima in the 412–414 mμ region [spectroscopic yield, 0.71 mg. (5.8%), based on ε = 140,000 of the main maximum of pure [30]annulene[21]]. The best representative fraction showed λ_{max}^{ether} 325 and 414 mμ (*E* 0.155 and 0.460); $\lambda_{max}^{dioxane}$ 328 and 427 mμ (*E* 0.585 and 1.595). The ultraviolet spectrum in benzene of this fraction is compared in Table II and Fig. 2 with that of the previously described [30]annulene.[21] On admixture with a sample of crystalline [30]annulene[21] and careful chromatography, no separation could be observed.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF MICHIGAN, ANN ARBOR, MICH.]

Comparative Rates of Homolysis of *exo* and *endo* Bonds in Norbornane and Norbornene Systems

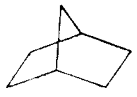
BY MICHAEL M. MARTIN AND DON C. DE JONGH

RECEIVED APRIL 25, 1962

A kinetic study of the decompositions of *t*-butyl *exo*- and *endo*-bicyclo[2.2.1]heptane-2-percarboxylate and *exo*- and *endo*-bicyclo[2.2.1]hept-5-ene-2-percarboxylate has established that all four peresters decompose by a one-step, concerted loss of carbon dioxide. Comparison of the activation parameters for each pair of isomers indicates that homolysis of the *exo*-bond at C_2 is not assisted by the C_1–C_6 single bond or the C_5–C_6 double bond. Thus, non-classical radicals in these two systems can be ruled out in the rate-determining step.

Introduction

The products of free radical reactions involving the norbornane (I), norbornene (II), norbornadiene (III) and 2-methylenenorbornene (IV) systems can all be explained without postulating the intervention of non-classical free radicals. Norbornyl free radicals have been generated by hydrogen abstraction from norbornane derivatives,[1,2] by brominative decarboxylation of the silver salts of carboxylic acids in the dihydroaldrin series, a norbornane derivative,[3] by the decomposition of diacyl peroxides derived from dihydroaldrin carboxylic acids,[3] and by free radical addition reactions to norbornene derivatives.[4–6] In all cases, the products are best explained if they are derived from a radical having the classical structure V, rather than the non-classical structure VI. The free radical addition of *p*-thiocresol to norbornadiene leads to mixtures of the *exo*-5-norbornen-2-yl aryl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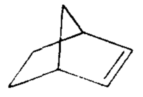
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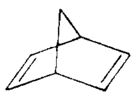
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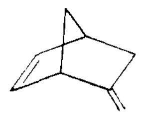
IV

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[1] E. C. Kooyman and G. C. Vegter, *Tetrahedron*, **4**, 382 (1958).

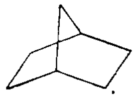
[2] S. J. Cristol and L. K. Gaston, *J. Org. Chem.*, **26**, 4672 (1961).

[3] S. J. Cristol, J. R. Douglas, W. C. Firth and R. E. Krall, *J. Am. Chem. Soc.*, **82**, 1829 (1960).

[4] S. J. Cristol and G. D. Brindell, *ibid.*, **76**, 5699 (1954).

[5] J. A. Berson and W. M. Jones, *ibid.*, **78**, 6045 (1956).

[6] N. LeBel, *ibid.*, **82**, 623 (1960).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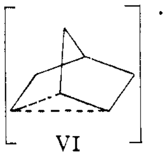
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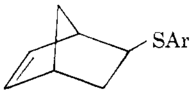

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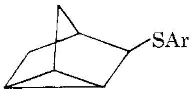

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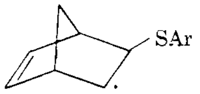

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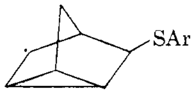

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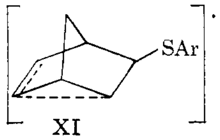
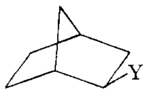


XI

thioether VII, formed by 1,2-addition, and the 3-nortricyclyl aryl thioether VIII, formed by homoconjugative addition.[7] The ratio of tricyclic product to bicyclic product depends upon the initial thiol concentration. This requires that there be present at least two interconvertible radical species which give rise to products. The simplest assumption is that these are the two classical radicals IX and X. Comparable results have been obtained in the free radical addition of carbon tetrachloride, chloroform and bromotrichloromethane to 2-methylene-5-norbornene.[8]

Thus, non-classical radicals such as VI and XI have been found to be unimportant in the product-determining step of free radical processes involving these ring systems. However, it is still possible that the rate-determining step leads to a non-classical structure which can either continue the chain leading to product, or rearrange to the classical radical. The nature of the product of the rate-determining step is more conveniently studied kinetically. Interpretation of studies of the general reactivity of double bonds in these strained ring systems[4,8–10] is generally complicated by the difficulty of assessing differences in steric factors in rigid bicyclic systems and less strained systems such as cyclohexene and octene.

It was the purpose of this work to study a system which would allow a kinetic comparison of the rates of homolytic cleavage of bonds *exo* and *endo* to the ethano bridge in a norbornane derivative and *exo* and *endo* to the etheno bridge in a norbornene derivative, that is, to compare the rates of homolysis of the C–Y bond in structure XII and XIII and in XIV and XV. As enunciated by Winstein[11] and Roberts,[12] in their studies of the solvolytic behavior of compounds of the type XII–XV, participation by the C_1–C_6 single bond or the C_5–C_6 double bond is possible only when the departing group is *exo*. Hence, if non-classical radicals are formed, homolytic cleavage of an *exo*-C–Y bond should be accelerated over that for an *endo*-C–Y bond.



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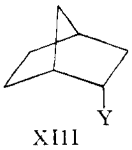
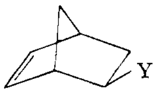
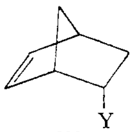


XIII

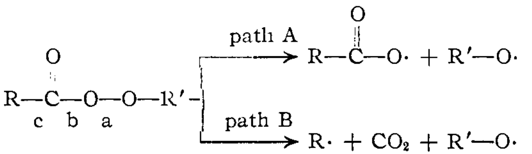


XIV



XV

The compounds chosen for this study were the *t*-butyl peresters of *exo*- and *endo*-bicyclo[2.2.1]-heptane-2-carboxylic acid (XII and XIII, Y = CO_3Bu-*t*) and *exo*- and *endo*-bicyclo[2.2.1]hept-5-ene-2-carboxylic acid (XIV and XV, Y = CO_3Bu-*t*). Bartlett[13] has established that the free radical decomposition of peresters (reaction 1) is rather delicately poised between two alternative mechanistic pathways, non-concerted (path A) and concerted (path B). When the alkyl radical R· is of a stable type (benzyl, *t*-butyl, trichloromethyl), there is simultaneous cleavage of bonds a and c, producing carbon dioxide in the rate-determining step. In addition to the stretching of bonds a and c, the transition state for such a decomposition requires that rotation of bond b from carbonyl carbon to oxygen be restricted because the elimination of the alkyl radical and *t*-butoxy radical is a *trans* elimination. When the alkyl radical R· is not so stable (methyl, phenyl, hydrogen,[14] 2-phenylethyl or 3-phenylpropyl[15]), then only bond a cleaves in the rate-determining step, and the carboxylate radical subsequently loses carbon dioxide. Furthermore, the mechanism by which a particular perester decomposes can be characterized by the values of the activation parameters, ΔH^* and ΔS^*. Peresters which decompose by a mechanism in which there are no rotational restrictions in the transition state, as is the case in a non-concerted decomposition which produces a carboxylate radical which is not conjugated with any other unsaturated moiety, are associated with values of ΔH^* greater than 35 kcal./mole and ΔS^* greater than 13 e.u. On the other hand, peresters which decompose by a mechanism in which the rotation of one bond is restricted at the transition state, as is the case in a concerted decomposition which produces an alkyl radical such as *t*-butyl, in which the radical carbon atom is not conjugated with any unsaturated moiety, are associated with values of ΔH^* between 30 and 35 kcal./mole and ΔS^* between 6 and 13 e.u. If there are further rotational


$$\mathrm{R\underset{c}{-}\overset{\overset{O}{\|}}{C}\underset{b}{-}O\underset{a}{-}O{-}R'} \begin{cases} \xrightarrow{\text{path A}} \mathrm{R{-}\overset{\overset{O}{\|}}{C}{-}O\cdot + R'{-}O\cdot} \\ \xrightarrow{\text{path B}} \mathrm{R\cdot + CO_2 + R'{-}O\cdot} \end{cases} \qquad (1)$$
XVI

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[7] S. J. Cristol, G. D. Brindell and J. A. Reeder, *J. Am. Chem. Soc.*, **80**, 635 (1958).

[8] E. S. Huyser and G. Echegaray, *J. Org. Chem.*, **27**, 429 (1962).

[9] M. S. Kharasch and H. N. Friedlander, *ibid.*, **14**, 239 (1949).

[10] J. Gressan, A. Rajbenbach and M. Szwarc, *J. Am. Chem. Soc.*, **83**, 3003 (1961).

[11] (a) S. Winstein and D. Trifan, *ibid.*, **71**, 2953 (1949); **74**, 1147, 1154 (1952); (b) S. Winstein, H. M. Walborsky and K. Schreiber, *ibid.*, **72**, 5795 (1950); (c) S. Winstein, B. K. Morse, E. Grunwald, H. W. Jones, J. Corse, D. Trifan and H. Marshall, *ibid.*, **74**, 1127 (1952); (d) S. Winstein and M. Shatavsky, *ibid.*, **78**, 592 (1956).

[12] (a) J. D. Roberts and C C. Lee, *ibid.*, **73**, 5009 (1951); (b) J. D. Roberts and W. Bennett, *ibid.*, **76**, 4623 (1954).

[13] (a) P. D Bartlett and R R. Hiatt, *ibid.*, **80**, 1398 (1958); (b) P. D. Bartlett and D. M. Simon, *ibid.*, **82**, 1753 (1960); (c) P. D. Bartlett and C. Rüchardt, *ibid.*, **82**, 1756 (1960); (d) P. D. Bartlett, E. P. Benzing and R. E. Pincock, *ibid.*, **82**, 1769 (1960).

[14] R. E. Pincock, *ibid.*, **84**, 312 (1962).

[15] M. M. Martin, *ibid.*, **84**, 1986 (1962).

restrictions in the alkyl radical produced, ΔH^* and ΔS^* are lowered still further.

The ability of the C_1–C_6 single bond in the norbornane ring system, or the C_5–C_6 double bond in the norbornene system, to stabilize a free radical developing at C_2 can be studied by ascertaining the mechanism of the decompositions of the four peresters XII–XV ($Y = CO_3Bu$-*t*). If there is σ- or π-participation, then it should be reflected in the rates and activation parameters for the decompositions of the two pairs of *exo* and *endo* isomers. Either the *exo* isomer should decompose by a concerted path, the *endo* by a non-concerted path, or if both decompositions are concerted, the enthalpy of activation for the *exo* isomer should be less than that for the *endo* isomer. If there is no σ- or π-participation, then the rates and activation parameters for the decompositions of the two pairs of isomers should be the same, whether the mechanism is concerted or non-concerted.

Experimental

Materials.—**Cumene** from the Eastman Kodak Co. was shaken with three portions of concentrated sulfuric acid, once with water, three times with 5% sodium bicarbonate, again with water, dried over magnesium sulfate, and distilled, b.p. 151–152°.

Chlorobenzene was distilled, b.p. 130–131°, shaken with three portions of concentrated sulfuric acid, once with water, three times with 5% sodium bicarbonate, again with water, dried successively over calcium chloride, calcium sulfate and phosphorus pentoxide, and distilled, b.p. 130–130.5°.

The peresters were prepared by the slow addition of the acid chloride in low boiling petroleum ether (30–60°) to an ice-cooled petroleum ether solution of *t*-butyl hydroperoxide and pyridine. For every mole of acid chloride used, 1.1 moles of pyridine and 2.2 moles of *t*-butyl hydroperoxide were employed. The mixture was stirred for 2 hours at 0°, then warmed to room temperature. Water was added to the mixture, and the petroleum ether layer was washed with 10% sulfuric acid, 10% sodium carbonate and water. The solution was dried with magnesium sulfate, then passed through a short Florisil column. Solvent was removed under vacuum, and finally the residue was pumped for several hours on a rotating concentrator to remove traces of solvent. Peresters prepared and purified in this way exhibit no extraneous bands in the hydroxyl and carbonyl regions of the infrared.

exo-t-**Butyl bicyclo[2.2.1]heptane-2-percarboxylate (XII)** was prepared in 93% yield. The material was a white solid, m.p. 27°, exhibiting a carbonyl stretching maximum at 1780 cm.$^{-1}$.

Anal. Calcd. for $C_{12}H_{20}O_3$: C, 67.89; H, 9.50. Found: C, 68.13; H, 9.38.

endo-t-**Butyl bicyclo[2.2.1]heptane-2-percarboxylate (XIII)** was prepared in 94% yield. The material was a white solid, m.p. 34°, exhibiting a carbonyl stretching maximum at 1780 cm.$^{-1}$.

Anal. Calcd. for $C_{12}H_{20}O_3$: C, 67.89; H, 9.50. Found: C, 67.67; H, 9.41.

exo-t-**Butyl bicyclo[2.2.1]hept-5-ene-2-percarboxylate (XIV)** was prepared in 77% yield. The material was a colorless oil, melting about 11°, exhibiting a carbonyl stretching maximum at 1780 cm.$^{-1}$.

Anal. Calcd. for $C_{12}H_{18}O_3$: C, 68.53; H, 8.63. Found: C, 68.22; H, 8.66.

endo-t-**Butyl bicyclo[2.2.1]hept-5-ene-2-percarboxylate (XV)** was prepared in 75% yield. The material was a colorless oil, melting at about 15°, exhibiting a carbonyl stretching maximum at 1780 cm.$^{-1}$.

Anal. Calcd. for $C_{12}H_{18}O_3$: C, 68.53; H, 8.63. Found: C, 68.82; H, 8.80.

Procedure for Kinetic Runs.—A weighed sample of the perester in a 5.00-ml. volumetric flask was dissolved in the solvent, and aliquots of this solution were sealed in ampoules. No effort was made to conduct the reaction under a nitrogen atmosphere since air was found to have no effect on the rates. A sample of this solution was considered to represent zero time. The ampoules were immersed simultaneously in an oil-bath maintained at a constant temperature within ± 0.05°. Ampoules were removed periodically from the oil-bath, chilled in ice-water, opened, and the solutions stored at 5° until analyzed. Points were taken until 55 to 93% of the original perester had decomposed. One ampoule was kept in the bath until decomposition was complete. This sample was considered to represent infinite time.

Determination of Relative Concentration of Peresters by Infrared.—The analytical method was essentially the one described by Bartlett and Hiatt.[13a] The carbonyl band of the peresters in the 1780 cm.$^{-1}$ region was used to follow their disappearance. The analyses were carried out in matched 0.1-mm. cells on a Perkin–Elmer model 21 infrared spectrophotometer. All samples of a given run were allowed to warm to room temperature, and the transmission of each was measured in turn, while both increasing and decreasing frequencies, and average values were taken. The maximum error in this measurement is around 1%.

Treatment of Data.—For the *exo* and *endo* saturated peresters XII and XIII, and the *exo* unsaturated perester XIV, rate constants were calculated from a least squares slope of plots of log P/P_0 *vs.* time, where P is perester concentration at any given time and P_0 is initial perester concentration. The ratio P/P_0 was calculated from the expression

$$P/P_0 = \frac{\log T_\infty - \log T_P}{\log T_\infty - \log T_0}$$

where T_∞ is the percentage transmission at infinite time, T_P is the percentage transmission of any given sample, and T_0 is percentage transmission at zero time.

The plots of log P/P_0 *vs.* time were linear, and first-order rate constants were determined by calculating the slope of the least squares line.

The enthalpy of activation, ΔH^*, was obtained from the least squares slope of the line given by log k/T *vs.* $1/T$ for runs at 94.5°, 101.9° and 112.0°. The entropy of activation, ΔS^*, was calculated from the expression

$$k = \frac{k'T}{h} e^{\Delta S^*/R} e^{-\Delta H^*/RT}$$

where k is the first-order rate constant at temperature T, k' is the Boltzmann constant, h is the Planck constant, and R is the gas constant.

The treatment described above is not applicable to the *endo* unsaturated perester XV, because of a parallel reaction of the perester which produces 6-hydroxynorcamphane-2-carboxylic acid lactone (XVII), having an absorption maximum at 1790 cm.$^{-1}$, and strong absorption at 1778 cm.$^{-1}$. Thus, although the change in transmission at 1778 cm.$^{-1}$ is clearly first order, it does not represent a measure of the desired rate constant, because the ratio "P/P_0", calculated as above, does not measure the perester concentration ratio, due to the lactone present in the partially decomposed mixture. The rate constants for the two parallel first-order processes were separated as follows. The lactone XVII was prepared[16] and its extinction coefficients at 1778 cm.$^{-1}$, the perester maximum, and at 1790 cm.$^{-1}$, the lactone maximum, were determined. The ratio of the rate constants for the two competing processes is given by the expression

$$\frac{k_2}{k_1} = \frac{\%\ \text{yield lactone}}{100 - \%\ \text{yield lactone}}$$

where k_2 is the rate constant for lactone formation and k_1 is the rate constant for reaction 1. The lactone yield was determined by measuring its concentration in the sample representing infinite time. The kinetic procedure was the same as that described above. The samples were analyzed by disconnecting the scanning mechanism of the infrared spectrophotometer at 1778 cm.$^{-1}$, and viewing each sample in turn. The observed optical density of any sample is a sum of the contributions due to the undecomposed perester and the lactone produced. Thus, $\text{O.D.}_{\text{obs.}} = \epsilon_P lP + \epsilon_l lL$, where O.D._{obs} is the observed optical density, ϵ_P

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[16] J. D. Roberts, E. R. Trumbull, W. Bennett and R. Armstrong, 1st. ed., *J. Am. Chem. Soc.*, **72**, 3116 (1950).

and ϵ_l are the extinction coefficients at 1778 cm.$^{-1}$ for perester and lactone, respectively, l is path length, and P and L represent the perester and lactone concentrations at any given time. From the kinetic treatment of parallel first-order reactions[17]

$$P = P_0 e^{-(k_2 + k_1)t} \text{ and } L = \frac{k_2}{k_2 + k_1} P_0 (1 - e^{-(k_2 + k_1)t})$$

where t is time and zero subscripts refer to initial concentration. By substitution of the expressions for P and L into the equation for the observed O.D., and making use of the known value for the ratio k_2/k_1, it is possible to solve for k_1 and k_2. An average value for all of the points of a given run can then be taken.

Determination of Products.—The amount of carbon dioxide evolved during a decomposition was determined gravimetrically by noting the increase in weight of a tube filled with Ascarite. A sample of the perester was weighed into the reaction flask and the solvent was introduced from a pipet. Solutions were approximately 0.1 *M*. Prepurified nitrogen from a cylinder was then passed through a tube filled with Ascarite and Dehydrite into the reaction flask to a point a few cm. above the surface. The top of the condenser was connected to a trap cooled in a Dry Ice–acetone-bath, then to a tube filled with Dehydrite, then two tubes filled with Ascarite, and finally to a bubbler. The system was purged with nitrogen, maintaining the reaction flask at room temperature, until the Ascarite tube nearest the reaction flask reached a constant weight. Then the reaction flask was immersed in the oil-bath, maintained at a constant temperature, and the Ascarite tube nearest the reaction flask was periodically weighed by stopping the nitrogen flow at the tank, clamping off rubber tubing, and removing the Ascarite tube. The second Ascarite tube simply protected the first from atmospheric carbon dioxide and did not increase in weight. The reaction was allowed to proceed until the Ascarite tube reached a constant weight.

The lactone XVII was isolated from the decomposition of the *endo* unsaturated perester XV in cumene at 113°, by removing solvent and volatile products by distillation at aspirator pressure. The residue was placed on a Florisil column in low boiling (30–60°) petroleum ether. Bicumyl was eluted in petroleum ether, and then the lactone was eluted with ether. The crude lactone was sublimed twice at 50° and atmospheric pressure, then crystallized from pentane; m.p. 154–155° (reported[16] 154.2–155.2°). The lactone so isolated had the same retention time on v.p.c. as the authentic material, and a mixed melting point of the two was not depressed.

Other organic products were not isolated and rigorously characterized, but were satisfactorily identified by infrared and vapor phase chromatography.

Results

Rate Constants.—The kinetic data for the decompositions of the *t*-butyl esters of *exo*-bicyclo-[2.2.1]heptane-2-percarboxylate (XII), *endo*-bicyclo[2.2.1]heptane-2-percarboxylate (XIII), *exo*-bicyclo[2.2.1]hept-5-ene-2-percarboxylate (XIV) and *endo*-bicyclo[2.2.1]hept-5-ene-2-percarboxylate (XV) are summarized in Tables I–IV, respectively.

TABLE I

RATE OF DECOMPOSITION OF *t*-BUTYL *exo*-BICYCLO[2.2.1]-HEPTANE-2-PERCARBOXYLATE

Init. concn., *M*	Solvent	T, °C. (±0.05)	$k \times 10^4$, sec.$^{-1}$
0.0474	Cumene	94.45	0.605
.2345	Cumene	94.45	0.592
.0497	Cumene	101.90	1.53
.0968	Cumene	101.90	1.36
.1908	Cumene	101.90	1.28
.0613	Cumene	112.10	4.72
.2461	Cumene	112.10	4.32
.2375	Chlorobenzene	94.45	0.886
.0480	Chlorobenzene	101.90	1.43
.1944	Chlorobenzene	101.90	2.28
.2520	Chlorobenzene	112.10	8.85

TABLE II

RATE OF DECOMPOSITION OF *t*-BUTYL *endo*-BICYCLO[2.2.1]-HEPTANE-2-PERCARBOXYLATE

Init. concn., *M*	Solvent	T, °C. (±0.05)	$k \times 10^4$, sec.$^{-1}$
0.0465	Cumene	94.45	0.527
.1983	Cumene	94.45	0.456
.0510	Cumene	101.90	1.12
.0980	Cumene	101.90	1.16
.1012	Cumene	101.90	1.20
.2085	Cumene	101.90	1.04
.0499	Cumene	111.90	3.57
.2010	Cumene	111.90	3.46
.1856	Chlorobenzene	94.45	0.969
.0480	Chlorobenzene	101.90	1.33
.0517	Chlorobenzene	101.90	1.25
.0948	Chlorobenzene	101.90	1.96
.1994	Chlorobenzene	111.90	6.53

TABLE III

RATE OF DECOMPOSITION OF *t*-BUTYL *exo*-BICYCLO[2.2.1]-HEPT-5-ENE-2-PERCARBOXYLATE

Init. concn., *M*	Solvent	T, °C. (±0.05)	$k \times 10^4$, sec.$^{-1}$
0.0508	Cumene	94.45	0.448
.2183	Cumene	94.45	0.424
.0501	Cumene	101.90	1.18
.0957	Cumene	101.90	1.19
.1007	Cumene	101.90	1.11
.1990	Cumene	101.90	1.05
.0503	Cumene	112.10	3.97
.2105	Cumene	112.10	3.45
.2218	Chlorobenzene	94.45	0.559
.0561	Chlorobenzene	101.90	0.934
.1039	Chlorobenzene	101.90	1.53
.2023	Chlorobenzene	101.90	1.25
.2202	Chlorobenzene	112.10	5.00

TABLE IV

RATE OF DECOMPOSITION OF *t*-BUTYL *endo*-BICYCLO[2.2.1]-HEPT-5-ENE-2-PERCARBOXYLATE

Init. concn., *M*	Solvent	T, °C. (±0.05)	$k \times 10^4$, sec.$^{-1}$
0.1148	Cumene	94.50	0.311
.1148	Cumene	101.90	0.735
.1109	Cumene	112.00	2.48

Except for the *endo* unsaturated perester, decompositions were carried out in two solvents, cumene and chlorobenzene, at three different temperatures, and over a fourfold variation in concentration. In cumene, the plots of log P/P_0 show a high degree of linearity, correlation coefficients ranging from 0.992–1.000. Furthermore, the rate constants determined from these graphs at any given temperature are constant, within experimental error, over a fourfold variation in initial perester concentration. Evidence for first-order kinetics, uncomplicated by induced decompositions, thus seems convincing. In chlorobenzene, the rate constants at any given temperature are seen generally to increase with increasing initial perester concentration, and to be larger than the corresponding rate constant in cumene, except when initial

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(17) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," First Ed., John Wiley and Sons, Inc., New York, N. Y., 1953, p. 147.

perester concentration is low. This suggests that in chlorobenzene induced decomposition is being observed. Apparently, the radicals which bring about the induced decomposition in chlorobenzene are trapped by hydrogen abstraction from the cumene, producing cumyl radicals, which dimerize rather than react with the perester.

Activation Parameters.—From the kinetic data of Tables I–IV, it is possible to calculate the activation parameters for the four decompositions studied. These are summarized in Table V. The correlation coefficients for all four Arrhenius plots are 0.999+. The error in ΔH^* is of the order of 0.5 kcal./mole, in ΔS^* of the order of 1.5 e.u. The *exo* and *endo* isomers of both the saturated peresters XII and XIII and the unsaturated peresters XIV and XV are seen to have the same activation parameters, within experimental error.

TABLE V

ACTIVATION PARAMETERS FOR THE DECOMPOSITIONS OF THE PERESTERS XII–XV

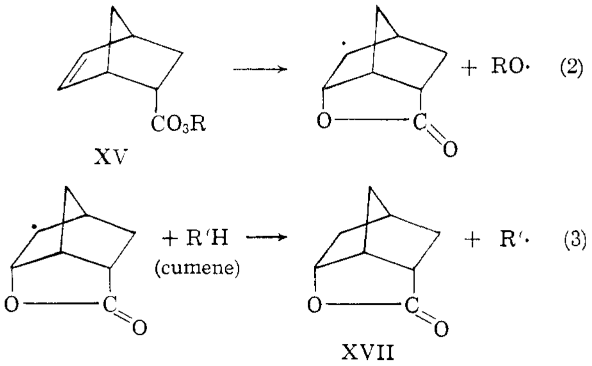
Perester	ΔH^*, kcal./mole	ΔS^*, e.u.
XII	31.4	7
XIII	31.1	6
XIV	33.0	11
XV	32.6	9

Products.—In Table VI the yields of carbon dioxide resulting from decompositions in cumene at 109.3° are indicated. These yields are accurate to about 5%. Except in the case of the *endo* unsaturated perester XV, the yields are very nearly quantitative. The lower yield of carbon dioxide in this case is due to the formation of the lactone XVII by reactions 2 and 3. This transformation involves the direct reaction of the double bond with the peroxidic linkage, and is analogous to the molecule-induced decompositions which have been shown to be responsible for the formation of cyclohexyl acetate during the decomposition of acetyl peroxide in cyclohexene.[18] Such a double bond induced decomposition is particularly favorable in perester XV because of the intramolecular nature of the reaction. The activation parameters for the reaction are $\Delta H^* = 30.2$ kcal./mole, $\Delta S^* = 1$ e.u.

TABLE VI

CARBON DIOXIDE YIELDS IN CUMENE AT 109.3°

Perester	XII	XIII	XIV	XV
CO_2 yield, %	98	92	94	69



XV

XVII

Other organic products were not isolated, but were adequately characterized by infrared and gas phase chromatography. The infrared spectra of decompositions carried out in cumene showed the absence of any absorption due to simple esters, which could be the products of induced decompositions. From all four peresters, acetone and *t*-butyl alcohol were produced from the *t*-butoxy radical. No products could be detected which might arise from the carboxylate radical. The infrared spectra were free of any absorption which might be due to a carboxylic acid, and no acidic material could be extracted with base from the decomposition mixtures. This, of course, is consistent with the high yields of carbon dioxide. The alkyl radical from the two saturated peresters produced only one major product, norbornane (I). Two major products, norbornene and nortricyclene, resulted from decompositions of the two unsaturated peresters in toluene, cumene and *p*-cymene. In cumene at 97.3°, the ratio of norbornene to the more stable nortricyclene[19] was 2:3 for both unsaturated peresters.

Discussion

When the activation parameters for the decompositions of the four peresters XII–XV are included in Bartlett and Hiatt's[13a] enthalpy-entropy correlation, all four are found to fall in with those peresters which decompose by a mechanistic pathway in which the rotation of one bond is restricted at the transition state. This means that all four peresters are decomposing by the one-step, concerted loss of carbon dioxide (path B). The high yield of carbon dioxide and the absence of carboxylic acids among the products are consistent with the concerted nature of the decomposition. Furthermore, the activation parameters for each pair of isomeric *endo*- and *exo*-peresters are the same within experimental error. Consequently, it must be concluded that it is no more energetically favorable for an *exo*-bond to undergo homolytic scission than it is for an *endo*-bond. From this it must be concluded that neither σ- nor π-participation is a significant driving force in the formation of free radicals in the norbornane and norbornene systems studied.

The higher enthalpies of activation associated with the unsaturated perester probably indicate that more strain is introduced when a dehydronorbornyl system produces a dehydronorbornyl free radical than when a norbornyl system produces a norbornyl free radical. More must be learned about the nature of hybridization of the radical carbon atom in these systems before these small differences can be interpreted with certainty, however.

Non-classical norbornyl and dehydronorbornyl free radicals have thus been shown to be unimportant in both the rate-determining step and the product-determining step. It is interesting to speculate on why a cation developing at C_2 by the cleavage of an *exo*-bond should be stabilized by σ- or π-participation while a free radical is not.

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(18) J. C. Martin and E. H. Drew, *J. Am. Chem. Soc.*, **83**, 1232 (1961).

(19) P. R. Schleyer, *ibid.*, **80**, 1700 (1958).

The resonance energy of the allyl radical is about 35% that of the allyl cation.[20] The decreased ability of an α-vinyl group to stabilize a radical compared to a cation is due to electron repulsion arising from the presence of an additional electron in the molecular orbital.[21] Furthermore, it has been calculated that a β-vinyl group is roughly 40% as effective at stabilizing a cation than is an α-vinyl group.[22] Apparently the added electron repulsion in the radical simply outweighs what little stabilization might result from delocalization in a non-classical structure. It is also possible that the different properties of norbornyl and dehydronorbornyl cations and radicals are due to differences in hybridization about a cationic carbon atom and a radical carbon atom. Alternatively, the difference in the cation and radical might be explained by considering C_2, C_5 and C_6 to define a homoaromatic structure[23] in which one carbon atom, C_1, intervenes between C_2 and C_6, and two carbon atoms, C_3 and C_4, intervene between C_2 and C_5. In such a case, the cation, having two electrons in the homoaromatic system, would be expected to be more stable than the radical with its three electrons. Whatever the reason, the formation of non-classical structures is not observed during the rate-determining or product-determining stages of reactions proceeding by way of free radicals at C_2 of a norbornane or norbornene ring system.

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(20) A. G. Harrison and F. P. Lossing, *J. Am. Chem. Soc.*, **82**, 1052 (1960).

(21) A. Streitwieser, Jr., *ibid.*, **82**, 4123 (1960).

(22) M. Simonetta and S. Winstein, *ibid.*, **76**, 18 (1954).

(23) S. Winstein and J. Sonnenberg, *ibid.*, **83**, 3244 (1961).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA, BERKELEY 4, CALIF.]

1,2-Dihydrocyclopent[jk]fluorene

BY BERMA L. MCDOWELL,[1] GERALD SMOLINSKY[2] AND HENRY RAPOPORT

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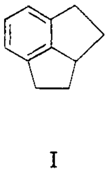
In order to obtain further data on the effects of bending a benzene ring, the strained hydrocarbon 1,2-dihydrocyclopent[jk]fluorene (IV) has been prepared and some of its properties have been determined. Synthesis by pyrolysis of the lead salt of 1-carboxyfluorene-9-acetic acid (V) was unsuccessful. However, by approaching the synthesis through a substituted indan and forming the fluorene by decomposition of diazotized *o*-(1-indanyl)-aniline (XXIX), the cyclopent[jk]fluorene ring system was prepared. As was the case with the previous three compounds of this series,[3] IV displayed properties characteristic of a bent benzene ring—a distinct bathochromic shift with decreased extinction coefficient in its ultraviolet absorption and olefinic-like reactivity with hydrogen and perbenzoic acid.

Introduction.—The objective of a series of investigations[3] has been to synthesize strained aromatic hydrocarbons in which the central benzene ring is forced out of planarity by a fused cyclopentano system. The diminished resonance stabilization, brought about by decreased overlap of the π-orbitals in a warped system, should be evidenced in increased susceptibility of that benzene ring to oxidation and reduction and in other behavior tending toward that of "cyclohexatriene." The ultraviolet absorption bands of such a molecule are expected to show a bathochromic shift and a decreased extinction coefficient when compared with those of a similarly substituted but non-strained planar system. The energy of the excited states of the two compounds would be comparable, but the ground state energy of the strained compound would be higher, thus resulting in a lower energy of transition. There would also be less fine structure in the spectrum of the strained molecule, probably as a result of the increased complexity of vibrational transitions.[4]

These predictions have been confirmed in several strained aromatic hydrocarbons of the above type which have been synthesized: 2,2a,3,4-tetrahydro-1H-cyclopent[cd]indene (I),[3a] 2,2a,3,3a,4,5-hexahydro-1H-cyclopent[jkl]-*as*-indacene (II)[3b] and fluoradene (III).[3c] All three compounds are easily hydrogenated over a palladium-on-carbon catalyst, II and III are readily attacked by perbenzoic acid, and all three show the expected spectral properties (see Table III).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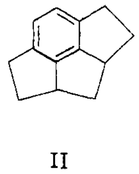
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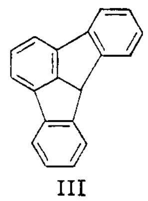
III

1,2-Dihydrocyclopent[jk]fluorene (IV) should represent a strained system intermediate between I and III. It is the preparation and properties of this substance that are the subject of this report.

Synthesis.—We anticipated that pyrolysis of the lead salt of 1-carboxyfluorene-9-acetic acid (V)

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(1) National Institutes of Health Predoctoral Fellow.

(2) National Science Foundation Predoctoral Fellow.

(3) (a) H. Rapoport and J. Z. Pasky, *J. Am. Chem. Soc.*, **78**, 3788 (1956); (b) H. Rapoport and G. Smolinsky, *ibid.*, **82**, 1171 (1960); (c) H. Rapoport and G. Smolinsky, *ibid.*, **82**, 934 (1960).

(4) See L. L. Ingraham in M. S. Newman "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1956, p. 500, and other references on strain in aromatic systems given in footnote 3b.