[Contribution from the Department of Chemistry, Massachusetts Institute of Technology]

Acid-catalyzed Equilibrations of Endocyclic and Exocyclic Olefins[1,2]

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Methylenecycloalkanes and 1-methylcycloalkenes have been equilibrated in acetic acid at 25° containing *p*-toluenesulfonic acid. The amounts of the isomers present at equilibrium and the approximate rates of equilibration were determined by gas chromatography. The equilibrium constants are: 1-methylcyclopentene/methylenecyclopentane 1144, 1-methylcyclohexene/methylenecyclohexane 240, 1-methylcycloheptene/methylenecycloheptane 74.4, and 1-methylcycloöctene/methylenecycloöctane 598. Methylenecycloalkanes were found to be absent in the equilibrium mixtures of the nine- and ten-membered cyclic olefins. *trans*-1-Methylcyclodecene was formed initially almost as rapidly as the *cis* isomer in the isomerization of methylenecyclodecane, and subsequently decreased in amount to an equilibrium value of *cis/trans* 99.5/0.5. A possible explanation of this phenomenon is discussed.

The question of the relative stabilities of methylenecycloalkanes and their endocyclic isomers recently has been the subject of some controversy. Brown[3] proposed that in *exo–endo* equilibria involving five- and six-membered cyclic olefins, methylenecyclopentane should be relatively more stable than methylenecyclohexane. Turner and Garner,[4] on the other hand, reported that the heat of isomerization of methylenecyclopentane to its endocyclic isomer is larger by 1.5 kcal. than the heat of isomerization of methylenecyclohexane to 1-methylcyclohexene. The same authors studied the acid-catalyzed isomerization of methylenecyclopentane and methylenecyclohexane in acetic acid at 100° and found the products to contain only the endocyclic isomers; these results have since been substantiated in other laboratories.[5,6] The amount of methylenecycloheptane in equilibrium with 1-methylcycloheptene in acetic acid at reflux temperature was reported[6] not to exceed 2%. This result is in agreement with the negative heat of isomerization of methylenecycloheptane.[4] No quantitative data concerning the relative stabilities of exocyclic and endocyclic double bonds in larger rings are reported in the literature,[7] although it has been known for some time that 1-methylcycloöctanol[8] gives rise to 1-methylcycloöctene rather than the exocyclic isomer on acid-catalyzed dehydration.[8] The present investigation, concerned with the determination of the equilibrium constants between methylenecycloalkanes and 1-methylcycloalkenes containing five- to ten-membered rings, was undertaken to obtain precise data on the influence of ring size on *exo–endo* equilibria.

Results

The olefins were isomerized in oxygen-free acetic acid containing 0.25% *p*-toluenesulfonic acid at 25°. The olefin concentration employed was 10% (by volume). Under these conditions no polymerization occurred except in several (but not all) equilibrations of methylenecyclopentane and 1-methylcyclopentene. The disappearance of the methylenecycloalkanes was followed kinetically by taking aliquots at intervals and analyzing them by gas chromatography. The half-lives of the methylenecycloalkanes were calculated from the first-order plots obtained in this way. The equilibria were approached from both sides and equilibrium was considered to be reached when the composition of the olefin mixture did not change over a period of twenty-four hours (seventy-two hours in the case of the six-membered cyclic olefins). The major products were isolated by gas chromatography and identified by their infrared spectra. In addition to the olefins, the mixtures of products from the equilibrations of the five-, six- and seven-membered cyclic olefins were found to contain varying amounts of the corresponding 1-methylcycloalkanols and their acetates. The alcohols did not arise by hydrolysis of the acetates during isolation since samples of the pure acetates were found to be stable under the conditions employed. The results are summarized in Table I.

Since the equilibria of the nine- and ten-membered cyclic olefins were so completely on the sides of the endocyclic isomers, no precise values for the equilibrium constants for the *exo/endo* equilibria could be determined. However, since 0.1% of the methylenecycloalkanes could have been detected by gas chromatography under the conditions employed,[9] it can be stated that $K_{endo/exo}$ must be greater than 1000 ($\Delta F^0 < -4.0$ kcal./mole). There was no evidence for the formation of the (unknown) *trans*-1-methylcycloöctene by isomerization of methylenecycloöctane. The product formed was *cis*-1-methylcycloöctene containing 0.5% of an unidentified olefin. *trans*-1-Methylcyclononene, of which an authentic sample was available,[10] was found to be absent, within the limits of detectibility by gas chromatography under the conditions employed,[9] in the equilibrium mixture of the nine-membered cyclic olefins. During the equilibration of methylenecyclodecane the surprising observation was made that *trans*-1-methylcyclodecene was initially formed at a rate only slightly slower than the *cis* isomer (Fig. 1). After the concentration of the *trans*-olefin had reached a maximum value of 37% (of the total olefin mixture), it decreased at a

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[1] Supported in part by the Office of Ordnance Research, U. S. Army, under Contract No. DA-19-020-ORD-4542.

[2] Described in part in a communication by A. C. Cope, D. Ambros, E. Ciganek, C. F. Howell and Z. Jacura, This Journal, **81**, 3153 (1959).

[3] H. C. Brown, *J. Org. Chem.*, **22**, 439 (1957); H. C. Brown, J. H. Brewster and H. Shechter, This Journal, **76**, 467 (1954).

[4] R. B. Turner and R. H. Garner, *ibid.*, **80**, 1424 (1958).

[5] R. A. Benkeser and J. J. Hazdra, *ibid.*, **81**, 228 (1959).

[6] W. J. Bailey and W. F. Hale, *ibid.*, **81**, 651 (1959).

[7] A summary of references pertinent to the stabilities of the exocyclic and endocyclic isomers of five- and six-membered cyclic olefins is found in ref. 4; *cf.* also B. R. Fleck, *J. Org. Chem.*, **22**, 439 (1957).

[8] M. Godchot and M. Cauquil, *Compt. rend.*, **185**, 1202 (1927); A. C. Cope and H. C. Campbell, This Journal, **74**, 179 (1952); H. C. Brown and M. Borowski, *ibid.*, **74**, 1894 (1952).

[9] See footnote *f* of Table I.

[10] A. C. Cope, E. Ciganek, C. F. Howell and E. E. Schweizer, to be published.

TABLE I

EQUILIBRIA BETWEEN METHYLENECYCLOALKANES $\overbrace{(CH_2)_{n-1}C}=CH_2$ AND 1-METHYLCYCLOALKENES $(CH_2)_{n-2}(CH{=})C{-}CH_3$ IN ACETIC ACID AT 25°

Olefin isomerized		Half-life, min.	Composition of olefin mixt. at equilibrium[a,b]		$K_{endo/exo}$[c]	$\Delta F^0_{isom.}$[d] (*exo* → *endo*), kcal./mole at 25°	$\Delta H^0_{isom.}$,[e] kcal./mole
n	Position of double bond		% *endo*	% *exo*			
5	*exo*	10	99 91	0.09	1144 ± 51	−4.17 ± 0.03	−3.9
5	*endo*	..	99.91	.09			
6	*exo*	296	99.56	.44	240 ± 13	−3.24 ± .03	−2.4
6	*endo*	..	99.62	.38			
7	*exo*	42	98.67	1.33	74.4 ± 0.8	−2.55 ± .01	−2.3
7	*endo*	..	98.73	1.27			
8	*exo*	11	99.81	0.19	598 ± 68	−3.79 ± .07	
8	*endo*	..	99.89	.11			
9	*exo*	30	100 0 *cis*[f]	.0[f]			
9	*endo-trans*[g]	4	100.0 *cis*[f]	.0[f]			
10	*exo*	22	99.5 *cis* 0.5 *trans*	.0[f]			
10	*endo-cis*[h]	..	99.6 *cis* 0.4 *trans*	.0[f]			
10	*endo-trans*[i]	163	99.4 *cis* 0.6 *trans*	.0[f]			

[a] Mean values of two equilibrations, rounded off to two decimal places. [b] In the equilibration of the five-, six- and seven-membered cyclic olefins, the following amounts (% of total products) of 1-methylcycloalkanols and 1-methylcycloalkyl acetates were formed: $n = 5$, alcohol, 0.3; acetate, 20–24; $n = 6$, alcohol, 2–14; acetate, 30–39; $n = 7$, alcohol, 2–4; acetate, 4–7. [c] Mean value of the equilibrium constants obtained from either side of the equilibrium using compositions of the olefin mixtures to the third decimal place. [d] Calculated using the equation $\Delta F^0 = -RT \ln K$ *endo/exo*. [e] Ref. 4. [f] The limits of detectibility by gas chromatography under the conditions employed of the isomers found to be absent in the equilibrium mixtures of the nine- and ten-membered cyclic olefins are estimated to be: methylenecyclononane, 0.1%; *trans*-1-methylcyclononene, 0.2%; methylenecyclodecane, 0.1%. [g] Mixture of methylenecyclononane (4.8%), *trans*-1-methylcyclononene (14%) and *cis*-1-methylcyclononene (81.2%). [h] Contained 0.2% of *trans*-1-methylcyclodecene. [i] Mixture of methylenecyclodecane (2.2%), *trans*-1-methylcyclodecene (35.5%) and *cis*-1-methylcyclodecene (62.3%). [j] *K cis/trans* = 199 ± 11. [k] $\Delta F^0_{isom.\ trans \rightarrow cis} = -3.13 \pm 0.03$ kcal./mole.

rate (half-life 172 minutes) identical within experimental error with the rate of isomerization of an authentic sample[10] of *trans*-1-methylcyclodecene (half-life 163 minutes) under the same conditions. Further proof of the structure of the *trans*-olefin was derived by comparison of its infrared spectrum with the spectrum of an authentic sample.[10]

Discussion

The results summarized in Table I show that in the common rings (five- to seven-membered) the amount of methylenecycloalkane present at equilibrium increases with increasing ring size. The values of ΔF^0 calculated from the equilibrium constants fall in the same order as the values of ΔH^0 determined by Turner from heats of hydrogenation.[4] From our values of ΔF^0 and the ΔH^0 values of ref. 4, it is possible to calculate the entropy changes accompanying the isomerization of the methylenecycloalkanes to their endocyclic isomers. The ΔS^0 values (cal./mole°) are: +0.9 for the five-membered, +2.8 for the six-membered and +0.8 for the seven-membered isomer pairs, indicating that in all cases the methylenecycloalkane is conformationally more restricted than the endocyclic isomer, which moreover possesses the additional rotational freedom around the C–CH$_3$ bond. The fairly large value in the six-membered case is somewhat surprising, since from an inspection of models methylenecyclohexane would appear to be rotationally less restricted than the endocyclic olefin. It must be borne in mind, however, that all these values were determined in acetic acid solution and that consequently the degree of solvation will have an effect on the entropy change.[11]

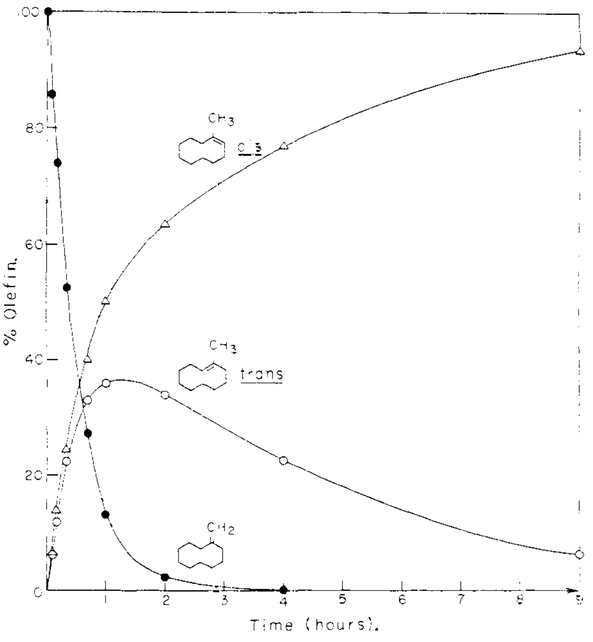

Fig. 1.—Rate of isomerization of methylenecyclodecane to *cis*- and *trans*-1-methylcyclodecene in acetic acid containing *p*-toluenesulfonic acid at 25°.

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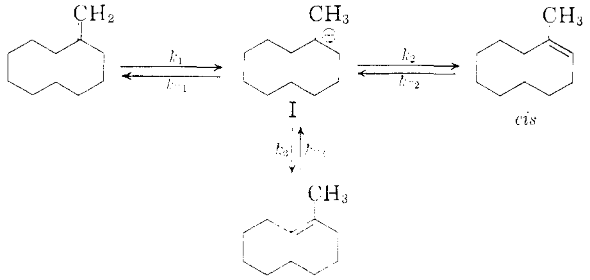
(11) A. C. Cope, P. T. Moore and W. R. Moore, THIS JOURNAL, **82**, 1744 (1960).

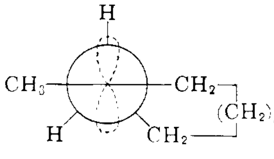
Turner and Garner[4] also determined the heats of isomerization of the ethylidenecycloalkanes to the 1-ethylcycloalkenes having five- and six-membered rings. In these compounds the degree of substitution of the double bond is the same in both the exocyclic and endocyclic isomer. The enthalpy values (ΔH^0) for the isomerization of ethylidenecyclopentane (-1.3 kcal./mole) and of ethylidenecyclohexane (-1.2 kcal./mole) to their endocyclic isomers differ very little. If the entropy change is larger for the isomerization of ethylidenecyclohexane than for ethylidenecyclopentane (as is the case in the corresponding methylene compounds), then the *endo*/*exo* ratio will be larger for the six-membered ring than for the five-membered ring as predicted by Brown.[3]

In the medium-sized rings included in this study the amount of exocyclic isomer present in the equilibrium mixture is very small; this is readily explained by the relief of ring strain which accompanies the introduction of a second trigonal center that occurs on isomerization of the methylenecycloalkane to the 1-methylcycloalkene. It is interesting to compare the free energies of isomerization of *trans*-1-methylcyclononene (< -3.8 kcal./mole) and *trans*-1-methylcyclodecene (-3.1 kcal./mole) to their *cis* isomers with the corresponding values[11] (calculated at 25°) for the unsubstituted cyclic olefins, *trans*-cyclononene (-3.8 kcal./mole) and *trans*-cyclodecene (-2.2 kcal./mole). Obviously introduction of a methyl group increases the strain in the *trans* relative to the *cis* isomer.

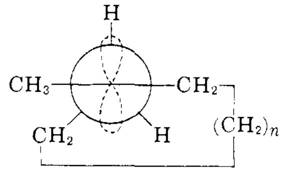
The intermediate formation of considerable amounts of *trans*-1-methylcyclodecene in the isomerization of methylenecyclodecane (Fig. 1) can be explained in terms of rate differences, assuming that the equilibration proceeds as formulated in the equation.



The exocyclic olefin adds a proton to form the carbonium ion I, possibly *via* a π-complex.[12] Assuming that in the transition state leading to elimination, the leaving proton will be in the plane of the empty orbital (8 in formula Ia and Ib) of the carbonium ion, then Ia and Ib represent the rotational isomers of the carbonium ion I which will give rise to *cis*- and *trans*-cyclodecene, respectively. The fact that the rates of formation of the *cis* isomer (k_2) and of the *trans* isomer (k_3) are approximately equal ($k_2 \sim k_3$) (Fig. 1) can be explained by assuming that the transition states leading to the two endocyclic olefins (possibly *via* their π-complexes) resemble the carbonium ion I more closely than the products, in which the equilibrium strongly favors the *cis* isomer (footnote *j* in Table I). Models show that there should not be much difference in strain between the two rotational isomers Ia and Ib. The rates of the reverse reaction, the protonation of *cis*- and *trans*-1-methylcyclodecene to give I, must be different and $k_{-3} > k_{-2}$, from the observed value of $K_{endo/exo}$ and the fact that k_2 and k_3 are nearly equal.



Ia



Ib

The formation of tertiary alcohols and acetates in the equilibrations of the methylenecycloalkanes and 1-methylcycloalkenes having five-, six- and seven-membered rings deserves some comment. Formation of these by-products is largest in the six-membered olefin (see footnote *b*, Table I), which is in accord with Brown's I-strain theory.[13] The relatively large amounts of tertiary alcohols formed in all three cases probably arise because of the presence of water in the glacial acetic acid used for the equilibrations. Water is known[14] to be a much better nucleophile than acetic acid.

Experimental[15]

Olefins.—The methylenecycloalkanes used for equilibrations (except for methylenecyclononane) were prepared by the pyrolysis of the corresponding N,N-dimethylcycloalkylmethylamine N-oxides.[10,16] The olefins obtained in this manner (including methylenecycloheptane, which has previously been reported[16] to contain 0.3% of 1-methylcycloheptene) were found to be free of their endocyclic isomers as determined by gas chromatography (see below). Small amounts (1 and 3%, respectively) of two unidentified impurities were found to be present in the methylenecyclononane that was used for equilibration (prepared by the Hofmann elimination reaction of N,N-dimethylcyclononylmethylamine methohydroxide) and were not removed; their concentration did not change significantly during the equilibration. The *cis*-1-methylcycloalkenes were obtained by addition of methylmagnesium iodide to the corresponding ketones followed by acid-catalyzed dehydration of the resulting tertiary alcohols.[6,10,16] The five- to eight-membered cyclic olefins obtained in this manner contained varying amounts (0.5–5%) of the exocyclic isomers; the *cis*-1-methylcyclodecene was contaminated by 20% of the *trans* isomer. Final purification of the *cis* isomers was effected by preparative gas chromatography followed by short-path distillation of the collected material. A mixture containing more *trans*-1-methylcyclononene than is present in the equilibrium mixture (81.2% of *cis*-1-methylcyclononene, 14.0% of *trans*-1-methylcyclononene and 4.8% of methylenecyclononane) was obtained by pyrolysis of N,N-dimethyl-1-methylcyclononylamine N-oxide[10] and used in the equilibration studies of *trans*-1-methylcyclononene. A mixture containing more *trans*-1-methylcyclodecene than is present in the equilibrium mixture (62.3% of *cis*-1-methylcyclodecene, 35.5% of *trans*-1-methylcyclodecene and 2.2% of methylene-

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(12) R. W. Taft, Jr., This Journal, **74**, 5372 (1952); H. Kwart and L. B. Weisfeld, *ibid.*, **80**, 4671 (1958), and references cited there.

(13) H. C. Brown and K. Ichikawa, *Tetrahedron*, **1**, 221 (1957), and references cited there.

(14) C. G. Swain, R. B. Mosely and D. E. Bown, This Journal, **77**, 3731 (1955).

(15) Boiling points are uncorrected. We are indebted to Dr. S. M. Nagy and his associates for analyses and to Mrs. N. Alvord for infrared spectra, which were determined with a Perkin-Elmer model 21 spectrometer.

(16) A. C. Cope, C. L. Bumgardner and E. E. Schweizer, This Journal, **79**, 4729 (1957).

cyclodecane) was prepared in a similar manner and used without further separation.

Equilibrations.—Glacial acetic acid containing 0.25 g. of *p*-toluenesulfonic acid monohydrate per 100 ml. was transferred into a 10-ml. volumetric flask. The solution was boiled until the vapors just reached the top of the flask which was then capped as quickly as possible with a rubber serum cap. The cap was punctured with a hypodermic needle attached to a nitrogen-filled balloon and the flask was placed in a constant temperature bath at 25° for one hour before adding the olefin (one-tenth the volume of the acetic acid solution). Samples (0.5 ml.) were withdrawn at appropriate intervals with a hypodermic syringe and added to 5 ml. of 25% aqueous potassium carbonate solution. Pentane (0.5 ml.) was added, the flask was agitated and the solution diluted to approximately 10 ml. with water. The pentane layer was analyzed by gas chromatography.

Gas Chromatography.—Gas chromatographic analyses were carried out using 180 × 0.8-cm. Pyrex tubes packed with 48–100 mesh C-22 firebrick (Johns–Manville) which was coated with the appropriate stationary phase. The samples were eluted with helium at 15 p.s.i., and thermal conductivity cells were used as detectors. The stationary phases employed were: (A) 35% (by weight) of a saturated solution (at room temperature) of silver nitrate in diethylene glycol; (B) 30% (by weight) of a 52% solution of silver nitrate in tetraethylene glycol; (C) 30% (by weight) of Silicone oil (Dow–Corning 550) on base-washed firebrick; (D) 30% (by weight) of 4-methyl-4-nitropimelonitrile.[17] Column A was used (column temperature in brackets) to analyze mixtures of methylenecyclopentane and 1-methylcyclopentene (33°). Mixtures of the endocyclic and exocyclic isomers of the six-, seven- and eight-membered cyclic olefins were analyzed using stationary phase B (50–70°); this was also used to separate methylenecyclononane from *cis*-1-methylcyclononene (90°) and to analyze mixtures of methylenecyclodecane and *cis*- and *trans*-1-methylcyclodecene (90°). Stationary phase D was used to separate *cis*-1-methylcyclononene from the *trans* isomer (90°). Mixtures of the 1-methylcycloalkanols, their acetates and of the corresponding olefins (without separation of the isomers) were analyzed using stationary phase C (110–190°). The compositions of the mixtures were computed from the chromatograms by determining the ratios of the individual peak areas.[18]

Isolation and Identification of Products.—The methylenecycloalkanes present in small amounts in the equilibrium mixtures of the five- to eight-membered cyclic olefins were identified by their retention times on gas chromatography. The 1-methylcycloalkenes, 1-methylcycloalkanols and 1-methylcycloalkyl acetates which were the major products of the equilibrations were isolated by gas chromatography and identified by their infrared spectra.

A small amount (0.5%) of an unidentified olefin was formed in the equilibration of methylenecyclooöctane; it was not detected in the products from the isomerization of 1-methylcyclooöctene. This unknown compound could not have been *trans*-1-methylcyclooöctene (which is as yet unknown), since it was found to be stable to acid and to have a retention time in gas chromatography on a silver nitrate column comparable to that of *cis*-1-methylcyclooöctene. Judging from the properties of its next higher homolog, *trans*-1-methylcyclooöctene would be expected to be extremely sensitive to acid and to be retained on a silver nitrate column much longer than the *cis* isomer.

Authentic samples of 1-methylcyclopentanol,[19] 1-methylcyclohexanol[20] and 1-methylcycloheptanol[21] were prepared from the corresponding ketones and methylmagnesium iodide. The acetates were prepared from the alcohols by the method of Nevitt and Hammond.[22]

1-Methylcyclopentyl acetate was obtained analytically pure in 65% yield, b.p. 66–67° (30 mm.), $n^{25}\text{D}$ 1.4291.

1-Methylcyclohexylacetate, obtained in 56% yield, had b.p. 75–76° (17 mm.), $n^{25}\text{D}$ 1.4403–1.4414.

1-Methylcycloheptyl acetate, obtained in 83% yield, had b.p. 74–74.5° (8 mm.), $n^{25}\text{D}$ 1.4501.

Stability of 1-Methylcycloalkyl Acetates to Hydrolysis.—A sample of 0.1 ml. of 1-methylcyclohexyl acetate was dissolved in 1 ml. of a 0.25% solution of *p*-toluenesulfonic acid monohydrate in glacial acetic acid, and the acetate was immediately re-isolated and analyzed using the methods described above for the equilibrium mixtures. 1-Methylcyclohexanol was found to be completely absent. The same result was obtained with 1-methylcycloheptyl acetate.

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[17] H. A. Bruson, U. S. Patent 2,361,251; *C. A.*, **39**, 2079 (1945).

[18] E. Cremer and R. Müller, *Z. Elektrochem.*, **55**, 217 (1951); M. Dimbat, P. E. Porter and F. H. Stross, *Anal. Chem.*, **28**, 290 (1956).

[19] N. Zelinski and S. Namjetkin, *Ber.*, **35**, 2683 (1902).

[20] N. Zelinski, *ibid.*, **34**, 2877 (1901).

[21] O. Wallach, *Ann.*, **345**, 139 (1906).

[22] T. D. Nevitt and G. S. Hammond, THIS JOURNAL, **76**, 4124 (1954).

CAMBRIDGE 39, MASS.

[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

Peresters. III.[1] *t*-Butyl Phenylperacetate, Trichloroperacetate and Trimethylperacetate

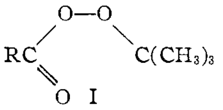
BY PAUL D. BARTLETT AND DONALD M. SIMONS[2]

RECEIVED AUGUST 18, 1959

The decomposition of *t*-butyl trimethylperacetate, *t*-butyl trichloroperacetate and *t*-butyl phenylperacetate has been studied in the temperature range 58–88°. Kinetic studies of all three peresters indicate a first-order concerted cleavage to yield carbon dioxide, *t*-butoxy and *t*-butyl, trichloromethyl or benzyl radicals. There is also a prominent acid-catalyzed ionic decomposition of *t*-butyl trichloroperacetate which can be suppressed by pyridine. Activation parameters are summarized in Table VI. The ΔH^* values suggest near equality for the stabilization energies of *t*-butyl and trichloromethyl radicals, each being about 80% as stable as benzyl. Bond-energy methods[11] lead to values of 12, 12 and 24.5 kcal. for the stabilization energies of these same radicals.

Introduction

Evidence has been presented[1a,3] that a series of peresters of general composition I decompose thermally with concerted rupture of an O–O bond and a C–C bond to produce carbon dioxide and the free radicals $(CH_3)_3CO\cdot$ and $R\cdot$ whenever $R\cdot$ is so constituted as to have a degree of stabilization considerably exceeding that of the methyl or phenyl radical. The three esters described in this paper were the first representatives of this series prepared in



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[1] (a) Part I, P. D. Bartlett and R. R. Hiatt, THIS JOURNAL, **80**, 1398 (1958); (b) part II, P. D. Bartlett and B. T. Storey, *ibid.*, **80**, 4954 (1958).

[2] National Science Foundation Post-doctoral Fellow, 1952–1953.

[3] P. D. Bartlett, *Experientia Suppl.*, **VII**, 275 (1957).