The crude methobromides precipitated almost quantitatively when a mixture of an ethereal solution of the ester base and a four molar excess of methyl bromide was allowed to remain at room temperature for 2 days and was then placed in a refrigerator for several days.

ANN ARBOR, MICHIGAN

[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

Stereochemistry of Allylic Rearrangements. VII. The Acid-catalyzed Hydrolysis of *cis* and *trans*-5-Methyl-2-cyclohexenyl *p*-Nitrobenzoate in Aqueous Acetone[1]

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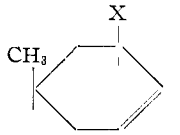
RECEIVED JULY 5, 1955

The kinetics of the hydrolysis of *cis*-(Ic) and *trans*-5-methyl-2-cyclohexenyl *p*-nitrobenzoate (IIc) in 80% aqueous acetone at 80 and 100° have been investigated to obtain information concerning the nature of intermediates involved in solvolysis and allylic rearrangements. The hydrolysis involves alkyl-oxygen cleavage and is catalyzed by perchloric acid. In the presence and absence of acid the polarimetric and titrimetric rate constants, k_α and k_t, are reproducible and steady during the reactions. The rate of the acid-catalyzed hydrolysis is proportional to the perchloric acid concentration over the concentration range investigated (to 0.1 *M*). At an acid concentration of 0.05 *M*, where the acid-catalyzed hydrolysis is essentially isolated from the uncatalyzed process, k_α and k_t are indistinguishable (within the combined experimental errors). In the absence of acid, $k_\alpha > k_t$ for both geometric isomers (*i.e.*, internal return is observed). The observation that internal return occurs during the uncatalyzed hydrolysis but not during the acid-catalyzed hydrolysis is consistent with the concept that ion-pair intermediates are involved in internal return. The greater polarimetric than titrimetric rate for the uncatalyzed hydrolysis is due to partial racemization of the reactant by an intramolecular allylic rearrangement—geometric isomerization does not occur—prior to hydrolysis. In this case the hydrolysis evidently involves the reversible formation of an intermediate which can at present best be described as an ion-pair which is irreversibly converted to product. The reversible step (internal return) represents the S_Ni' isomeric allylic rearrangement.

Introduction

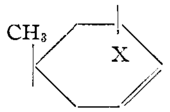
In the work described in previous papers in this series it was found that internal return[3] is involved in the solvolysis of the isomeric 5-methyl-2-cyclohexenyl acid phthalates (Ia and IIa) in aqueous acetone[4] and chlorides (Ib and IIb) in ethanol and acetic acid.[5] In each case the method[3] of comparing polarimetric (k_α) and titrimetric (k_t) first-order rate constants was used to measure internal return and it was found that this phenomenon does not result in the interconversion of the *cis* (I) and *trans* (II) isomers. Similar results were obtained in a study of the isomeric allylic rearrangement of the acid phthalates (Ia and IIa) in acetonitrile.[6] In this case it was observed that with both isomers, racemization is more rapid than geometric isomerization. As pointed out in previous papers in this series all of these observations appear to be consistent with the idea[3] that a common intermediate, presumably an ion-pair,[3,7] is involved in solvolysis and internal return (which in an allylic system corresponds to the S_Ni'[8] isomeric allylic rearrangement).[4]

This present work was undertaken to obtain information concerning the intramolecular (S_Ni') rearrangement of allylic esters and the nature of the presumably common intermediate involved in this process and solvolysis. In this connection we investigated the uncatalyzed and acid-catalyzed hydrolysis of *cis*- (Ic) and *trans*-5-methyl-2-cyclohexenyl *p*-nitrobenzoate (IIc) in aqueous acetone. In the uncatalyzed hydrolysis, alkyl-oxygen cleavage results in the formation of ions, and ion-pair intermediates are possible. In the acid-catalyzed hydrolysis, where the conjugate acid of the ester undergoes alkyl-oxygen cleavage, ion-pair intermediates are not possible. According to the ion-pair interpretation,[3] internal return is possible in the uncatalyzed hydrolysis but not in the acid-catalyzed hydrolysis. We have indeed observed that internal return is observed in the uncatalyzed hydrolysis, *i.e.*, $k_\alpha > k_t$, but not in the acid-catalyzed hydrolysis.



I

a, X = $O_2CC_6H_4CO_2H$
b, X = Cl
c, X = $O_2CC_6H_4NO_2$



II

a, X = $O_2CC_6H_4CO_2H$
b, X = Cl
c, X = $O_2CC_6H_4NO_2$

Results

The hydrolyses of 0.05 *M* Ic and IIc in 80% acetone[9] at 80 and 100° are first order and are catalyzed by perchloric acid. The polarimetric (k_α) and titrimetric (k_t) first-order rate constants (pseudo first order for the acid-catalyzed reactions) were determined in the absence of perchloric acid and at an acid concentration of 0.05 *M*. The results of the kinetic experiments are presented in Table I.

The titrimetric first-order rate constants (k_t) were determined by periodically titrating the *p*-nitrobenzoic acid produced. The constants were steady over the ranges that the reactions were followed (to 80% completion in some cases) for both the acid-catalyzed and uncatalyzed reactions.

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[1] This work was supported by the Office of Ordnance Research.

[2] National Science Foundation Fellow, 1954–1955.

[3] S. Winstein and R. Heck, THIS JOURNAL, **74**, 5584 (1952), and previous papers in this series; S. Winstein, E. Clippinger, A. H. Fainberg and G. C. Robinson, *ibid.*, **76**, 2597 (1954); *Chem. and Ind.*, 664 (1954).

[4] H. L. Goering and E. F. Silversmith, THIS JOURNAL, **77**, 1129 (1955).

[5] H. L. Goering, T. D. Nevitt and E. F. Silversmith, *ibid.*, **77**, 5026 (1955).

[6] H. L. Goering, J. P. Blanchard and E. F. Silversmith, *ibid.*, **76**, 5409 (1954).

[7] D. J. Cram, *ibid.*, **74**, 2129 (1952).

[8] C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p. 596.

[9] The 80% acetone was prepared by mixing 4 volumes of purified acetone with one volume of water at 25°.

TABLE I

HYDROLYSIS OF 0.05 M *cis*- AND *trans*-5-METHYL-2-CYCLOHEXENYL p-NITROBENZOATE IN 80% (BY VOLUME)[a] AQUEOUS ACETONE

Expt.	Isomer	Temp., °C.	$[HClO_4]^b$ ($10^2 M$)	$[LiClO_4]^b$ ($10^2 M$)	Method[c]	$10^2 k_\alpha$ or $k_t{}^d$ (hr.$^{-1}$)	$k_c{}^{e,f}$ (l. mole^{-1} hr.$^{-1}$)
1	*cis*	79.99	5.25	0.0	P	4.76 ± 0.11	
2a	*cis*	79.99	5.25	0.0	T	4.67 ± 0.11	0.92
2b	*cis*	79.99	5.25	0.0	T	4.82 ± 0.09	0.95
3	*cis*	79.99	0.00	5.0	T	0.172 ± 0.003	
4	*cis*	79.99	0.00	0.0	T	0.153 ± 0.004	
5	*cis*	79.99	0.00	10.0	T	0.194 ± 0.002	
6	*cis*	79.99	10.76	0.0	T	10.8 ± 0.2	1.05
7	*cis*	79.99	3.19	0.0	T	2.68 ± 0.04	0.82
8	*cis*	79.99	2.98	7.5	T	3.19 ± 0.05	1.07
9a	*cis*	99.83	0.00	0.0	P	2.18 ± 0.07	
9b	*cis*	99.83	0.00	0.0	P	2.10 ± 0.05	
10a	*cis*	99.83	0.00	0.0	T	1.24 ± 0.04	
10b	*cis*	99.83	0.00	0.0	T	1.22 ± 0.01	
11	*cis*	99.83	5.25	0.0	T	44.2 ± 0.3	9.0
12	*cis*	49.85	5.25	0.0	T	0.089 ± 0.002	0.0166
13	*trans*	79.99	5.25	0.0	P	27.4 ± 0.3	
14	*trans*	79.99	5.25	0.0	T	26.6 ± 0.5	5.4
15	*trans*	79.99	0.00	0.0	T	0.164 ± 0.001	
16	*trans*	79.99	0.00	5.0	T	0.20 ± 0.005	
17	*trans*	99.83	0.00	0.0	P	2.04 ± 0.01	
18	*trans*	99.83	0.00	0.0	T	1.33 ± 0.02	

[a] Based on volumes of pure components at 25° before mixing. [b] Indicated concentrations are for 25°. [c] P = polarimetric and T = titrimetric. [d] Apparent first-order rate constants and mean deviation of the 6 to 9 determinations during the reaction. [e] Specific second-order catalytic constant, corrected for expansion of the solvent. [f] The values of $k_{t([SH^+]=0)}$ used to calculate k_c were for the same ionic strength as those of the acid-catalyzed reactions.

Each value of k_t in Table I is the average value (and mean deviation) of 6 to 9 determinations during the reaction.

The polarimetric constants (k_α) were determined from the rate of loss of optical activity of solutions of active Ic and IIc. In all cases the reactions resulted in complete loss of optical activity and the first-order constants were steady throughout the reaction. Both the polarimetric and titrimetric constants were reproducible (within the combined mean deviations) in the absence or presence of added perchloric acid. In all cases where the polarimetric and titrimetric rates were compared the reactions were carried out simultaneously in the same thermostat and the solvent (containing perchloric acid for the acid-catalyzed reactions) was taken from the same stock solution. Typical experiments illustrating the first-order behavior of the polarimetric and titrimetric rates are included in the Experimental section.

The observed relationship between the rate of formation of p-nitrobenzoic acid ($ArCO_2H$), *i.e.*, the titrimetric rate, and the concentrations of ester (Ic or IIc) and lyonium ion ($SH^\oplus$) (*i.e.*, the concentration of perchloric acid) is

$$d[ArCO_2H]/dt = k_{t([SH^\oplus]=0)}\,[\text{ester}] + k_c[SH^\oplus][\text{ester}] \qquad (1)$$

The last term of this equation disappears in the absence of perchloric acid—the relative magnitudes of $k_{t([SH^\oplus]=0)}$ and k_c are such that catalysis by 0.05 M p-nitrobenzoic acid produced in the reaction cannot be detected (see below)—and the value of $k_{t([SH^\oplus]=0)}$ is the steady first-order titrimetric rate constant in the absence of perchloric acid. As shown in Table I, $k_{t([SH^\oplus]=0)}$ increases with ionic strength as would be expected, *cf.* expts. 3, 4 and 5 and expts. 15 and 16. Since the change in lyonium ion concentration, $[SH^\oplus]$, during the hydrolysis is negligible (see below), the hydrolysis is first order in the presence of perchloric acid. The relationship between the observed first-order constant (k_t) and the constants in equation 1 is

$$k_t = k_{t([SH^\oplus]=0)} + k_c[SH^\oplus] \qquad (2)$$

The values of the second-order catalytic constant (k_c) given in Table I were calculated from this relationship using values of $k_{t([SH^\oplus]=0)}$ for the same ionic strength as that of the acid-catalyzed reaction. All concentrations are given for 25° and the values of k_c given in Table I have been corrected for thermal expansion of the solvent.

In order to estimate the increase in lyonium ion concentration during the hydrolysis of Ic or IIc the dissociation constant of p-nitrobenzoic acid in 80% acetone[9] was determined by the half-neutralization method.[10] The value of K_a at 25° was found to be 5.0×10^{-7}.[11] From this constant it can be determined that the increase in $[SH^\oplus]$ during the hydrolysis of 0.05 M Ic or IIc in the presence of 0.05 M perchloric acid is only 0.001%.[12] For the hydrolysis in the absence of perchloric acid the value of $[SH^\oplus]$ is *ca.* 1.6×10^{-4} [12] at the completion of the reaction. Since k_c, which decreases with ionic strength, is not known for zero ionic strength

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[10] H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publ. Corp., New York, N. Y., 1943, pp. 316–325.

[11] A solution of hydrogen chloride in 80% acetone was used for calibration so that corrections for the junction potential at the glass electrode would not be necessary.

[12] This value probably represents an upper limit since the dissociation constants of carboxylic acids are in general lower at 80 and 100° (the reaction temperatures) than at 25°. See J. F. J. Dippy and H. D. Jenkins, *Trans. Faraday Soc.*, **37**, 366 (1941).

the effect of the formation of 1.6×10^{-4} *M* lyonium ion on the instantaneous rate constant cannot be determined. A reasonable value for k_c ($\mu = 0$) indicates that the instantaneous first-order rate constant should not increase by more than a few per cent. and this is indeed consistent with the observation that k_t does not show any detectable trends.

The data in Table I show that at constant ionic strength the rate of the acid-catalyzed hydrolysis of Ic is proportional to the perchloric acid concentration over the range of concentrations investigated, *cf.* the values of k_c for expts. 6 and 8. Comparison of k_c at different ionic strengths shows that this constant increases with ionic strength. A similar increase in the pseudo first-order rate constant ($k_c[SH^\oplus]$) with ionic strength has previously been observed[13] for the acid-catalyzed solvolysis of *t*-butyl 2,4,6-trimethylbenzoate in aqueous ethanol, a reaction that is similar to the present one in that alkyl-oxygen cleavage is involved.

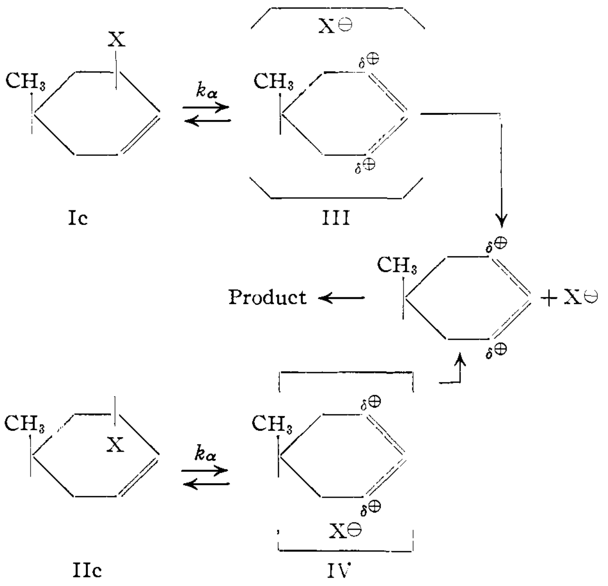
The ratio of $k_{t([SH^\oplus]=0)}$ to k_t at various acid concentrations (both constants for the same ionic strength) corresponds to the fraction of ester hydrolyzed by the uncatalyzed process. The magnitudes of this ratio calculated from the data in Table I show that at an acid concentration of 0.05 *M* (or higher) the acid-catalyzed hydrolysis is essentially isolated from the uncatalyzed process (at an acid concentration of 0.05 *M* 3.6% of Ic and 0.7% of IIc react by the uncatalyzed process).

As shown in Table I, $k_\alpha > k_t$ for the hydrolysis of Ic and IIc in the absence of acid, *cf.* expts. 9 and 10 and expts. 17 and 18. In the presence of 0.05 *M* perchloric acid k_α and k_t are within experimental error for Ic and IIc, *cf.* expts. 1 and 2 and expts. 13 and 14. The specific first-order rate constant for the excess loss of optical activity during the uncatalyzed hydrolysis is $(k_\alpha - k_t)$.[14] From the magnitude of this steady first-order constant the optical activity of the unhydrolyzed ester can be determined for any time during the hydrolysis. For Ic at 100° $(k_\alpha - k_t) = 9.4 \times 10^{-3}$ hr.$^{-1}$ which corresponds to a half-life of 73.7 hr. The unhydrolyzed ester recovered from a 0.05 *M* solution of *dl*-Ic in 80% acetone after 73.6 hr. at 100° was found to be pure Ic by an analytical method (infrared analysis) which enables the detection of 2% of the geometric isomer in either Ic or IIc. In a similar experiment the unhydrolyzed ester was recovered from a 0.05 *M* solution of *dl*-IIc after 97.6 hr. (one half-life for racemization of the unhydrolyzed ester) at 100° and found to be pure IIc. Since the esters were isolated in such a way that isomers could not possibly be fractionated these experiments demonstrate that geometric isomerization is not associated with the excess loss of optical activity. These results are similar to the previous observation[4,5] that internal return does not result in geometric isomerization in the 5-methyl-2-cyclohexenyl system.

Discussion

The experimental results for the uncatalyzed hydrolysis of Ic and IIc are consistent with the mechanism previously suggested for the solvolysis of the isomeric acid phthalates[4] and chlorides,[5] which is reproduced in Chart I ($X = O_2CC_6H_4NO_2$). The kinetic experiments clearly show that the ester, rather than the conjugate acid of the ester, is the reactive species (catalysis by the *p*-nitrobenzoic acid produced during the reaction is not observed) and internal return is involved, *i.e.*, $k_\alpha > k_t$. The fact that the complete loss of optical activity is cleanly first order implies[15] that alkyl-oxygen cleavage is involved. This type of cleavage would be expected in view of the observation of Kenyon and co-workers[16] that alkyl-oxygen cleavage is involved in the hydrolysis of allylic esters in neutral and weakly alkaline solution. Perhaps the most obvious evidence that alkyl-oxygen cleavage is involved in the present case is the fact that Ic and IIc hydrolyze more rapidly than cyclohexyl *p*-nitrobenzoate by factors of 240 and 260 in the absence of acid, and 62 and 350 in the presence of 0.05 *M* perchloric acid in 80% acetone at 100°.[17] Since there is no apparent reason why an allylic ester should undergo acyl-oxygen cleavage more readily than the saturated analog, these data show that beyond all reasonable doubt, alkyl-oxygen cleavage is involved in the acid-catalyzed as well as the uncatalyzed hydrolysis of Ic and IIc.

CHART I



As previously pointed out,[4] internal return in allylic systems evidently corresponds to the S_Ni'[8] isomeric allylic rearrangement. The intramolecular nature of the rearrangement (internal return),

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[13] V. R. Stimson and E. J. Watson, *J. Chem. Soc.*, 2848 (1954).

[14] See S. Winstein and K. C. Schreiber, THIS JOURNAL, **74**, 2165 (1952).

[15] Optically active alcohol would result from acyl-oxygen cleavage and in the case of the *trans* isomer the alcohol and ester have rotations of the same magnitude. Although initially formed optically active alcohols racemize under the conditions of the hydrolysis[4] (especially in the presence of added perchloric acid) it seems unlikely that active alcohol would react sufficiently faster than the ester under any conditions so that acyl-oxygen cleavage would result in a clean first-order complete loss of optical activity.

[16] J. Kenyon, *et al.*, *J. Chem. Soc.*, 85 (1936); 575 (1936); 1697 (1939); 18 (1942).

[17] The value of k_t for cyclohexyl *p*-nitrobenzoate in 80% acetone at 100° is 5.1×10^{-5} hr.$^{-1}$ in the absence of acid and 0.0071 hr.$^{-1}$ in the presence of 0.05 *M* perchloric acid (*i.e.*, $k_c = 0.14$ l. mole^{-1} hr.$^{-1}$).

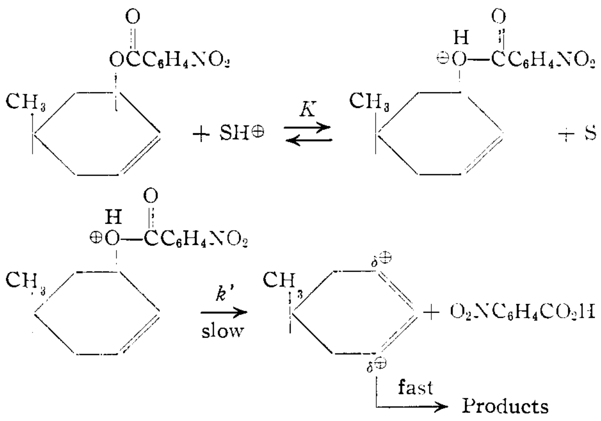
which in the present system results in the interconversion of enantiomers, is apparent from the kinetic behavior[14] and the fact that racemization is exclusive of geometric isomerization. Regardless of the mechanism, the specific first-order rate constant for the conversion of one enantiomer to the other (*i.e.*, allylic rearrangement) is $(^1/_2)\ (k_\alpha - k_t)$. Since this constant remains steady during the uncatalyzed hydrolysis of Ic and IIc (and Ia and IIa[4]), even though acid is being formed, it is clear that contrary to Braude's repeated claim,[18] acid catalysis is not a necessary requirement for the isomeric rearrangement of allylic esters. Although the alkyl-oxygen cleavage of Ic and IIc is subject to specific acid-catalysis (*i.e.*, the conjugate acid of the ester undergoes alkyl-oxygen cleavage more readily than the ester) as would be expected[19] it is clear from the present work and from earlier work[4,6,16] that acid catalysis is not a necessary requirement for this type of cleavage in reactive allylic systems.

In the case of the acid-catalyzed hydrolysis internal return is not observed (*i.e.*, $k_\alpha = k_t$) and the kinetic data are adequately accommodated by the carbonium ion mechanism[20] in its simplest form, which is illustrated for Ic in Chart II. The relationship between the observed pseudo first-order rate constant, k_t or k_α, and the constants in the chart is

$$k_\alpha = k_t = Kk'[\mathrm{SH}]^{\oplus}$$

The experimental Arrhenius activation energy, E_a[21] (calculated from values of k_c, expts. 2, 11 and 12) for Ic is 30.2 kcal., which is of the magnitude generally observed for acid-catalyzed hydrolysis involving alkyl-oxygen cleavage.[13]

CHART II



Evidence that a common intermediate is involved in internal return and solvolysis, as indicated in Chart I, has previously been discussed.[3-6] Such intermediates have previously been represented as ion-pairs and are represented as such in Chart I. Denny[22] has recently reported the pertinent observation that in the intramolecular rearrangement of 9-decalyl hydroperoxide benzoate to 1,6-epoxycyclodecyl benzoate, a rearrangement which involves internal return,[23] the oxygen atoms of the migrating benzoate moiety do not become equivalent but instead the carbonyl oxygen atom retains its identity. This suggests that the degree of separation of the ions in intermediates involved in internal return is somewhat less than previously[3-7] implied. In view of the compelling evidence that these intermediates have considerable ionic character[3-7,24] it seems best to represent them as ion-pairs until more evidence concerning the intimate structural details is available.

An obvious corollary of the ion-pair interpretation[3] is that internal return is possible for $\mathrm{S_N1}$-type reactions of RX if the departing (or migrating) group, X, is neutral prior to reaction, but not if this group is positively charged. If our previous assumption[4] that the $\mathrm{S_Ni'}$ isomeric allylic rearrangement of allylic esters involves internal return is correct, it follows that the acid-catalyzed counterpart of this intramolecular rearrangement is not possible. Presumably the acid-catalyzed isomeric rearrangements involve external return[3] (*i.e.*, dissociation followed by recombination of the carbonium ion with the solvent) or a concerted process of the type suggested by Braude and co-workers[25] in which a solvent molecule attacks the γ-carbon and displaces a similar molecule. In the present work we have found that this indeed appears to be the case in the 5-methyl-2-cyclohexenyl system. In the uncatalyzed hydrolysis, alkyl-oxygen cleavage results in the formation of ions and internal return is observed. As illustrated in Chart II, the rate-determining step for the acid-catalyzed hydrolysis is alkyl-oxygen cleavage of the conjugate acid of the ester. In this case oppositely charged ions are not formed and internal return is not observed.[26]

Experimental[27]

Materials.—*dl-cis-*, m.p. 93.5–94.0°; *dl-trans-*, m.p. 87.0–87.4°, and (−)-cis-5-methyl-2-cyclohexenyl *p*-nitrobenzoate, $[\alpha]^{25}\mathrm{D}$ −68.2° (*c* 1.3, acetone) were prepared by the method described previously.[28] (+)*trans*-5-Methyl-2-cyclohexenyl *p*-nitrobenzoate, m.p. 81.8–82.5°, $[\alpha]^{25}\mathrm{D}$ 101° (*c* 1.3, acetone) was prepared from (+)-*trans*-alcohol in the usual manner.[28] Cyclohexyl *p*-nitrobenzoate was prepared from cyclohexanol by the method used to prepare Ic and IIc.[28] After three recrystallizations from pentane, it had m.p. 49.4–49.8° (lit.[29] 50°).

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[18] E. A. Braude, *J. Chem. Soc.*, 794 (1948); E. A. Braude, *Ann. Reports on Prog. Chem.*, **46**, 114 (1949); *Quart. Rev. Chem. Soc.*, **4**, 417 (1950).

[19] Ref. 8, p. 779.

[20] It appears that this mechanism was first suggested by H. Burton and C. K. Ingold, *J. Chem. Soc.*, 904 (1928). See also W. G. Young, *et al.*, THIS JOURNAL, **74**, 608 (1952); E. D. Hughes, C. K. Ingold, *et al.*, *J. Chem. Soc.*, 8 (1948); J. Kenyon, *et al.*, *ibid.*, 18 (1942); and previous papers in these three series.

[21] Since $k_c = Kk'$, E_a is the sum of the activation energy of the rate-determining alkyl-oxygen cleavage and ΔH for the preceding equilibrium (Chart II).

[22] D. B. Denny, THIS JOURNAL, **77**, 1706 (1955).

[23] P. D. Bartlett and J. L. Kice, *ibid.*, **75**, 5591 (1953); H. L. Goering and A. C. Olson, *ibid.*, **75**, 5853 (1953).

[24] This is indicated for the present system by the sensitivity of the rate constant for the formation of the intermediate (k_α) and the constants for the processes that depend on the rate of formation of the intermediate, internal return ($k_\alpha - k_t$) and solvolysis (k_t), toward varying the ionizing power of the solvent (ref. 4).

[25] H. C. Barany, E. A. Braude and J. A. Coles, *J. Chem. Soc.*, 2093 (1951).

[26] W. A. Bonner and C. J. Collins, THIS JOURNAL, **77**, 99 (1955), have recently observed that internal return is not involved in the acid-catalyzed alkyl-oxygen cleavage of 1,2,2-triphenylethyl acetate in acetic acid and attributed this to the fact that ion-pair formation is not possible in this reaction.

[27] All melting points are corrected.

[28] H. L. Goering and J. P. Blanchard, THIS JOURNAL, **76**, 5405 (1954).

[29] S. M. McElvain, "The Characterization of Organic Compounds," The Macmillan Co., New York, N. Y., 1949, p. 194.

The solvent for the kinetic experiments, 80% acetone, was prepared by mixing four volumes of pure acetone[30] and one volume of conductivity water. The volumes were carefully measured at 25° and water containing the calculated amount of perchloric acid (reagent grade) was used for the acid-catalyzed experiments. A 0.05 *M* solution of perchloric acid in 80% aqueous acetone, after being kept at 80° for 50 hours, did not contain α,β-unsaturated ketones (ultraviolet spectrum) which indicates that the acetone does not undergo acid-catalyzed self-condensation under the conditions of the kinetic experiments.

The lithium perchlorate used in some of the experiments was dried to constant weight by heating to 100° for 16 hours *in vacuo*.

Kinetic Experiments.—All standard solutions were prepared at 25°. The polarimetric and titrimetric rates were determined by the previously described method.[4] The perchloric acid concentrations were determined by titrating aliquots of the stock solutions at 25°. The values of k_c (Table I) were corrected for the decrease in perchloric acid concentration resulting from the thermal expansion of the solvent by use of the following data. When 3.480 ml. (measured at 25°) of 80% aqueous acetone was sealed in a calibrated tube and heated, it was found that the volume increased to 3.581 ml. at 49.85°, 3.732 ml. at 79.99° and 3.837 ml. at 99.83°. Typical kinetic experiments are summarized in Tables II and III.

Isolation of Unsolvolyzed *p*-Nitrobenzoates from Aqueous Acetone.—Fifty ml. of 0.05*M* solutions of *cis*- and *trans*-5-methyl-2-cyclohexenyl *p*-nitrobenzoates in 80% aqueous acetone was sealed in ampules and heated at 99.83° for one half-life for racemization of the esters (measured by $(k_\alpha - k_t)$). The solution was concentrated to *ca.* 10 ml. under reduced pressure after which 50 ml. of water was added, and the concentration process repeated. This was continued until the distillate gave a negative test for unsaturation (bromine in carbon tetrachloride), *i.e.*, until all of the 5-methyl-2-cyclohexenol had been removed. During this process the temperature of the residue did not exceed 60°.

The mixture was concentrated to *ca.* 5 ml. and the mixture of 5-methyl-2-cyclohexenyl *p*-nitrobenzoate and *p*-nitrobenzoic acid was collected by filtration. The aqueous filtrate was extracted once with chloroform. The residue was stirred with 10 ml. of chloroform and the insoluble *p*-nitrobenzoic acid was removed by filtration and washed thoroughly with chloroform. The chloroform extracts were combined, washed with an equal volume of 5% sodium hydroxide solution and dried over calcium chloride. The chloroform was evaporated under a stream of filtered air, and the infrared spectrum of a chloroform solution of the residue was determined.

The spectra showed no absorption in the -OH region, indicating the complete absence of water, 5-methyl-2-cyclohexenol and *p*-nitrobenzoic acid. The relative quantities of the isomeric *p*-nitrobenzoates was calculated from the relative absorptions at 10.59 μ (where only the *cis* isomer absorbs) and 11.00 μ (where only the *trans* isomer absorbs). The spectrum of the ester recovered from the partial hydrolysis of the *cis-p* nitrobenzoate was indistinguishable from that of authentic *cis-p*-nitrobenzoate (Ic). The spectrum of the material recovered from the partial solvolysis of *trans-p*-nitrobenzoate was indistinguishable from that of pure *trans-p*-nitrobenzoate (IIc).

TABLE II

TITRIMETRIC RATE OF HYDROLYSIS OF 0.05 *M* *cis*-5-METHYL-2-CYCLOHEXENYL *p*-NITROBENZOATE IN 80% ACETONE AT 100° (EXPT. 10b)

Time (hr.)	0.04909 *M* NaOH,[a] ml.	$10^2 k_t$ (hr.$^{-1}$)
0.0	0.000	
15.3	0.857	1.21
26.8	1.384	1.19
39.3	1.923	1.22
63.5	2.712	1.21
72.1	2.961	1.22
89.9	3.401	1.24
112.3	3.815	1.25
	Av.	1.22 ± 0.01

[a] Amount of base required to titrate 4.965-ml. aliquots.

TABLE III

POLARIMETRIC RATE OF HYDROLYSIS OF 0.05 *M* *cis*-5-METHYL-2-CYCLOHEXENYL *p*-NITROBENZOATE IN 80% ACETONE AT 100° (EXPT. 9b)

Time (hr.)	$\alpha^{25}\text{D}$[a]	$10^2 k_\alpha$ (hr.$^{-1}$)
0.0	−3.399	
18.1	−2.294	2.17
40.5	−1.423	2.15
52.5	−1.119	2.12
64.5	−0.894	2.07
77.9	−0.698	2.03
88.8	−0.558	2.04
	Av.	2.10 ± 0.05

[a] Observed rotation of reaction mixture in a 4-dm. tube.

Independent control experiments showed that: (a) the isomeric *p*-nitrobenzoates are stable under the conditions of the isolation, and (b) as little as 2% of either isomer in the other can be detected by the analytical method used.

Determination of the Dissociation Constant of *p*-Nitrobenzoic Acid in 80% Aqueous Acetone.—The dissociation constant was determined by the half-neutralization method,[10] using a Beckman *p*H meter (Model G) with a Beckman calomel electrode (No. 1170) and a Beckman Type E High *p*H glass electrode. The instrument was calibrated with a 0.001272 *M* solution of hydrochloric acid in 80% acetone (assuming complete dissociation). A 0.003 *M* solution of *p*-nitrobenzoic acid in 80% acetone was titrated with 0.05 *M* base. The solution was stirred thoroughly after each increment of base was added. A plot of *p*H against base added was made (using forty determinations during the titration) and pK_a (the *p*H at the half-neutralization point) was found to be 6.30.

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[30] J. K. Kochi and G. S. Hammond, THIS JOURNAL, **75**, 3445 (1953).