Cram and co-workers[9] have studied the ultraviolet absorption spectra of the paracyclophanes and closely related compounds. Some of them must be greatly distorted and show great bathochromic shifts of the B-band. In these cases, the benzene ring must adopt a "boat-like" conformation.

Ingraham concluded that the shift of the secondary band of the strained paracyclophanes are mostly due to $2p\sigma$ interaction between rings.[10] His conclusion was based much on the appearance of a first principal band which is also found in the strained derivatives here studied, where no such interaction can take place.

In view of the results here reported one is inclined to consider that the great shifts found also in the cyclophanes are mostly due to benzene ring warping.

Pentamethyltrichloromethylbenzene (XIII), a homomorph of VIII, has been recently reported.[11] Its ultra-violet absorption spectrum (see Table I) is "abnormal." There is no fine structure of the secondary band, and it is located about 20 mμ away from its "expected" place.[12]

(9) D. J. Cram, N. L. Allinger and H. Steinberg, THIS JOURNAL, **76**, 6132 (1954).

(10) L. L. Ingraham, J. Chem. Phys., **18**, 988 (1950); M. S. Newman, "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1956, pp. 498–501.

(11) R. J. Rolih, unpublished preparation; see H. Hart and R. W. Fish, THIS JOURNAL, **80**, 5894 (1958).

(12) Due to the smaller substituent effect of the methyl group in polymethylbenzenes the secondary band is found at shorter wave lengths. Examples: Pentamethylbenzene,[13] 269, 275, 279 mμ, vs.

According to Platt[14] it is possible to assign to each benzene substituent a vector called spectroscopic moment, from which the maximum extinction may be calculated. This calculation fails, however, with most of the highly substituted benzene derivatives here studied. However, some interesting sequences that can be drawn from it agree with the data: examples: 1, I < III < IV < V < VIII < XII; 2, VI < VIII < VII; 3, VI < XI; 4, X < XI < XII.

Experimental

An Uvispek Hilger Spectrophotometer was used. Benzene-free cyclohexane was the solvent. All the substances but pentamethyltrichloromethylbenzene were obtained in this Laboratory and were purified by recrystallization from the suitable solvents until they melted sharply, and dried under high vacuum. The 2,3,4,5,6-pentachloro-1-chloromethylbenzene and 2,3,4,5,6-pentachloro-1-dichloromethylbenzene, which usually contaminate each other, were purified by chromatography on alumina grade A.

pentachlorobenzene, 289, 299 mμ. Hexamethylbenzene,[13] 270, 279 mμ, vs. hexachlorobenzene, 291, 298 mμ.

(13) H. Conrad-Billroth, Z. physik. Chem., **B29**, 170 (1935).

(14) J. R. Platt, J. Chem. Phys., **19**, 263 (1951).

Intermediates and Transition States in Reactions of Allylic and Homoallylic Systems. I. Free Energy Relationships in the Reactions of α-Aryl-γ-methylallyl and α-Methyl-γ-arylallyl p-Nitrobenzoates

BY RICHARD A. SNEEN

p-Nitrobenzoate esters of α-aryl-γ-methylallyl and α-methyl-γ-arylallyl alcohols have been solvolyzed in aqueous dioxane solutions of varying composition. All of the esters investigated solvolyzed by uncatalyzed first-order processes involving alkyl–oxygen fission. In the case of the α-aryl esters, solvolysis (k_S) was accompanied by a concurrent, intramolecular, first-order rearrangement (k_R) to the allylic isomer. In 70 volume per cent. aqueous dioxane the rates of these competing reactions were nearly equal. The total rate of reaction ($k_S + k_R$) of each of the α-aryl isomers was found to be ca. 325 greater than the solvolysis rate of the corresponding γ-aryl ester. Substitution of a p-methyl substituent into the phenyl ring of the solvolyzing esters furnished a rate enhancement of ca. 10.0 in the case of each of the measured rate constants (k_S, k_R) of the α-phenyl ester and ca. 8.4 for the solvolysis of the allylic γ-phenyl ester. The reactions of the four esters under investigation showed relatively large solvent sensitivities, a change in solvent from 70 to 60 volume per cent. aqueous dioxane enhancing the reaction rates by factors of ca. 3.2 ($m \simeq 0.7$) for the rearrangement processes, k_R, and of ca. 4.0–5.0 ($m \simeq 0.85$–1.0) for the hydrolysis reactions. The kinetic results permit a calculation of the ground state free energy differences between pairs of allylic isomers. The γ-aryl esters (which contain a styrene-type chromophore) are found to be 3.2 ± 0.1 kcal./mole more stable than the isomeric α-aryl esters. The greatly enhanced rates of reaction of the α-aryl isomers over their isomers are due chiefly to this difference in ground state energies.

Introduction

In recent years a number of investigations of solvolysis reactions of isomeric allylic halides and esters have uncovered some interesting facets of carbonium ion behavior. A paper by Young, Winstein and Goering[1] reported that the first-order acetolysis of α,α-dimethylallyl chloride is

accompanied by an essentially intramolecular rearrangement to the isomeric γ,γ-dimethylallyl chloride. These authors preferred to interpret their results in terms of a common ion-pair intermediate produced from either isomeric chloride and capable of giving rise either to covalent chlorides by internal return or to solvolysis product. de la Mare and Vernon[2] have also investi-

(1) W. G. Young, S. Winstein and H. L. Goering, THIS JOURNAL, **73**, 1958 (1951).

(2) P. B. D. de la Mare and C. A. Vernon, J. Chem. Soc., 2504 (1954).

gated this system in the solvents 75 per cent. aqueous ethanol and absolute ethanol. These authors noted that a similar rearrangement process accompanies solvolysis in the former solvent system but not in the latter. Their data require that, if an intermediate is involved in the formation of rearrangement products, it cannot be a dissociated carbonium ion.

The solvolytic behavior of several other pairs of isomeric allylic systems have since been investigated and in every case the general behavior exhibited by these systems parallels that noted with the dimethylallyl chlorides, a simultaneous operation of both intramolecular rearrangement and solvolysis processes is observed. Perhaps the most thorough investigation has been carried out by Goering and his co-workers[3] who utilized the various geometric and optical isomers of derivatives of the 5-methylcyclohex-2-enyl system in a number of interesting investigations. These researchers used a combination of polarimetric and titrimetric kinetic techniques to determine the relative rates of the competing rearrangement and solvolysis reactions which their various systems undergo. The relative importance of these competing reactions was shown to be remarkably insensitive to changes in the nature of the leaving group (chloride,[3b] acid phthalate, [3c] p-nitrobenzoate[3a]) or of the solvent (ethanol, [3b] acetic acid,[3b] aqueous acetone[3a,3c]). Goering interprets his data in terms of an ion-pair intermediate, common to both reactions. His results require that this ion-pair possess a certain degree of covalent bonding; alternatively, the electrostatic forces of attraction between the ion-pair components must be sufficiently strong to retain configuration.

Other allylic systems whose solvolyses have been investigated include phenylvinylcarbinyl chloride in aqueous dioxane and ethanol,[4] and α,γ-dimethylallyl acid phthalate in aqueous acetone.[5]

That solvolysis reactions of the type under discussion take place *via* ion-pair intermediates, common to both solvolysis and rearrangement, appears to be accepted by most current chemical opinion. An alternative view, first proposed by de la Mare and Vernon,[2] requires the operation of two separate simultaneous reactions: an intramolecular SNi reaction leading to the rearranged chloride, accompanied by an SN1 ionization reaction[6] furnishing allylic carbonium ion which can react further to give product. However, this latter view appears to be inconsistent with experimental facts, as has been argued convincingly by Streitwieser[7] and by Winstein and Robinson.[8]

We have studied the allylically related α-phenyl-γ-methylallyl (Ia) and α-methyl-γ-phenylallyl (IIa) p-nitrobenzoates as well as the α-p-

tolyl-γ-methylallyl (Ib) and α-methyl-γ-p-tolylallyl (IIb) p-nitrobenzoates. Our attention was first drawn to these pairs of compounds as a result of some rather unexpected findings obtained in a recent study in which the rates of solvolysis of a series of 6-substituted cholesteryl p-toluenesulfonate esters were measured.[9] We undertook this work in an attempt to gain insight into the factors responsible for the observed order of reactivity in this homoallylic series.

Results

All of the esters used in the present work were prepared by conventional methods from the corresponding alcohols. Both allylic phenyl esters are known compounds.[10] The phenyl alcohols were prepared by the action of the methyl or phenyl Grignard reagent on the appropriate aldehyde. α-p-Tolyl-γ-methylallyl alcohol was prepared from the p-tolyl Grignard reagent and crotonaldehyde and was rearranged to the more stable α-methyl-γ-p-tolylallyl alcohol by acetic acid in aqueous acetone. The *trans* orientation of substituents about the double bond in three of these alcohols is inferred from their synthesis from *trans*-α,β-unsaturated aldehydes. The *trans* orientation in α-methyl-γ-p-tolylallyl alcohol follows from the findings of Kenyon and co-workers[10] that the analogous rearrangement of *trans*-α-phenyl-γ-methylallyl alcohol furnished its *trans*-allylic isomer, *trans*-α-methyl-γ-phenylallyl alcohol.

The pertinent kinetic data are collected in Table I. The four p-nitrobenzoate esters were allowed to solvolyze in aqueous dioxane solutions containing varying amounts of water. At appropriate time intervals aliquots of the reacting solution were quenched in dry acetone and titrated to the phenolphthalein end-point with *ca.* 0.02 N standard sodium hydroxide. In nearly all of the runs carried out at temperatures of 50° or greater, ampoules sealed under nitrogen were used. Essentially all of the rate constants given in Table I were averages of from ten to fifteen separate kinetic points; the precision within any one run was usually of the order of 2–3%. Most of the runs were carried to 80–90% reaction with no detectable drift in rate constants (except as noted below).

In general, the γ-aryl isomers had liberated more than 100% of the theoretical acid after ten half-lives (>99.9% reaction) and the titer increased further with time. Presumably the solvent undergoes a slow hydrolysis and oxidation to furnish acid.[11] Accordingly the rates of hydrolysis of the γ-aryl esters reported in Table I have been calculated from the usual first-order rate expression using the theoretical rather than the experimental infinity titers. Fortunately this acid-producing side reaction becomes important only after about 75% reaction. Later kinetic points have been excluded in calculating the average rate constants. A typical kinetic run is included in the Experimental section.

(3) (a) H. L. Goering and E. F. Silversmith, THIS JOURNAL, 77, 6249 (1955); (b) H. L. Goering, T. D. Nevitt and E. F. Silversmith, *ibid.*, 77, 5026 (1955); (c) H. L. Goering and E. F. Silversmith, *ibid.*, 77, 1129 (1955).

(4) G. Valkanas and E. S. Waight, *Proc. Chem. Soc.*, 10 (1959).

(5) H. L. Goering and R. W. Greiner, THIS JOURNAL, 79, 3464 (1957).

(6) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, pp. 311 and 596.

(7) A. Streitwieser, Jr., *Chem. Revs.*, 56, 571 (1956).

(8) S. Winstein and G. C. Robinson, THIS JOURNAL, 80, 169 (1958).

(9) R. A. Sneen, *ibid.*, 80, 3971, 3977, 3982 (1958).

(10) (a) J. Kenyon, S. M. Partridge and H. Phillips, *J. Chem. Soc.*, 85 (1936); (b) 207 (1937).

(11) This side reaction was minimized when aliquots of the reaction mixture were sealed under nitrogen.

TABLE I

RATES OF SOLVOLYSIS OF SOME ALLYL p-NITROBENZOATES IN AQUEOUS DIOXANE

[ROpNB]a × 10²	Solvent,b % dioxane	Temp., °C.	k, sec.⁻¹ × 10⁶	Infinity,c %
α-Phenyl-γ-methyl^d				
2.27	60	25.0	70.7 ± 1.5^e	61.5
1.54	60	25.0	74.4 ± 1.4	58.2
2.42	70	25.0	17.5 ± 0.5^e	51.5
	70	25.0	18.2 ± 0.7^j	49.3 ± 0.5^j
1.35	70	50.0	306 ± 8	50.7
1.77	80	50.0	79.2 ± 1.7	39.6
α-p-Tolyl-γ-methyl^d				
1.81	60	25.0	740 ± 11^e	63.2
1.49	60	25.0	736 ± 18	63.7
1.65	70	25.0	186 ± 5^e	50.2
	70	25.0	180 ± 2^j	53.2 ± 1.0^j
1.50	80	25.0	39 ± 2	36.8
α-Methyl-γ-phenyl^f				
2.27	60	50.0	6.19 ± 0.16	..
2.16	60	65.0	32.6 ± 0.4	..
2.26	60	75.0	98.0 ± 1.3	..
2.30	70	50.0	1.49 ± 0.02	..
2.20	70	65.0	8.50 ± .19	..
2.10	70	75.0	24.6 ± .4	..
..	60	50.0	6.0 ± .4^g	..
..	70	50.0	1.46 ± .07^g	..
..	60	25.0	0.250^h	
..	70	25.0	0.0570^h	
α-Methyl-γ-p-tolyl^f				
	60	50.0	51.0 ± 0.6^j	
2.05	60	65.0	252 ± 5	
	70	50.0	11.8 ± 0.1^j	
2.07	70	65.0	63.1 ± 1.2	
2.20	70	75.0	184 ± 5	
..	70	50.0	11 ± 1^g	
..	60	25.0	2.14^h	
..	70	25.0	0.475^h	

a [Alkyl p-nitrobenzoate]ᵢₙᵢₜᵢₐₗ. b Volume per cent. c Percentage of the theoretical acid liberated after ten half-lives. d Rate constants calculated from experimental infinity titers. e These four kinetic runs were carried out simultaneously using homogeneous samples of the esters and of the mixed solvents. The values have been used in calculating the ratios in the succeeding tables. f Rate constants calculated from theoretical infinity titers. g These are the calculated rates at which acid was liberated from the infinity solutions resulting from reaction of the corresponding α-aryl p-nitrobenzoate. h These rate constants were obtained by extrapolation of the data at higher temperatures, using the thermodynamic data of Table II. j Average of two or more separate runs.

The α-aryl esters reacted at a sufficiently fast rate under all conditions to make the acid-producing side reaction of negligible importance. Infinity titers after ten and twenty half-lives of reaction were constant within experimental error. However, both α-phenyl-γ-methyallyl and α-p-tolyl-γ-methylallyl p-nitrobenzoate liberated less than the theoretical amount of acid; depending on the composition of the solvent, these esters gave only from 37–64% of the theoretical acid by this initial fast reaction. Accordingly, these rate constants were calculated from the equation

$$\frac{1}{t} \ln \frac{[HX]_\infty - [HX]_0}{[HX]_\infty - [HX]_t} = k$$

where $[HX]_\infty$, $[HX]_0$ and $[HX]_t$ represent the concentrations of titrated acid at infinite time (ten half-lives), zero time and time t, respectively. It can be shown that the rate constant so determined is equal to the sum of the rate constants for two simultaneous first-order processes for the disappearance of starting material, an acid-producing hydrolysis and a rearrangement to unreactive isomer.

In some cases the infinity solutions resulting from reaction of each of the α-aryl compounds for ten half-lives were transferred to a constant temperature bath at 50.0°. At this temperature the acid titers increased further with time. Rough rate constants for these slower reactions were calculated using the theoretical infinity titers based on the original concentration of the α-aryl ester. The rate constants so calculated are included in Table I and can be seen to agree within experimental error with the rate constants for reaction of the corresponding γ-aryl-α-methylallyl esters under the same conditions. Data from a typical run have been included in the Experimental section.

In order to compare the widely-differing rate constants of the four esters under comparable conditions it was necessary to extrapolate data for the γ-aryl esters from higher temperatures to 25.0° Accordingly, the thermodynamic functions of activation, $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$, have been determined for the γ-aryl isomers from data at 50.0 and 75.0°. The extraplated rates of reaction of the γ-aryl esters at 25.0° have been calculated using these functions and are recorded in Table I. The functions are collected in Table II. A plot of

TABLE II

THERMODYNAMIC FUNCTIONS OF ACTIVATION FOR THE REACTIONS OF SOME SUBSTITUTED ALLYL p-NITROBENZOATES IN AQUEOUS DIOXANE

Allyl p-nitrobenzoate	Solvent, % dioxane	Reaction	$\Delta H^{\ddagger}$, kcal./mole	$\Delta S^{\ddagger}$, e.u.
α-Phenyl-γ-methyl	70	$k_{RX} = k_R + k_S$	21.0	−10.0
	70	k_S	21.2	−10.4
	70	k_R	20.8	−11.8
α-Methyl-γ-phenyl	70	$k_{R'X}$	24.4	−10.0
	60	$k_{R'X}$	24.0	− 8.5
α-Methyl-γ-p-tolyl	70	$k_{R'X}$	24.0	− 7.9
	60	$k_{R'X}$	22.4	− 9.0

log k vs. $1/T$ for each of the γ-aryl esters at each solvent composition was linear over the temperature range 50–75°. Table III lists the ratios of

TABLE III

RATES OF SOLVOLYSIS OF ISOMERIC PAIRS OF ALLYLIC ESTERS IN AQUEOUS DIOXANE

Allyl p-nitrobenzoates	Solvent, % dioxane	Temp., °C.	Ratio ($k_{RX}/k_{R'X}$)
α-Phenyl^a	60	25.0	283
γ-Phenyl	70	25.0	307
	70	50.0	206
α-p-Tolyl^b	60	25.0	346
γ-p-Tolyl	70	25.0	392

a $k_{α\text{-phenyl-γ-methyl}}/k_{α\text{-methyl-γ-phenyl}}$.   b $k_{α\text{-p-tolyl-γ-methyl}}/k_{α\text{-methyl-γ-p-tolyl}}$.

rates of pairs of allylic isomers. The rate enhancements accompanying p-methyl substitution are presented in Table IV, and in Table V the effects of varying solvent composition on the rates of the various reactions are compared.

TABLE IV

RATE ENHANCEMENTS ACCOMPANYING p-METHYL SUBSTITUTION IN SOME ALLYLIC p-NITROBENZOATE ESTERS IN AQUEOUS DIOXIDE

Allyl p-nitrobenzoates	Solvent, % dioxane	Temp., °C.	Reaction	Ratio $(k_{p\text{-Me}}/k_H)$
α-p-Tolyl[a]	60	25.0	Total	10.4
α-Phenyl	60	25.0	Hydrol.	10.7
	60	25.0	Rearrang.	10.0
	70	25.0	Total	10.6
	70	25.0	Hydrol.	10.4
	70	25.0	Rearrang.	10.9
γ-p-Tolyl[b]	60	50.0		8.15
γ-Phenyl	60	65.0		7.73
	70	50.0		7.92
	70	65.0		7.43
	70	75.0		7.49
	60	25.0		8.56
	70	25.0		8.33

[a] $k_{\alpha\text{-}p\text{-tolyl-}\gamma\text{-methyl}}/k_{\alpha\text{-phenyl-}\gamma\text{-methyl}}$. [b] $k_{\alpha\text{-methyl-}\gamma\text{-}p\text{-tolyl}}/k_{\alpha\text{-methyl-}\gamma\text{-phenyl}}$.

TABLE V

SOLVENT EFFECTS ON REACTION RATES OF SOLVOLYSIS OF SOME ALLYL p-NITROBENZOATE ESTERS IN AQUEOUS DIOXANE

Allyl p-nitrobenzoate	Temp., °C.	Reaction	k_{60}/k_{70}[a]	k_{70}/k_{80}[b]
α-Phenyl-γ-methyl	25	Total	4.04	
	25	Hydrol.	4.82	
	25	Rearrang.	3.21	
	50	Total		3.86
	50	Hydrol.		4.95
	50	Rearrang.		3.15
α-p-Tolyl-γ-phenyl	25	Total	3.98	
	25	Hydrol.	5.02	
	25	Rearrang.	2.94	
α-Methyl-γ-phenyl	50		4.15	
	65		3.84	
	75		3.98	
	25		4.22	
α-Methyl-γ-p-tolyl	50		4.27	
	65		4.00	
	25		4.51	

[a] Ratio of rates in 60 and 70 volume per cent. aqueous dioxane. [b] Ratio of rates in 70 and 80 volume per cent. aqueous dioxane.

Discussion

The solvolytic behavior exhibited by the isomeric pairs of esters in the present study parallels very closely the behavior of other previously studied allylic systems[1-5]; the reactive α-aryl esters undergo simultaneous acid-producing solvolysis reactions and rearrangements to the considerably more stable γ-aryl esters. The so-formed γ-aryl esters are essentially unreactive under the conditions of their formation and this fact simplifies the evaluation of the rate constant, k_{RX}, for the destruction of the α-aryl esters. The rate constant, k_{RX}, evaluated in this way can be shown to be

equal to the sum of the rate constants for acid-producing solvolysis, k_S, and rearrangements k_R. The gross transformations, without commitment as to details of mechanism, can be described by the empirical scheme

a, R = phenyl
b, R = p-tolyl
$k_{RX} = k_R + k_S$
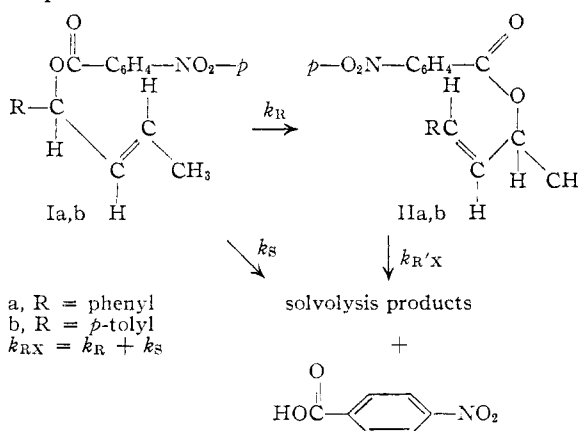
The discrepancy between the amount of acid actually produced after ten half-lives of reaction of the α-aryl esters and that calculated for 100% solvolysis results from a concurrent rearrangement to the more stable γ-aryl isomers. This is shown by the observation that infinity solutions ($\geqslant 10$ half-lives) of the reaction mixtures resulting from solvolysis of the α-aryl ester, when allowed to react further at higher temperatures, produced acid at a rate within experimental error of that determined for the corresponding authentic γ-aryl-α-methylallyl p-nitrobenzoates (see Table I).

All four of the allylic esters studied react exclusively by alkyl–oxygen fission. This conclusion follows from the following observations. The rate of reaction of even the slowest-solvolyzing ester, γ-phenyl-α-methyallyl p-nitrobenzoate, can be calculated to be ca. 7000 times greater than that of cyclohexyl p-nitrobenzoate.[12] As Goering [3a] has pointed out for a similar allylic p-nitrobenzoate, there is no apparent reason why the allylic ester should undergo acyl–oxygen cleavage more readily than the saturated analog. Further evidence for alkyl–oxygen fission is found in the high sensitivities of the reactant esters to ionizing power of the solvent[13] (see Table V) and to p-methyl substitution $(k_{p\text{-tol}}/k_{C_6H_5} \cong 9)$ (see Table IV).

That the reactions under discussion involve heterolytic cleavage of the neutral ester, uncatalyzed by acid, is shown by the constancy of the integrated rate constants during the course of reaction. Since p-nitrobenzoic acid is liberated in the course of solvolysis, any important acid-catalyzed component of the reaction would have been revealed by rising rate constants.

The intramolecular nature of the rearrangement has been established by the following observations. First, no trend was noticed with time in the calculated values of the integrated rate constants during the course of reaction. Further, although the addition of 0.186 M sodium p-nitrobenzoate to a

(12) Goering[3a] reports a value of 1.4 × 10⁻⁸ sec.⁻¹ for the rate of solvolysis of this compound in 80% aqueous acetone at 100°.

(13) A. H. Fainberg and S. Winstein, THIS JOURNAL, 78, 2770 (1956), and other papers in this series.

solvolyzing mixture of the α-phenyl ester resulted in a decreased rate constant, the effect was relatively small and of the same magnitude as observed with comparable concentrations of the non-common ion-containing salt, sodium benzoate.[14]

Identification of the solvolysis products of the various esters studied in this work has been hindered by the rapid isomerization (presumably acid-catalyzed) of the α-aryl-γ-methyallyl alcohols.[15] However, by analogy with numerous results reported in the literature for similar allylic systems solvolyzing by an SN1-type process in a solvent of relatively high ionizing power,[16] it seems highly probable that both isomeric allylic alcohols are produced on solvolysis of either ester and in essentially the same ratio from either ester.

The significance of the rate ratios summarized in Tables III, IV and V will be discussed in detail in later sections of this paper. Briefly, the more salient features will be pointed out here. Table III indicates that for each isomeric pair of esters the α-aryl-γ-methylallyl ester is found to be appreciably more reactive than its isomer by rate factors of ca. 300–400. Table IV contrasts the effect of p-methyl substitution into each of the allylic phenyl esters, the α-phenyl ester proved to be slightly more sensitive to such substitution, a rate enhancement of ca. 10.5 being observed, whereas the rate of reaction of the α-phenyl ester was increased by a factor of ca. 8.5 at the same temperature. Table V indicates that all of the esters investigated show similar sensitivities to changes in the ionizing power of the solvent, a rate enhancement of ca. 4.0[17] accompanying the change in solvent from 70 to 60 volume per cent. aqueous dioxane.

Quantitative Treatment of Data.—The solvolytic behavior exhibited by the isomeric allylic esters studied in this work can be described by Scheme 1,[18] an adaptation of the mechanism originally proposed by Young, Goering and Winstein[1] for the acetolysis of α,α-dimethylallyl chloride. It will be seen that this scheme involves the formation of the same intermediate tight ion-pair[19] from each

(14) Unpublished work.

(15) Unpublished work in these laboratories (Mr. A. Rosenberg) suggests that methanolysis of α-phenyl-γ-methylallyl p-nitrobenzoate at 35.0° produces, in addition to ca. 22% of the rearranged γ-phenyl ester, the methyl ethers of the α-phenyl and γ-phenyl alcohols in a ratio of ca. 1:2.

(16) R. H. DeWolfe and W. G. Young, Chem. Revs., 56, 753 (1956).

(17) This corresponds to a value for the substrate constant,[13] m, of 0.9; t-butyl chloride, a compound assumed to react almost exclusively by a limiting or SN1 process, has m = 1.00 at 25.0°; see ref. 13.

(18) Throughout the discussion which follows the rate constants described in Scheme 1 as well as in the empirical formulation (vide supra) will retain these definitions. In particular k_{RX} and $k_{R'X}$ refer to the experimentally determined total rates of reaction of the α-aryl-γ-methylallyl and α-methyl-γ-arylallyl p-nitrobenzoates, respectively. Further, the symbols RX and R'X will always refer to the α-aryl and γ-aryl esters, respectively.

(19) The bonding in these intermediates must be quite strong. This conclusion follows from the studies of Kenyon[10] in which it was shown that various rearrangements of derivatives of α-phenyl-γ-methylallyl alcohol take place by stereospecific processes. Similarly, Goering[3] has shown that ion-pair formation from certain derivatives of the 5-methyl-2-cyclohexenyl system is not accompanied by geometric isomerization. Further, Goering[5] has quoted an unpublished result of W. E. Doering in which the rearrangement of α-phenyl-γ-methylallyl p-nitrobenzoate, under unspecified conditions, furnished
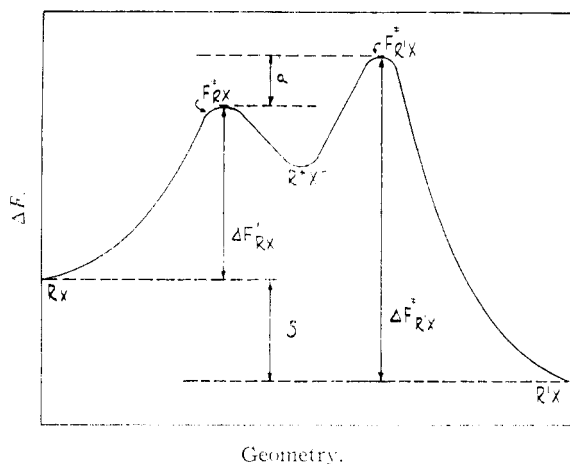
isomeric ester in a relatively high energy step (k_1 and k_2). The unstable intermediate so formed can then proportion itself by any of several fast reactions; it can undergo internal return (k_{-1} and k_{-2}) to form starting ester or rearranged ester or it can dissociate irreversibly (k_3) to carbonium ion which subsequently reacts with solvent in fast reactions to give the isomeric alcohols.[20]

SCHEME 1
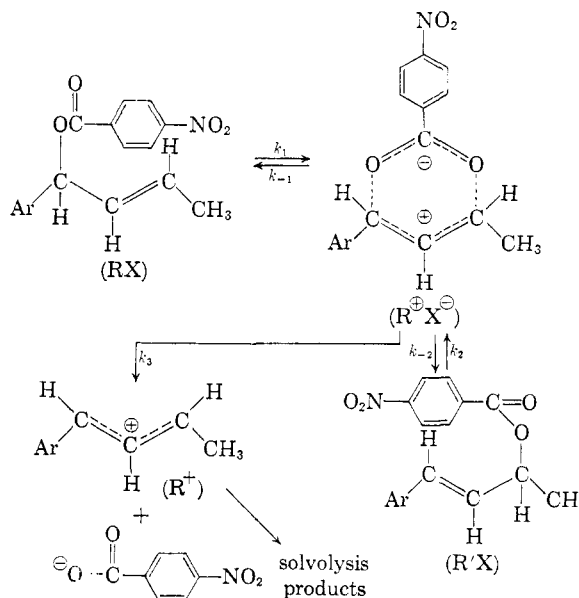
One of our aims in undertaking this work was the quantitative description of the various processes involved in reactions of allylic systems in terms of their free energy profile diagrams. It can be shown that if the ion-pair dissociation reaction (k_3 in Scheme 1) had proved to be reversible a nearly complete analysis of the rates defined in Scheme 1 could be achieved from the experimentally determined kinetic data for the allylic phenyl esters, with and without added p-nitrobenzoate anion.[21] In particular, the differences in ground state energies of the allylic isomers could be calculated. Early kinetic experiments in the presence of sodium p-nitrobenzoate suggested that this dissociation was reversible at moderate concentrations of anion.[14] However, it was later shown that all of the facts could be explained in terms of normal salt effects.

However, an alternative approach is available for the calculation of differences in ground state energy between the allylic isomers. The quantities used in this derivation are defined by the free energy diagram of Fig. 1, and correspond to the definitions of rate constants of Scheme 1[22] reproduced below in abbreviated form.

the allylic isomer in which the original carbonyl oxygen has become the alkyl oxygen in the product.

(20) The inclusion of the dissociated carbonium ion, R+, in this reaction scheme is required by the results of competition experiments with azide ion.[14]

(21) A similar analysis would be possible on the basis of a dual mechanism scheme, analogous to that suggested by de la Mare and Vernon[2] for the solvolysis of α,α-dimethylallyl chloride, if the ionization of either RX or R'X had proved to be reversible.

(22) The alternative dual mechanism scheme also lends itself to this sort of treatment. Interestingly, it predicts the same energy difference between isomers as does the intermediate scheme.

Geometry.

Fig. 1.—Free energy diagram for the reactions:
$$RX \rightleftharpoons R^+, X^- \rightleftharpoons R'X.$$

$$RX \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} R^\oplus X^\ominus \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} R'X$$

$$\downarrow k_3$$

solvolysis product

The solvolysis step, k_3, has not been explicitly included in the energy diagram. The reaction coördinate is considered to be geometry; e.g., at the extreme left the geometry corresponds to covalent RX in its environment and somewhere near the center of the diagram the geometry is that defined by the ion-pair, $R^\oplus X^\ominus$.

The following definitions and relations are apparent from the diagram

$$t = F_{R'X}^\ddagger - F_{RX}^\ddagger$$

$$s = F_{RX} - F_{R'X}$$

$$\Delta\Delta F^\ddagger = \Delta F_{R'X}^\ddagger - \Delta F_{RX}^\ddagger = t + s$$

This solution for the ground state energy differences requires that two assumptions be made: first, that the ratio k_{-1}/k_{-2} is a constant and independent of solvent (i.e., that t is a constant), at least over small intervals of varied solvent composition; and second, that the ground state free energies of the covalent allylic esters are similarly affected by a small change in solvent composition (i.e., that s is a constant). If these assumptions are granted, then the Principle of Microscopic Reversibility requires that the ratio k_1/k_2 be a constant over this same solvent composition interval.[23]

$$k_{-1}/k_{-2} = b \text{ (solvent independent)} \quad (1)$$

$$k_1/k_2 = c \text{ (solvent independent)} \quad (2)$$

Further, the ratio

$$k_3/k_{-2} = a \text{ (solvent dependent)} \quad (3)$$

is solvent dependent but experimentally measurable.

When solvolysis of R'X takes place, RX is sufficiently unstable to be treated as an unstable

intermediate subject to a steady state approximation. Then the relations 4 and 5 are established.

$$k_{RX} = \frac{k_1(k_{-2} + k_3)}{k_{-1} + k_{-2} + k_3} \quad (4)$$

$$k_{R'X} = \frac{k_2 k_3}{k_{-2} + k_3} \quad (5)$$

Making the proper substitutions from equations 1, 2 and 3 into equations 4 and 5, one finds

$$k_{RX} = \frac{k_2 c(k_{-2} + ak_{-2})}{bk_{-2} + k_{-2} + ak_{-2}} = \frac{ck_2(1 + a)}{1 + a + b} \quad (6)$$

$$k_{R'X} = \frac{ak_{-2}k_2}{k_{-2} + ak_{-2}} = \frac{ak_2}{1 + a} \quad (7)$$

Dividing equation 6 by 7 furnishes, after rearrangement, equation 8.

$$c = \frac{k_{RX}(1 + a + b)a}{k_{R'X}(1 + a)^2} = \frac{ak_{RX}}{k_{R'X}(1 + a)^2}b + \frac{ak_{RX}}{k_{R'X}(1 + a)} \quad (8)$$

Now, since values of a, k_{RX} and $k_{R'X}$ have been experimentally determined at two solvent compositions, and since b and c are assumed independent of solvent changes, there result two linear equations in two unknowns, b and c, which can be solved for these unknowns. The results of these calculations from data in 60 and 70 volume per cent. dioxane are collected in Table VI.[24]

TABLE VI

CALCULATED GROUND STATE FREE ENERGY DIFFERENCES BETWEEN ALLYLIC ISOMERS AND RATIOS OF RATE CONSTANTS FOR ISOMERIZATION REACTIONS[a]

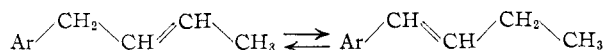| Allyl p-nitro-benzoates	$b = \frac{k_{-1}}{k_{-2}}$	$c = \frac{k_1}{k_2}$	$\Delta F = F_{RX} - F_{R'X} = s,$ kcal./mole
Phenylmethyl	1.53	276	3.07
p-Tolylmethyl	1.12	306	3.32

[a] Calculated from eq. 8.

Ground State Energies, Reactivity and Electrical Effects.—The exalted reactivity of the α-arylallyl esters over their isomeric γ-aryl esters (Table III) is not unexpected since the latter compounds contain a resonance-stabilized styrene-type system. Interestingly, our calculations show that this difference in rate is due almost wholly to this ground state energy difference; the respective transition states are of nearly identical energy (Table VI). The conjugation energy of the styrene system present in the γ-aryl isomers has been calculated to be ca. 3.2 kcal./mole. Since there is no obvious reason to suppose that the

(23) These assumptions seem eminently reasonable; that k_{-1}/k_{-2} should be quite independent of solvent follows from the obvious similarities of the two transition states involved. Further the ground state energy difference (s) between covalent esters should also be relatively insensitive to solvent composition.

(24) An alternative method of calculation can be solved for a minimum difference in ground state energy between the allylic isomers. From the quantities defined above, the equation can be rigorously derived

$$s = F_{RX} - F_{R'X} =$$

$$RT \ln \frac{[1 - k_{-2}/(k_{-2} + k_3)][k_{-2}/(k_{-2} + k_3)]k_{RX}}{[k_{-1}/(k_{-1} + k_{-2} + k_3)]k_{R'X}}$$

Experimentally each of these terms has been measured except for the fraction in the denominator, $k_{-1}/(k_{-1} + k_{-2} + k_3)$. However, since this fraction must be less than unity, a minimum value for s can be determined. Using the data from Table I and a value of unity for the denominator fraction, one calculates a minimum value of 2.53 ± 0.03 kcal. for s, the difference in ground state energies for the isomeric phenylmethyl esters under varying conditions of solvent and temperature, and a minimum value of 2.68 ± 0.04 kcal. for the difference in ground state energy of the isomeric p-tolylmethyl esters in varying solvent systems. Interestingly, equations derived from the dual mechanism scheme[2] predict these same numerical values for s.

ester function will significantly affect the stabilities of the α- and γ-isomers in different ways, it would seem that this conjugation energy should be a fairly good measure of the free energy difference for the isomerization reaction,[25]
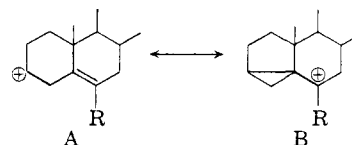
$$Ar \overset{CH_2}{\diagdown}{CH} \overset{CH}{\diagup}{\diagdown}{CH_3} \rightleftarrows Ar \overset{CH}{\diagup}{\diagdown}{CH} \overset{CH_2}{\diagup}{\diagdown}{CH_3}$$

It is tempting to attempt to analyze the ratios k_{-1}/k_{-2}, recorded in Table VI, as a function of the structure of the allylic systems. However, the experimental uncertainties in the kinetic data used to obtain these values, together with the assumptions necessary in order to solve for these ratios, makes their uncertainities fairly large. It is reassuring that each of the investigated systems gave a value for this ratio of a similar magnitude.

Another interesting facet of the present results is brought out by the data of Table IV where the kinetic effects of p-methyl substitution are compared. It will be noted that the rates of reaction at 25° for both allylic esters are increased by factors varying from 8–11 by a p-methyl group. The magnitude of the rate enhancements effected by a p-methyl group leaves no doubt that the rate-determining steps of all of these reactions are of SN1 or limiting type[26] and that considerable charge has been generated in the transition state. Of more interest for our present purposes is the observation that the rates of both α- and γ-p-tolyl isomers have rates accelerated by quite similar factors over the corresponding α- and γ-phenyl esters.[27]

If one assumes that the ground state free energies of the allylic esters are affected similarly by p-methyl substitution, it follows that their respective transition states are stabilized to nearly the same extent by this substituent. Thus the electrical effect of the p-methyl group is transmitted with nearly undiminished force through the conjugated double bond in spite of the greatly increased ground state stability of the γ-aryl ester.

The findings have implications for some unusual reactivities noted in a recent study[9] of the rates of ionization of some 6-substituted cholesteryl p-toluenesulfonates in 90 volume per cent. aqueous dioxane. The relative rates of reaction of the esters of cholesterol, 6-methylcholesterol, 6-phenylcholesterol and 6-p-tolylcholesterol, were found to be 1.00:75:0.324:0.457. The rate enhancement effected by introduction of the 6-methyl group was interpreted in terms of the increased

(25) Using the parameters evaluated by Taft and Kreevoy, a quantity which these authors call the "extra resonance energy of conjugation" of the styrene chromophore can be assessed from our experimental data. This quantity measures, presumably, the stabilization by resonance interaction after correction for inductive and hyperconjugative effects. This treatment results in a correction factor of 1.0 kcal./mole to be added to our experimentally determined resonance energy of 3.2 kcal./mole. The sum, 4.2 kcal./mole, is in very good agreement with the corresponding energy calculated for styrene, 4.3 kcal./mole; R. W. Taft, Jr., and M. M. Kreevoy, THIS JOURNAL, 79, 4011 (1957); M. M. Kreevoy and R. W. Taft, Jr., ibid., 79, 4016 (1957); R. W. Taft, Jr., in M. S. Newman, "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1956, p. 591.

(26) See ref. 7, pp. 591 and 648.

(27) The acceleration in rate for the γ-isomer corresponds to an increased stabilization energy ca. 90% as large as that of the α-aryl isomer.

stabilization provided by this group to the transition state.

The actual decrease in reaction rate noted on introduction of the 6-phenyl group was unexpected. Several possible explanations for this inversion in reactivity were suggested. The present results shed some light on this problem. In the first place the conjugation energy of the styrene chromophore has been shown in the present work to be ca. 3.2 kcal./mole. If the phenyl ring in 6-phenylcholesteryl p-toluenesulfonate is assumed to be coplanar with the Δ⁵-double bond, a stabilization energy of ca. 3.2 kcal./mole must be gained back in the transition state by electron delocalization from the phenyl ring if the rate is not to be depressed relative to the unsubstituted ester. However, this postulated decrease in ground state energy of the starting material cannot completely rationalize the low reactivity of 6-phenylcholesteryl tosylate. This follows from the observed insensitivity of the rates of solvolysis of 6-phenylcholesteryl tosylate to p-methyl substitution, the observed rate ratio, $k_{p\text{-tolyl}}/k_{phenyl}$ being only 1.41. In the present study it has been found that the ground state stabilities of the α- and γ-arylallyl esters had only a very small effect on the sensitivity to p-methyl substitution $k_{p\text{-tol}}/k_{phenyl} \cong 9$. These results then require that in the transition state for ionization of 6-arylcholesteryl p-toluenesulfonates only a small amount of positive charge can reside on C_6; in other words, the canonical resonance form, B, is quite unimportant in the transition state when R is an aryl ring. The reasons for the relative unimportance of this structure are still somewhat obscure.[28]

Experimental

α-Phenyl-γ-methylallyl p Nitrobenzoate.—To a magnetically stirred, ice-water-cooled solution of α-phenyl-γ-methylallyl alcohol[10b] (3.583 g., 2.42 mmoles) in 15 ml. of pyridine (distilled from calcium hydride) was added 4.22 g. (2.28 mmoles) of p-nitrobenzoyl chloride in small portions. After the addition had been completed (5 min.), an additional 15 ml. of pyridine was added and the reaction was allowed to proceed with stirring for an additional 45 minutes. The reaction mixture was then poured into ice-water with stirring, furnishing crystalline ester. The crude product was filtered, dissolved in ca. 50 ml. of ether, and the ethereal solution was washed with fresh water and dried (magnesium sulfate). Most of the ether was removed at water-pump pressure and pentane (ca. 50 ml.) was added. The resulting solution was allowed to stand overnight at −5°, furnishing 3.945 g. (58.5%) of α-phenyl-γ-methylallyl p-nitrobenzoate, m.p. 95–96°. Repeated crystallization from hexane furnished the analytical sample, m.p. 96.5–98° (lit.[10b] m.p. 99°).

Anal. Calcd. for $C_{17}H_{15}NO_4$: C, 68.67; H, 5.09. Found: C, 68.98; H, 4.85.

(28) An intermediate in the synthesis of each of the 6-substituted cholesteryl esters used in these kinetic studies⁹ was formed by the reaction of an appropriate Grignard reagent with 6-ketocholesteryl acetate (or alcohol). The original assignment of configuration to the newly-formed asymmetric center at C_6 (6β-aryl-6α-hydroxy), which was based on the direction of changes in the molecular rotation at the sodium D line, has been placed in doubt by rotatory dispersion measurements which indicate that the 6-phenyl group makes a dextrorotatory contribution (private communication, J. H. Brewster).

α-**Methyl-γ-phenylallyl** *p*-**Nitrobenzoate.**—The preparation of this compound followed the procedure described above for its allylic isomer; α-methyl-γ-phenylallyl alcohol[10a] (7.20 g., 48.6 mmoles) and *p*-nitrobenzoyl chloride (8.80 g., 47.4 mmoles) in 50 ml. of pyridine interacted to form, after one crystallization from pentane, 12.74 g. (90.6%) of α-methyl-γ-phenylallyl *p*-nitrobenzoate, m.p. 51–58°. Repeated crystallization furnished the pure ester, m.p. 59° (lit.[10a] m.p. 58–59°).

α-*p*-**Tolyl-γ-methylallyl alcohol** was prepared by the dropwise addition of a solution of crotonaldehyde (26 g.) in ethyl ether to a solution of the *p*-tolyl Grignard reagent (previously prepared by the addition of a solution of *p*-tolyl bromide (77.5 g.) in ether (70 ml.) to a suspension of 10.0 g. of magnesium turnings in 50 ml. of ether). The reaction was allowed to continue for 2 hours after the addition had been completed and the excess Grignard reagent was decomposed with methanol and then a saturated aqueous solution of ammonium chloride. The ethereal layer was removed, washed with water and dried overnight (potassium carbonate). Ether was removed at atmospheric pressure through a Vigreux column. Vacuum distillation of the residue furnished α-*p*-tolyl-γ-methylallyl alcohol, b.p. 117–120° (2 mm.). The distilled alcohol crystallized spontaneously to a solid mass. Repeated crystallization from pentane furnished the analytical sample, m.p. 48°.

Anal. Calcd. for $C_{11}H_{14}O$: C, 81.44; H, 8.70. Found: C, 81.44; H, 8.49.

α-**Methyl-γ-*p*-tolylallyl Alcohol.**—A suspension of the isomeric α-*p*-tolyl-γ-methylallyl alcohol (29.8 g.) in acetone (150 ml.), water (135 ml.) and glacial acetic acid (15 ml.) was allowed to react at room temperature for 3 hours with stirring. The reaction mixture was then neutralized to phenolphthalein with aqueous potassium hydroxide and diluted with ether. The resulting organic phase was washed with water and dried (magnesium sulfate). Removal of the ether at atmospheric pressure through a small Vigreux column and vacuum distillation of the residue furnished a quantitative yield of α-methyl-γ-*p*-tolylallyl alcohol, b.p. 95–97° (0.5 mm.). Careful fractionation through a small glass-bead column furnished the analytical sample, b.p. 113° (1 mm.)

Anal. Calcd. for $C_{11}H_{14}O$: C, 81.44; H, 8.70. Found: C, 81.44; H, 8.83.

α-*p*-**Tolyl-γ-methylallyl** *p*-**Nitrobenzoate.**—To a magnetically stirred, tap-water-cooled solution of α-*p*-tolyl-γ-methylallyl alcohol (4.56 g., 28.2 mmoles) dissolved in 20 ml. of anhydrous pyridine was added *p*-nitrobenzoyl chloride (4.84 g., 26.0 mmoles) in small portions. Stirring was continued for 30 minutes and the reacton mixture was then poured into ice-water and allowed to stand until the initially-formed oil had partly solidified. The water solution was decanted and the residue was triturated with ether. The resulting solution was filtered from the insoluble matter and dried (magnesium sulfate). Ether was removed at water-pump pressure until a total volume of *ca.* 20 ml. remained. The addition of hexane (*ca.* 50 ml.) caused the precipitation of a small amount of insoluble matter which was filtered off. The filtrate was cooled in Dry Ice-acetone, furnishing a first crop of α-*p*-tolyl-γ-methylallyl *p*-nitrobenzoate (1.90 g.). The mother liquor furnished an additional 2.25 g. of ester; total yield 51.4%. The analytical sample was prepared by repeated crystallization from pentane, m.p. 44.5–46.5°.

Anal. Calcd. for $C_{18}H_{17}NO_4$: C, 69.44; H, 5.55. Found: C, 68.87; H, 5.21.

α-**Methyl-γ-*p*-tolylallyl** *p*-**Nitrobenzoate.**—The synthesis of this compound was patterned after that described for α-phenyl-γ-methylallyl *p*-nitrobenzoate; α-methyl-γ-*p*-tolylallyl alcohol (4.19 g., 25.8 mmoles) and *p*-nitrobenzoyl chloride (4.57 g., 24.6 mmoles) furnished 4.44 g. (58.0%) of the ester, m.p. 91–94°. Repeated crystallization from pentane furnished the analytical sample, m.p. 95–96.5°.

Anal. Calcd. for $C_{18}H_{17}NO_4$: C, 69.44; H, 5.55. Found: C, 69.40; H, 5.31.

Preparation of Rate Solutions.—The solvent mixtures used in the present work, 60, 70 and 80 volume per cent. aqueous dioxane, were prepared by the addition of the appropriate number of aliquots of distilled carbonate-free water to the appropriate number of aliquots of dioxane, purified by

TABLE VII

SOLVOLYSIS OF 2.16 × 10⁻² *M* α-METHYL-γ-PHENYLALLYL *p*-NITROBENZOATE IN 60 VOLUME PER CENT. AQUEOUS DIOXANE AT 65.0°

[KOH] = 2.49 × 10⁻² *M*; blank = 0.078 ml.; Theoretical infinity titer = 4.345 + 0.078 = 4.423

Time, sec.	KOH, ml.	k, sec.$^{-1}$ × 10$^{5 a}$	Time, sec.	KOH, ml.	k, sec.$^{-1}$ × 10$^{5 a}$
. . .	0.125	. .	27180	2.685	3.32
3300	.550	3.16	33480	2.983	3.26
6480	.940	3.25	39360	3.240	3.28
9600	1.265	3.20	72900	4.190	3.99[b]
13920	1.690	3.24	160800 (∞)	4.645	. .
17820	2.050	3.32	190140 (∞)	4.670	. .
21780	2.330	3.30		Av.	3.26 ± 0.04

[a] Calculated from theoretical infinity titer. [b] Excluded from average.

TABLE VIII

SOLVOLYSIS OF 1.35 × 10⁻² *M* α-PHENYL-γ-METHYLALLYL *p*-NITROBENZOATE IN 70 VOLUME PER CENT. AQUEOUS DIOXANE AT 50.0°

[KOH] = 2.105 × 10⁻² *M*; blank = 0.076 ml.; theoretical infinity titer = 3.212 + 0.076 = 3.288 ml.

Time, sec.	KOH, ml.	k, sec.$^{-1}$ × 10$^{4 a}$
. . .	0.408	. .
755	.653	2.90
1440	.856	3.09
2160	1.000	2.98
3080	1.177	3.12
4640	1.365	3.16
6470	1.492	3.16
9820	1.587	3.00
14820 (∞)	1.652	. .
	Av.	3.06 ± 0.08

% of theory (1.652 − 0.076)/3.212 = 49.1%

Time, sec.	KOH, ml.	k, sec.$^{-1}$ × 10$^{6 b}$
. . .	1.742	. .
91070	1.933	1.45
178340	2.071	1.34
366680	2.384	1.46
534800	2.632	1.60
814820	3.003	. .
1147820	3.408	. .
1477220	3.904	. .
	Av.	1.46 ± 0.07

[a] Rates calculated from experimental infinity titer. [b] Rates calculated from theoretical infinity titer.

the method described by Fieser.[29] A weighed sample of an ester was then dissolved to a given volume of solution (usually 100 ml.) in a volumetric flask with the appropriate solvent mixture.

For the kinetic runs carried out at 25.0° these volumetric flasks were then placed in a constant temperature bath and 5-ml. aliquots of the reacting mixture were removed directly at appropriate time intervals, quenched, and titrated.

Sealed ampoules were used for most of the kinetic runs at 50.0°, 65.0 and 75.0°. Portions of the reaction mixture prepared in the volumetric flask were introduced into glass ampoules, sealed under nitrogen, and immersed in a constant temperature bath. At appropriate time intervals an aliquot of the reaction mixture was removed, quenched by pipetting into 10 ml. of acetone, and titrated with dilute potassium hydroxide to the phenolphthalein end-point.

A typical kinetic run for the solvolysis of γ-phenyl-α-methylallyl *p*-nitrobenzoate is presented in Table VII.

(29) L. F. Fieser, "Experiments in Organic Chemistry," D. C. Heath and Co., Boston, Mass., 1941, p. 369.

Table VIII illustrates the kinetic behavior observed on solvolysis of α-phenyl-γ-methylallyl p-nitrobenzoate. A fast initial rate was observed (63 min. half-life) followed by a much slower reaction (131 hr. half-life). The rate constants for the initial fast reaction have been calculated from the experimental infinity titer. The rate constants for the slower reaction were calculated from the theoretical infinity titer.

LAFAYETTE, IND.

Methoxy-mercuration of Acrylic Esters

BY KANAI LAL MALLIK AND MIHIR NATH DAS

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Methoxy-mercuration of methyl acrylate has been studied kinetically over the temperature range 35–50°. Second-order kinetics has been observed for the over-all reaction, the energy of activation being about 9 kcal./mole. The reaction is slightly accelerated by acetic acid, and strongly retarded by sodium acetate, propionate and butyrate. Nitrogen bases also exert an equally strong retarding effect on the reaction. The reaction with ethyl and butyl acrylates was studied at 45° and found to exhibit exactly similar features. The results strongly favor an ionic mechanism for the addition, involving the formation of a reactive carbonium ion by interaction between the unsaturated compound and undissociated mercuric acetate.

Mercuric salts have long been known to form addition products with unsaturated compounds, the reaction being generally very fast in methanol. Extensive and systematic studies have been conducted on some oxy-mercuration reactions by Wright and co-workers,[1] especially on methoxy-mercuration of cyclohexene. The rapid and quantitative addition of mercuric acetate to several unsaturated compounds in methanol has been utilized to a limited extent for the estimation of these compounds.[2] Vinyl and allyl esters readily react with mercuric acetate in methanol, but with acrylic and methacrylic esters the addition is much slower in the absence of catalysts. It seemed of interest to study this reaction with different types of substituted ethylenes in order to determine the effect of substituent groups which is expected to be of great help in elucidating the mechanism of the reaction. The present paper reports the results of kinetic studies on the addition of mercuric acetate to methyl, ethyl and butyl acrylates in methanol.

Experimental

Materials.—The acrylic esters were purified by the following procedure. The samples were repeatedly washed with caustic soda till free from inhibitors, and then were washed with distilled water. After drying with calcium chloride, the samples were fractionally distilled under reduced pressure in all-glass apparatus, the middle fraction being collected for the work. Only freshly distilled samples were used for the kinetic studies, the absence of peroxides being tested for with potassium iodide.

Mercuric acetate was prepared by dissolving pure mercuric oxide in reagent grade glacial acetic acid. The solution was carefully evaporated almost to dryness, and allowed to cool. The residue was kept in a vacuum desiccator for several days to remove the last traces of water and acetic acid. The sample of mercuric acetate so obtained was analyzed for purity by direct titration in propylene glycol-chloroform with standard hydrochloric acid in butanol, using thymol blue as indicator.[3] The purity was also checked by direct titration with standard alkali in aqueous acetone with phenolphthalein as indicator and further checked by titrating with standard nitric acid the alkali liberated by addition of potassium iodide.[4] The agreement between the alkali and acid titers indicated absence of free acid and also of basic acetate. The titration results indicated a purity of about 99.8%.

Extra pure methanol (Merck) was used as the reaction medium without any further treatment; $0.01-0.02N$ hydrochloric acid in butanol was used for the titration, being standardized against mercuric oxide after conversion to acetate.[2c]

Sodium acetate, propionate and butyrate solutions were prepared by dissolving reagent grade sodium carbonate in the respective acids, the excess acid being removed by evaporation. The sodium salts so obtained were dissolved in methanol and the solutions were analyzed by non-aqueous titration with standard hydrochloric acid in butanol, using thymol blue as indicator.

Triethanolamine and pyridine solutions were prepared by dissolving analytical grade reagent in methanol and standardized by titration with hydrochloric acid in butanol.

Solutions of acrylic esters and of mercuric acetate were prepared by weighing out the reactant into a measured volume of methanol, so as to give the desired concentrations.

Kinetic Measurements.—Reaction rates were measured at 35, 40, 45 and 50°. A larger range of temperature was precluded by experimental difficulties. The thermostat used for the work maintained a temperature with a maximum variation of ±0.05°. Most of the work was confined to 45°, and at this temperature, the initial concentration of mercuric acetate was in the range of 0.01–0.04 g. mole/liter, and for methyl acrylate the concentration was in the range of 0.01–0.22 g. mole/liter. The solutions of the reactants of desired concentrations were separately prepared in Jena bottles with glass stoppers and kept in the thermostat to attain the bath temperature. Equal volumes (usually 20 ml.) of each were then mixed together in a Jena bottle and the reaction was followed by analyzing 5-ml. portions of the mixture by titration with hydrochloric acid in butanol, using thymol blue as indicator.

Analytical.—The analytical method used is essentially based on the fact that one mole of mercuric acetate when titrated with hydrochloric acid in glycolic or alcoholic media consumes two equivalents of acid, whereas the mercurated product formed by addition takes up only one equivalent of acid per mole.[2c,2d] If v_0 ml. is the initial acid titer, and v ml. the titer at time t for 1 ml. of the reaction mixture and if N be the normality of the hydrochloric acid, the concentration of mercuric acetate at any stage is given by $(v - \frac{1}{2}v_0)N$ g. moles/liter.

(1) (a) T. Connor and G. F. Wright, THIS JOURNAL, **68**, 256 (1946); (b) A. G. Brook, A. Rodgman and G. F. Wright, J. Org. Chem., **17**, 988 (1952); (c) A. Brook and G. F. Wright, Can. J. Res., **28B**, 623 (1950); **29**, 308 (1951); (d) G. F. Wright, Chem. in Canada, **2**, 149 (1950); (e) W. R. R. Park and G. F. Wright, Can. J. Chem., **12**, 1088 (1957); (f) A. Rodgman and G. F. Wright, J. Org. Chem., **18**, 1617 (1953); (g) A. Rodgman, D. A. Shearer and G. F. Wright, Can. J. Chem., **36**, 1377 (1957).

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(3) M. N. Das, J. Indian Chem. Soc., **31**, 39 (1954).

(4) M. N. Das, Anal. Chem., **25**, 1406 (1953).