[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

Stereochemistry of Allylic Rearrangements. IX. The Solvolysis of *trans*-α,γ-Dimethylallyl Acid Phthalate in Aqueous Acetone[1]

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The polarimetric (k_α) and titrimetric (k_t) rate constants for the solvolysis of *trans*-α,γ-dimethylallyl acid phthalate (I) in aqueous acetone have been determined. At concentrations up to 0.1 M both k_α and k_t are steady during the reaction and $k_\alpha > k_t$ under all conditions at which the two were compared. The greater rate of loss of optical activity than of formation of solvolysis products is due to partial racemization of the reactant, by an isomeric intramolecular (SNi′) allylic rearrangement, prior to solvolysis. The data are consistent with a picture involving the reversible formation of a symmetrical ion-pair intermediate which is irreversibly converted to solvolysis products.

In earlier papers in this series[3,4] it was pointed out that an intermediate (an "internal ion-pair" intermediate according to Winstein's classification[5]) is involved in the ionization–dissociation step of carbonium-ion reactions in allylic systems. This intermediate can return to the original allylic compound or its allylic isomer by internal return—presumably this represents the mechanism of the SNi′[6] rearrangement of allylic compounds[3]—or dissociate to the allylic cation and the accompanying anion. In non-reactive solvents, *e.g.*, non-hydroxylic solvents, the dissociated carbonium ion and anion recombine; however, in hydroxylic solvents this recombination is completely diverted by solvolysis.[3,4] Thus, in hydroxylic solvents the SNi′ rearrangement is cleanly isolated from an intermolecular isomeric rearrangement.

Optically active symmetrical allylic systems, *i.e.*, systems with similar α- and γ-alkyl substituents, are especially well suited for studying the SNi′ rearrangement (internal return) which accompanies solvolysis. In such systems the SNi′ rearrangement results only in the interconversion of enantiomers and thus does not disturb the first-order rate of product formation but results in a larger rate of loss of optical activity (polarimetric rate) than of product formation (titrimetric rate). The first-order rate constant for the conversion of one enantiomer to the other by the SNi′ rearrangement is $(1/2)(k_\alpha - k_t)$ and thus can be determined readily from the polarimetric (k_α) and titrimetric (k_t) rate constants.[3,4]

As described in earlier papers in this series, internal return is involved in the solvolysis of the isomeric 5-methyl-2-cyclohexenyl chlorides in ethanol and acetic acid[4] and the corresponding acid phthalates[3a] and *p*-nitrobenzoates[3b] in aqueous acetone. In the present work we have examined the solvolysis of α,γ-dimethylallyl acid phthalate in aqueous acetone to determine the importance of internal return in this acyclic symmetrical allylic system relative to that in the 5-methyl-2-cyclohexenyl system.

Results

The α,γ-dimethylallyl acid phthalate used in the present work was apparently the pure *trans* isomer. That the material was homogeneous was indicated by a rather sharp reproducible melting point (89–90.5°) which was unchanged by recrystallization. The infrared spectrum of α,γ-dimethylallyl alcohol obtained by reduction of the pure acid phthalate with lithium aluminum hydride had a strong absorption band at 10.4 μ and no bands above 14 μ, which is characteristic of *trans*-1,2-disubstituted ethylenes.[7] The neutral equivalents of the samples of racemic and optically active acid phthalate used in the kinetic experiments were within 0.3% of the theoretical value.

The first-order polarimetric (k_α) and titrimetric (k_t) rate constants for the solvolysis of *trans*-α,γ-dimethylallyl acid phthalate (I) in 70, 80 and 90% aqueous acetone are given in Table I. The data are arranged so that the polarimetric rate constants are for the same conditions as the preceding titrimetric rate constants.

The polarimetric constants were determined from the rate of loss of optical activity of solutions of (+)-I. In all cases solvolysis resulted in complete loss of optical activity, and the polarimetric constants were steady over the range that the reaction was followed (88 to 94% completion). The observed first-order rate constants were reproducible and most of the values for $k\alpha$ given in Table I are average values of two independent kinetic experiments. A typical kinetic experiment is included in the Experimental section.

The titrimetric constants (k_t) were determined from the rate of increase in acidity of solutions of racemic I. In all cases the observed initial titer, *i.e.*, the titer of freshly prepared solutions prior to heating, agreed well with the calculated value. The observed infinity titers, however, were found to be approximately 2% less than the calculated values (twice the initial titer). Evidently this discrepancy is due to conversion of about 1% of the phthalic acid to phthalic anhydride under the conditions of the solvolysis experiments. In a control experiment the titer of a 0.05 M solution of phthalic acid in 90% acetone at 100° was determined periodically. The titer of this solution decreased slowly and after a period of time, corresponding to infinity time for the solvolysis, the percentage difference between the initial and final titers was the same as between the observed and calculated infinity titers.

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[3] (a) H. L. Goering and E. F. Silversmith, THIS JOURNAL, **77**, 1129 (1955); (b) **77**, 6249 (1955).

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

[5] S. Winstein, E. Clippinger, A. Fainberg, R. Heck and G. Robinson, *ibid.*, **78**, 328 (1956).

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

[7] R. S. Rasmussen, R. R. Brattain and P. S. Zucco, *J. Chem. Phys.*, **15**, 135 (1947).

TABLE I

POLARIMETRIC AND TITRIMETRIC RATE CONSTANTS FOR THE SOLVOLYSIS OF *trans*-α,γ-DIMETHYLALLYL ACID PHTHALATE IN AQUEOUS ACETONE

Acid phthalate, 10^2 *M*	Method[b]	k,[c,d] 10^3 hr.$^{-1}$	k_α/k_t[e]
	90% (vol.[a]) acetone, 99.81°		
7.50	T	110 ± 6[f]	
10.0	T	117 ± 4	2.52 ± 0.16
10.0	P	295 ± 8[f]	
5.00	T	108 ± 4	2.69 ± 0.14
5.00	P	291 ± 4	
2.50	T	102 ± 2	2.83 ± 0.17
2.50	P	289 ± 11[f]	
5.00[g]	T	11.9 ± 0.6	2.50 ± 0.14
5.00[g]	P	29.8 ± 0.1	
5.00[h]	T	3.97 ± 0.16	2.43 ± 0.13
5.00[h]	P	9.66 ± 0.11	
	80% (vol.[a]) acetone, 79.58°		
5.00	T	52.9 ± 0.9	1.89 ± 0.05
5.00	P	100 ± 1	
	70% (vol.[a]) acetone, 79.58°		
5.00	T	142 ± 2	1.68 ± 0.03
5.00	P	238 ± 2	

[a] Based on volumes of pure components at 25° before mixing. [b] T = titrimetric and P = polarimetric. [c] These are values for k_α (polarimetric determinations) and k_t (titrimetric determinations). [d] These values are the average (and mean deviation) of two or more independent kinetic experiments, except as noted. [e] Indicated uncertainty determined from limiting values for k_α and k_t. [f] These values are the average (and mean deviation) of from seven to thirteen determinations within a kinetic experiment. [g] Temperature, 79.58°. [h] Temperature, 70.12°.

Because the conversion of phthalic acid to phthalic anhydride is slow, the calculated rather than the observed infinity titers were used to calculate the first-order titrimetric constants. The constants obtained in this way did not show any significant trends in reactions followed to 75–85% completion. With one exception the values for k_t in Table I are average values of two or more independent kinetic experiments. A typical kinetic experiment is included in the Experimental section.

In order to establish that the solvolysis of I in aqueous acetone involves alkyl–oxygen cleavage, the rate of solvolysis of the saturated analog, 2-pentyl acid phthalate, in 90% acetone at 100° was determined. The rate constant for this compound under these conditions is $7.4 \pm 0.4 \times 10^{-4}$ hr.$^{-1}$ or 1/45 of that for I. Since there is no apparent reason why an allylic ester should undergo acyl–oxygen cleavage more readily than the saturated analog, the observed factor of 145 appears to be compelling evidence that the solvolysis of I involves exclusive alkyl–oxygen cleavage.

As shown in the final column of Table I the polarimetric rate exceeds the titrimetric rate under all conditions where the two were compared. The polarimetric rate constants increase slightly as the initial concentration of acid phthalate is increased, and the titrimetric constants show a somewhat larger increase with increase in concentration. This increase in rate presumably is due to a slight increase in the ionizing power of the medium as the acid phthalate concentration is increased. Both $k\alpha$ and k_t show marked increases as the ionizing power of the solvent is increased; *cf.* rates in 70% and 90% aqueous acetone. The titrimetric rate is slightly more sensitive than the polarimetric rate to increase in ionizing power of the solvent. Thus $k\alpha/k_t$ decreases as the ionizing power increases. This behavior is similar to that observed previously for the solvolysis of *cis*-5-methyl-2-cyclohexenyl acid phthalate in aqueous acetone.[3a]

Excellent linear plots are obtained when log $k\alpha$ or log k_t is plotted against the Y values[8] of the solvents. The slopes of these plots, m,[8] are 0.542 for k_t and 0.454 for k_α. These values are similar to those calculated[8] for the solvolysis of *cis*-5-methyl-2-cyclohexenyl acid phthalate in aqueous acetone[3a] (m = 0.472 for k_t and 0.429 for $k\alpha$). Thus both k_α and k_t show about the same sensitivity to changes in the ionizing power of the solvent in the two systems.

The activation parameters for loss of optical activity ($k\alpha$), solvolysis (k_t) and racemization or S_Ni′ rearrangement ($k_\alpha - k_t$) in 90% acetone are given in Table II. These data were determined from least-square plots of log k *vs.* $1/T$.

TABLE II

ACTIVATION PARAMETERS FOR THE SOLVOLYSIS OF 0.05 *M* α,γ-DIMETHYLALLYL ACID PHTHALATE IN "90%" AQUEOUS ACETONE[a]

	E_a[b] kcal./mole	log *A*	$\Delta H^\ddagger$,[b,c] kcal./mole	$\Delta S^\ddagger$,[b,c] e.u.
$k\alpha$	29.1 ± 0.2	12.974	28.4 ± 0.2	−1.61 ± 0.51
k_t	28.3 ± 0.6	12.077	27.6 ± 0.6	−5.71 ± 1.79
$(k\alpha - k_t)$	29.8 ± 0.8	13.156	29.0 ± 0.8	−0.77 ± 2.0

[a] These values were calculated from the rate constants at 70, 80 and 100° given in Table I. [b] The indicated uncertainties were calculated from the limiting values of the rate constants at 70 and 100°. [c] These values were calculated for 100°.

The present system is a little more reactive than the 5-methyl-2-cyclohexenyl system. In 90% aqueous acetone at 100°, $k\alpha$, k_t and $k\alpha - k_t$ are larger for I than for the isomeric 5-methyl-2-cyclohexenyl acid phthalates by factors of about 5, 3 and 7, respectively.

Discussion

The solvolysis of α,γ-dimethylallyl acid phthalate (I) is similar to that of the isomeric 5-methyl-2-cyclohexenyl acid phthalates[3a] in that $k_\alpha > k_t$ in each case. It appears that the present data are consistent with the mechanism suggested previously[3,4] for the solvolysis and rearrangement of allylic compounds. According to this picture, which is illustrated below for the present system—the indicated rotations for the enantiomers of I have been chosen arbitrarily—an "internal ion-pair"[5] intermediate (II) is common to solvolysis and intramolecular (S_Ni′) rearrangement. The first-order rate constant for loss of optical activity is k_α. That for formation of phthalic acid, *i.e.*, the titrimetric rate constant (k_t) is $k_\alpha\, k_2/(2k_1 + k_2)$, and that for the conversion of one enantiomer to the other is $1/2\ (k_\alpha - k_t)$.

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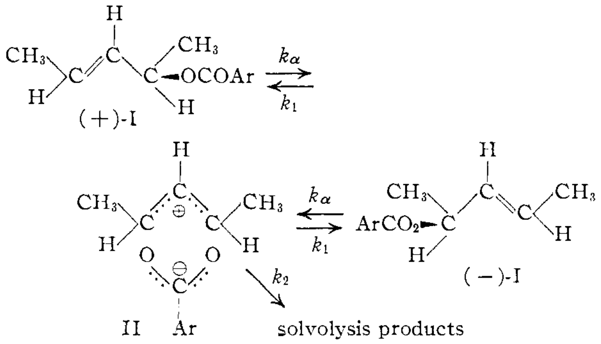
(8) A. H. Fainberg and S. Winstein, THIS JOURNAL, **78**, 2770 (1956).



In the present system the intramolecular rearrangement results in the interconversion of enantiomers providing that the planar allylic moiety in II has the indicated configuration. The steady polarimetric and titrimetric rates suggest that I reacts *via* the conformation corresponding to the indicated configuration for II, *i.e.*, the configuration with the α- and γ-methyl groups *cis*. If II had the other configuration (*i.e.*, with the methyl groups *trans*) the SNi′ rearrangement would result in the conversion of optically active *trans*-acid phthalate to optically active *cis*-acid phthalate. This would likely disturb the polarimetric and possibly also the titrimetric rate. Scale models also indicate that the configuration indicated for the α,γ-dimethylallylcarbonium ion in II is the more stable one.[9]

It has been shown recently that in the intramolecular rearrangement of α-phenyl-γ-methylallyl[10a] and α-phenylallyl *p*-nitrobenzoate[10b] the carbonyl oxygen atom in the reactant becomes the alkyl oxygen atom in the product. This suggests that there is some covalent bonding between the allylic carbon atoms and the oxygen atoms in the symmetrical intermediate II. However, from the way in which k_α responds to changes in the ionizing power of the solvent, it appears that there must be considerable charge separation in the intermediate.

Experimental

Materials.—*trans*-α,γ-Dimethylallyl alcohol, b.p. 116–121°, $n^{20}\text{D}$ 1.4280 (lit.[11] b.p. 116–121°, $n^{20}\text{D}$ 1.4280) was prepared according to the previously described method.[11,12] The alcohol was converted[12] to *dl-trans*-α,γ-dimethylallyl acid phthalate, m.p. 89–90.5° (lit.[12] 90–90.5°); neut. equiv. found 233.9, calcd. 234.2. The acid phthalate was resolved according to the method of Kenyon, *et al.*[12] The (+)-*trans*-α,γ-dimethylallyl acid phthalate obtained in this way had a melting point of 78–83.6° and $[\alpha]^{25}\text{D}$ 35.4° (l = 4, c 1.1, ethanol) (lit.[12] m.p. 82–84°, $[\alpha]\text{D}$ 38.3° for optically pure material).

Reduction of α,γ-Dimethylallyl Acid Phthalate with Lithium Aluminum Hydride.—The ester was reduced according to the method of Doering and Zeiss.[13] α,γ-Dimethylallyl alcohol, b.p. 116–121°, was isolated in 66% yield. The infrared spectrum of this material was found to have a strong band at 10.4 μ.

Kinetic Experiments.—The kinetic runs were carried out as described previously.[3a] Typical kinetic experiments are summarized in Tables III and IV.

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TABLE III

TITRIMETRIC RATE OF SOLVOLYSIS OF 0.05 *M* *trans*-α,γ-DIMETHYLALLYL ACID PHTHALATE IN 90% AQUEOUS ACETONE AT 99.81°

t, hr.	NaOH, ml.	$10^3 k_t$,[a] hr.$^{-1}$
init.	4.745	..
0.00	4.910	..
0.75	5.240	100
1.50	5.580	105
3.00	6.205	111
4.50	6.690	109
6.00	7.150	112
7.50	7.530	113
9.00	7.800	111
10.50	8.060	111
12.10	8.310	112
13.50	8.470	111
15.00	8.600	109
Obs. ∞	9.300	..
Theor. ∞	9.490	..
	Av.	109 ± 3

[a] Calculated from theoretical infinity titer.

TABLE IV

POLARIMETRIC RATE OF SOLVOLYSIS OF 0.05 *M* (+)-*trans*-α,γ-DIMETHYLALLYL ACID PHTHALATE IN 90% AQUEOUS ACETONE AT 99.81°

t, hr.	Obs.	$10^3 k_\alpha$, hr.$^{-1}$
0.000	+1.955	..
0.500	+1.723	303
1.500	+1.363	296
3.083	+0.955	302
4.500	+ .751	291
6.000	+ .603	285
7.500	+ .497	287
∞	+ .308	..
Solvent	+ .305	
	Av.	294 ± 6

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[9] The stereochemical relationship between the reactant and product for an SNi′ process in the *trans*-α,γ-dimethylallyl system has been discussed by W. G. Young, *et al.*, THIS JOURNAL, **77**, 4182 (1955).

[10] (a) W. E. Doering, private communication; (b) E. A. Braude and D. W. Turner, *Chemistry & Industry*, 1223 (1955).

[11] E. R. Alexander and R. W. Kluiber, THIS JOURNAL, **73**, 4304 (1951).

[12] H. W. J. Hill, J. Kenyon and H. Phillips, *J. Chem. Soc.*, 576 (1936).

[13] W. E. Doering and H. H. Zeiss, THIS JOURNAL, **72**, 147 (1950)