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Stereochemistry of Allylic Rearrangements. III. The Solvolysis of *cis*- and *trans*-5-Methyl-2-cyclohexenyl Acid Phthalate in Aqueous Acetone[1]

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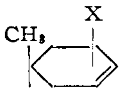
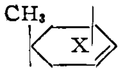
The polarimetric and titrimetric rates of solvolysis of *cis*-(Ia) and *trans*-5-methyl-2-cyclohexenyl acid phthalate (IIa) in aqueous acetone have been examined. The polarimetric rate constant (k_α) and titrimetric constant (k_t) are steady during the reaction and $k_\alpha > k_t$ under all conditions at which the two were compared. The greater polarimetric rate is due to partial racemization of the reactant, by an intramolecular process, prior to solvolysis. The kinetic behavior is consistent with the previous interpretation for internal return involving the formation of an ion pair intermediate which gives solvolysis product or returns to the racemic reactant. It is suggested that intramolecular (S$_N$i′) rearrangements of allylic acid phthalates which have been described in the literature are similar to the racemization involved in the present work and involve internal return from ion pair intermediates.

In the previous paper in this series[3] the kinetics and stereochemistry of the isomeric anionotropic rearrangement of *cis*-(Ia) and *trans*-5-methyl-2-cyclohexenyl acid phthalate (IIa) in acetonitrile were described. Evidence was presented which indicates that the isomeric rearrangement involves ionization (alkyl–oxygen cleavage) to the symmetrical hybrid 5-methyl-2-cyclohexenylcarbonium ion and hydrogen phthalate ion followed by recombination to form the rearranged ester. The observation that racemization is faster than geometric isomerization for both optically active Ia and IIa was attributed to internal return[4] which was interpreted in terms of ion-pair intermediates.

In order to obtain more information concerning the importance and nature of ion-pair intermediates in the ionization of the isomeric 5-methyl-2-cyclohexenyl acid phthalates we have investigated the solvolysis of these compounds in aqueous acetone solutions. In solvents of this type the isomeric rearrangement is completely diverted by the intervention of solvent and the previously developed[4] method of comparing polarimetric and titrimetric solvolysis constants can be used to determine the extent of internal return.



I



II

a, X = $O_2CC_6H_4CO_2H$
b, X = OH

The polarimetric (k_α) and titrimetric (k_t) first-order rate constants for the solvolysis of Ia in 50, 60, 80 and 90% aqueous acetone and for IIa in 80% aqueous acetone are shown in Table I. The titrimetric constants (calculated from the integrated expression for a first-order reaction) were determined at initial concentrations of 0.20 and 0.05 *M* from the rate of increase in acidity and were steady at both concentrations over the ranges that the reactions were followed. Each value of k_t in Table I is the average value (and mean deviation) of 6 or 7 determinations during the reaction.

The polarimetric constants (k_α) were determined from the rate of loss of optical activity of solutions of (−)-Ia and (+)-IIa. In all cases the solvolysis of active Ia and IIa resulted in the complete loss of optical activity. At concentrations of 0.05 *M* the constants determined from the relationship $\ln(\alpha_0/\alpha_t) = k_\alpha t$, where α_0 and α_t are observed rotations at zero time and time *t*, respectively, did not show any trends during the reaction. Typical experiments illustrating the first-order behavior of the polarimetric and titrimetric rates are shown in Fig. 1. The polarimetric solvolysis constants for Ia at concentrations of 0.20 *M* showed upward trends during the reaction and k_α for these experiments are given as ranges in Table I. In order to determine the cause of the increasing polarimetric constants the effect of phthalic acid (a product of the reaction) on the rate was investigated. The polarimetric constant for Ia at a concentration of 0.20 *M* in 80% acetone containing 0.20 *M* phthalic acid did not show any trends during the solvolysis and as shown by Table I was somewhat greater than the final value reached without added phthalic acid. It thus appears that phthalic acid, either by increasing the ionizing power of the medium or by acid catalysis, causes the upward trend in the polarimetric rate. The titrimetric constant, which is steady at concentrations of 0.20 *M*, also is increased (from 12.3 to 18.2 in 80% acetone) by 0.20 *M* phthalic acid. The upward trend of the polarimetric constants is puzzling in view of the fact that

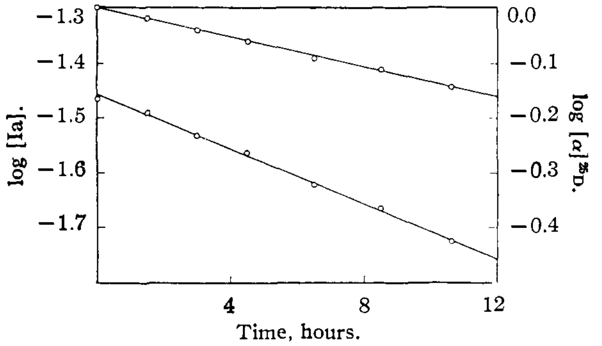


Fig. 1.—First-order rate of formation of phthalic acid (upper line, left-hand scale) and loss of optical activity (lower line, right-hand scale) during the solvolysis of (−)-*cis*-5-methyl-2-cyclohexenyl acid phthalate (Ia) in 90% aqueous acetone at 100°.

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[1] This work was supported in part by the Office of Ordnance Research and in part by the Research Commitee of the Graduate School with funds given by the Wisconsin Alumni Research Foundation.

[2] Shell Fellow 1954; du Pont summer research assistant 1953.

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

[4] S. Winstein and R. Heck, *ibid.*, **74**, 5584 (1952), and previous papers in this series.

the titrimetric constants remain steady under the same conditions.

TABLE I

POLARIMETRIC AND TITRIMETRIC RATE CONSTANTS FOR THE SOLVOLYSIS OF *cis*- AND *trans*-5-METHYL-2-CYCLOHEXENYL ACID PHTHALATE IN AQUEOUS ACETONE AT 99.95 ± 0.05°

Cmpd.	Solvent vol. % acetone[a]	(Acid phthalate) 10^2 M	% of reacn. followed	Method	k_α (10^2 hr.$^{-1}$)	k_t (10^2 hr.$^{-1}$)
Ia	90	5.00	45	Pol.	5.37 ± 0.22	
Ia	90	5.00	28	Tit.		3.08 ±0.07
IIa	90	5.00	61	Pol.	6.64 ± 0.45	
IIa	90	5.00	40	Tit.		3.92 ± .13
Ia	90	20.00	55	Pol.	5.7 to 7.0[b]	
Ia	90	20.00	35	Tit.		3.83 ± .04
Ia	80	5.00	81	Pol.	16.5 ± 1.0	
Ia	80	5.00	69	Tit.		11.1 ± .1
Ia	80	20.00	66	Pol.	15 to 18[b]	
Ia	80	20.00	53	Tit.		12.3 ± .4
Ia	80[c]	20.00	72	Pol.	24.0 ± 0.5	
Ia	80[c]	20.00	68	Tit.		18.2 ± .9
Ia	60	5.00	89	Pol.	70.9 ± 3.3	
Ia	60	5.00	81	Tit.		54.8 ± 1.2
Ia	60	20.00	87	Pol.	63 to 81[b]	
Ia	60	20.00	83	Tit.		59.4 ± 1.3
Ia	50	5.00	83	Pol.	134 ± 8	
Ia	50	5.00	75	Tit.		106 ± 2
Ia	50	20.00	95	Pol.	161 to 201[b]	
Ia	50	20.00	86	Tit.		105 ± 3

[a] Solvent compositions are based on the volumes of the pure liquids before mixing. [b] This is the range of the constant which drifted upward during the reaction. [c] The solvent contained 0.2 M phthalic acid.

As shown in Table I the polarimetric rate exceeds the titrimetric rate under all conditions where the two were compared. The effect of varying solvent composition on k_t, k_α and the ratio k_α/k_t is summarized in Table II. These data show that k_α and k_t are quite sensitive to solvent composition and that the ratio k_α/k_t decreases as ionizing power of the solvent increases. The effect of varying temperature on k_α, k_t and k_α/k_t in 60% acetone and the activation parameters are shown in Table III.

TABLE II

RATE CONSTANTS FOR THE SOLVOLYSIS OF 0.05 M *cis*-5-METHYL-2-CYCLOHEXENYL ACID PHTHALATE IN AQUEOUS ACETONE AT 99.95 ± 0.05°

Acetone, %	k_α, hr.$^{-1}$	k_t, hr.$^{-1}$	k_α/k_t
90	0.0537	0.0308	1.74
80	.165	.111	1.49
60	.709	.548	1.29
50	1.34	1.06	1.26

TABLE III

RATE CONSTANTS AND ACTIVATION PARAMETERS FOR THE SOLVOLYSIS OF *cis*-5-METHYL-2-CYCLOHEXENYL ACID PHTHALATE IN 60% AQUEOUS ACETONE

	80°	100°	$\Delta H^{\ddagger}$, kcal.	$\Delta S^{\ddagger}$, e.u.
k_α (10^2 hr.$^{-1}$)	8.15	70.9	27.6	−0.5
k_t (10^2 hr.$^{-1}$)	6.30	54.8	27.6	−0.6
$(k_\alpha - k_t)$(10^2 hr.$^{-1}$)	1.85	16.1	27.6	−1.2
k_α/k_t	1.29	1.29		

The solvolysis of Ia and IIa results in the formation of a mixture of *cis*-(Ib) and *trans*-5-methyl-2-cyclohexenol (IIb) together with phthalic acid. Unfortunately the 5-methyl-2-cyclohexenols isomerize under the conditions of the solvolysis and consequently the composition of the isolated mixture of methylcyclohexenols is not informative from a mechanistic viewpoint. *cis*-5-Methyl-2-cyclohexenol (Ib) is isomerized in 5.5 hours at 100° in 60% acetone (4.4 half-lives for the solvolysis of Ia) in the presence of 0.05 M phthalic or chloroacetic acid to a mixture that has the same composition (55% Ib and 45% IIb) as those isolated from the solvolysis of each of the isomeric acid phthalates in 60% acetone.

Because of the acid-catalyzed (Ib does not isomerize in aqueous acetone at 100° in the absence of acid) isomerization of the solvolysis products it is not possible to distinguish between acyl–oxygen and alkyl–oxygen cleavage by the usual method of comparing the configurations of the acid phthalates and the resulting alcohols.[5] There is, however, other evidence which indicates that alkyl–oxygen cleavage is involved. We have found that the ethanolysis of Ia involves exclusive alkyl–oxygen cleavage (ethyl 5-methyl-2-cyclohexenyl ether is the exclusive allylic product) and it seems most likely that the same type of cleavage is involved in the hydrolysis in aqueous acetone.

The effect of change in solvent composition on the solvolysis constants is consistent with an S$_N$1[6] mechanism (alkyl–oxygen cleavage). As shown in Fig. 2, when log k_t and log k_α are plotted against $(D - 1)/(2D + 1)$—where D is the dielectric constant of the solvent[7]—straight lines are obtained as predicted by the relationship derived[8] from the calculations of Kirkwood.[9] The k_a and k_t plots are nearly parallel with a slope of 2.5 which is similar to the value of 2.9 observed by Kochi and Hammond[10] for the solvolysis of benzyl and *p*-methylbenzyl *p*-toluenesulfonates in aqueous acetone. This suggests that the acid phthalates and *p*-toluenesulfonates undergo the same type of ionization in the rate-determining step.

Unsolvolyzed acid phthalate was recovered from partly solvolyzed solutions of Ia and IIa and examined to determine if geometric isomerization occurs during solvolysis. The first-order behavior of the titrimetric process indicates that geometric isomerization does not occur; however, the difference between k_t for Ia and IIa is small (Table I) and considerable isomerization would be required to cause a detectable kinetic disturbance. The acid phthalate recovered from a 0.20 M solution of *dl*-Ia in 80% acetone after 5.8 hours at 100° was shown to be pure Ia by infrared analysis. By using synthetic mixtures it was found that 1% of the geometric isomer can be detected in Ia or

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[5] (a) J. Kenyon, S. M. Partridge and H. Phillips, *J. Chem. Soc.*, 207 (1937); (b) M. P. Balfe, H. W. J. Hills, J. Kenyon, H. Phillips and B. C. Platt, *ibid.*, 556 (1942).

[6] C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, pp. 345 ff.

[7] The dielectric constants of the solutions were calculated from the data of H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publishing Corp., New York, N. Y., 1943, p. 118.

[8] S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941, pp. 419 ff.

[9] J. G. Kirkwood, *J. Chem. Phys.*, **2**, 351 (1934).

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

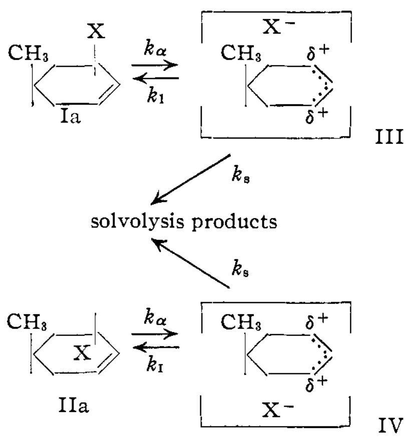
IIa by this analytical procedure. From the values of k_α and k_t it can be determined that at the time of isolation optically active acid phthalate would be racemized to the extent of 28%. In other words, 14% of the isolated acid phthalate was converted to its enantiomorph without simultaneous geometric isomerization. When the isolation experiment was repeated with the *trans*-acid phthalate IIa using the conditions described above for the *cis* isomer, the recovered acid phthalate was found to be pure IIa. From these experiments it is clear that geometric isomerization does not occur during the solvolysis of Ia and IIa and that the loss of activity associated with solvolysis is due to the simultaneous formation of solvolysis products and racemic reactant. The specific first-order rate constant for racemization is $(k_\alpha - k_t)$ and the effects of varying solvent composition and temperature on this constant are included in Table III and Fig. 2.

The available information indicates that the racemization, measured by $(k_\alpha - k_t)$, which occurs during the solvolysis of Ia and IIa, involves internal return as in the case of the solvolysis of *exo*-norbornyl *p*-bromobenzenesulfonate in acetic acid[11] and 3-phenyl-2-butyl-*p*-toluenesulfonate in ethanol, acetic acid and aqueous acetone.[12] The previous interpretation[4,12b] of internal return, which appears to be consistent with the present data, has been applied to the 5-methyl-2-cyclohexenyl system in chart I. According to this scheme, the solvolysis of Ia or IIa ($X = HO_2CC_6H_4CO_2$–), involves the formation of the corresponding ion pair III or IV, which either is converted to solvolysis products or returns to racemic reactant. Presumably the conversion of the ion pair to solvolysis products involves dissociation of the ion pair followed by the reaction of water with the 5-methyl-2-cyclohexenyl-carbonium ion. However, no information concerning this step in the solvolysis was obtained because of the instability of the products under the conditions of the solvolysis. The observed polarimetric specific rate constant (k_α) corresponds to the rate of formation of the ion pair which is necessarily optically inactive because of its symmetry. The titrimetric specific rate constant (k_t) and the rate constant for racemization $(k_\alpha - k_t)$ are related to the rate constants in Chart I as shown by equations 1 and 2.

$$k_t = k_\alpha k_s/(k_1 + k_s) \quad (1)$$

$$(k_\alpha - k_t) = k_\alpha k_1/(k_1 + k_s) \quad (2)$$

CHART I



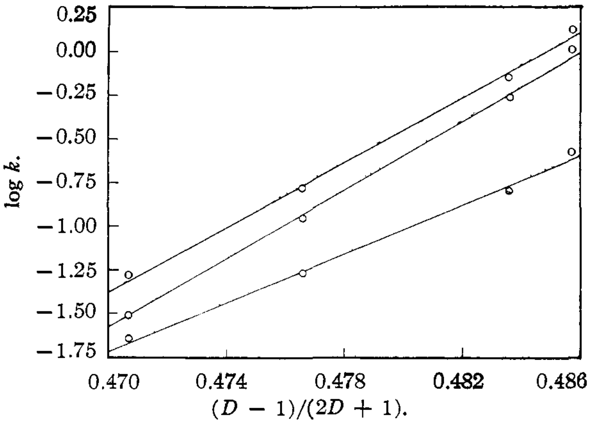


Fig. 2.—The effect of varying dielectric constant on the polarimetric k_α, titrimetric k_t and racemization $(k_\alpha - k_t)$ specific rate constants for the solvolysis of *cis*-5-methyl-2-cyclohexenyl acid phthalate (Ia) in aqueous acetone at 100°: upper line, k_α; middle line, k_t; lower line $(k_\alpha - k_t)$.

If this interpretation is correct the racemization without simultaneous geometric isomerization demonstrates that different ion pairs result from the isomeric acid phthalate and that each, by internal return, is converted exclusively to that isomeric acid phthalate from which it was formed. Thus in the present system it is possible to distinguish between internal and external return[13] (recombination of the dissociated 5-methyl-2-cyclohexenyl cation with hydrogen phthalate ion), because the latter would necessarily result in the isomerization of at least one and probably both of the isomeric acid phthalates.

The lack of isomerization shows that the process responsible for the discrepancy between k_α and k_t is an intramolecular process and does not involve external hydrogen phthalate ion. This is indicated also by the kinetic behavior. It has been pointed out previously[12a] that the process responsible for a larger polarimetric than titrimetric rate cannot involve the external anion formed in the solvolysis providing both k_α and k_t are steady throughout the solvolysis.

Other mechanisms besides the one shown in chart I can accommodate the known facts. For example, it is possible that the simultaneous processes, racemization and solvolysis, are completely independent and do not involve a common intermediate. The evidence indicates, however, that a common intermediate (an ion pair according to Chart I) is indeed involved in the two processes. This is indicated by the temperature independence of the ratio k_α/k_t (Table III) and the small effect of varying solvent on this ratio (Table II). In order to interpret the present data in terms of independent mechanisms for racemization $(k_\alpha - k_t)$ and solvolysis (k_t) the unlikely coincidence is

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[11] S. Winstein and D. Trifan, THIS JOURNAL, **74**, 1154 (1952).

[12] (a) S. Winstein and K. C. Schreiber, *ibid.*, **74**, 2165 (1952); (b) see also D. J. Cram, *ibid.*, **74**, 2129 (1952).

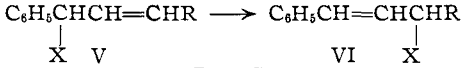
[13] This is the same phenomenon referred to as "Mass Law Effect" by C. K. Ingold, *et al.*, *J. Chem. Soc.*, 979 (1940).

required that the independent processes have identical activation energies and are similarly affected by changing the ionizing power of the solvent (Fig. 2). It indeed appears that the large effect of varying solvent or temperature on both racemization ($k_\alpha - k_t$) and solvolysis (k_t) and the small effect on k_α/k_t can best be explained in terms of a rate-determining formation of a common intermediate.

The downward trend in k_α/k_t with increasing dielectric constant of the solvent (Table II) parallels previous observations[12a,14,15] that the ratio of internal return to solvolysis decreases as ionizing power of the solvent increases. It has been pointed out[14] that this behavior is consistent with the ion-pair intermediate interpretation since the magnitude of k_α/k_t depends on the ratio k_1/k_s (equation 3) and the latter would be expected to decrease as ionizing power increases.

$$k_a/k_t = 1 + (k_1/k_s) \qquad (3)$$

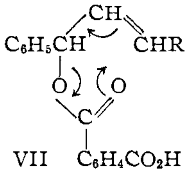
The conversion of optically active Ia or IIa to racemic material by way of the ion-pair intermediate is an intramolecular allylic rearrangement. Because of the symmetry of the present system the only structural change resulting from this rearrangement is the conversion of one enantiomorph to the other. In unsymmetrical allylic systems this process would result in an intramolecular isomeric rearrangement and it indeed appears that such rearrangements have been observed with certain allylic acid phthalates. Kenyon and co-workers have observed that under certain conditions optically active 1-phenyl-3-methylallyl acid phthalate[5a] (Va, X = $O_2CC_6H_4CO_2H$) and 1-phenyl-3-ethylallyl acid phthalate[16] (Vb) rearrange to the corresponding optically active 3-phenyl-1-alkylallyl ester (VI). Kenyon and co-workers[5a] originally proposed an SNi′[17] mechanism involving a four-membered cyclic transition state and later[18] suggested the cyclic mechanism VII to account for the intramolecular nature of the rearrangement indicated by the retention of activity during the rearrangement. More recently Catchpole, Hughes and Ingold[19] suggested a nine-membered cyclic (SNi′) mechanism involving the free carboxyl group of the acid phthalate. The latter mechanism



$$\underset{\mathrm{X}}{\mathrm{C_6H_5CH}}\mathrm{CH{=}CHR} \longrightarrow \mathrm{C_6H_5CH{=}CH}\underset{\mathrm{X}}{\mathrm{CHR}}$$

V VI

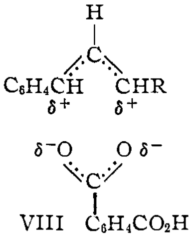
a, R = CH_3
b, R = C_2H_5



VII

features an "internal acid catalysis" and was suggested to accommodate the fact that salts of allylic acid phthalate (anions) rearrange less readily than the free acids.

It now appears that the so-called SNi′ rearrangements observed by Kenyon and co-workers are of the same type as the one involved in the racemization process in the present work and involve the formation of ion-pair intermediates (VIII) which are converted to the rearranged ester by internal return. This mechanism is consistent with the fact that the acid phthalates rearrange more readily than their salts (anions) since the rearrangement of the anion would involve a doubly charged anion in the ion-pair intermediate.



VIII

Experimental

Materials.—The isomeric 5-methyl-2-cyclohexenyl acid phthalates (Ia and IIa) and the isomeric 5-methyl-2-cyclohexenols (Ib and IIb) used in this work have been described previously.[20]

The aqueous acetone solvents were prepared by mixing the calculated volumes of acetone (fractionated from calcium chloride) and distilled water. The pure solvents were equilibrated at 25° prior to mixing and the solvent compositions are given as volume per cent. acetone at 25° based on the volumes of the components before mixing.

***cis*- and *trans*-Ethyl 5-Methyl-2-cyclohexenyl Ether.**—These ethers were prepared from the corresponding 5-methyl-2-cyclohexenols by the Williamson synthesis according to the method of Letsinger and Bobko.[21] *cis*-Ethyl 5-methyl-2-cyclohexenyl ether, b.p. 66–67° (21 mm.), n^{25}_D 1.4402, d^{25}_4 0.8690, *MR*D 42.55 (calcd. 42.74), was obtained in 67% yield.

Anal. Calcd. for $C_9H_{16}O$: C, 77.09; H, 11.50. Found: C, 76.98; H, 11.44.

trans-Ethyl 5-methyl-2-cyclohexenyl ether was obtained in 70% yield and has the following properties: b.p. 46–46.5° (10 mm.), n^{25}_D 1.4447, d^{25}_4 0.8663, *MR*D 43.06 (calcd. 42.74).

Anal. Calcd. for $C_9H_{16}O$: C, 77.09; H, 11.50. Found: C, 77.20; H, 11.77.

Kinetic Experiments.—All standard solutions were prepared at 25°. The polarimetric rates were determined as follows: Standard solutions of optically active 5-methyl-2-cyclohexenyl acid phthalate were prepared and distributed into ampules. The optical activity of the solution was determined periodically in the usual manner. The change in rotation during a kinetic experiment varied from 0.4 to 0.8° and the rotations were determined with a precision of ±0.003°.

The ampule technique also was used for the titrimetric determinations. The reactions were followed by periodically titrating a 20-ml. aliquot of reaction solution (measured at 25°) with standard 0.1 *N* aqueous sodium hydroxide to the phenolphthalein end-point. Solvent blanks were determined for each solvent. The change in titer during a kinetic experiment varied from 3 to 7 ml. and the titer of an 0.05 *N* solution of phthalic acid in aqueous acetone was found to be reproducible to within ±0.02 ml.

Isolation of Unsolvolyzed 5-Methyl-2-cyclohexenyl Acid Phthalates.—A solution of 0.50 g. (1.9 mmoles) of *cis*-5-methyl-2-cyclohexenyl acid phthalate (Ia), m.p. 78.4–

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[14] S. Winstein and K. C. Schreiber, THIS JOURNAL, **72**, 2171 (1952).

[15] H. L. Goering and A. C. Olson, *ibid.*, **75**, 5853 (1953).

[16] M. P. Balfe, J. Kenyon and D. Y. Waddan, *J. Chem. Soc.*, 1366 (1954).

[17] For the significance of this symbol see ref. 6, p. 596.

[18] M. P. Balfe and J. Kenyon, *Trans. Faraday Soc.*, **37**, 721 (1941).

[19] A. G. Catchpole, E. D. Hughes and C. K. Ingold, *J. Chem. Soc.*, 8 (1948).

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

[21] R. L. Letsinger and E. Bobko, *ibid.*, **75**, 2649 (1953).

79.1°, in 40 ml. of 80% aqueous acetone was sealed in an ampule and placed in the 99.95° thermostat. After 5.8 hours the ampule was opened and the solvent evaporated under a stream of filtered air. The residue was extracted with chloroform and the insoluble phthalic acid was removed by filtration. The chloroform solution was extracted with three 10-ml. portions of ice-cold 5% sodium hydroxide which were combined and shaken with several portions of ether to remove the 5-methyl-2-cyclohexenol. The aqueous solution was acidified and the acid phthalate, which separated as an oil, was separated by extraction with chloroform. This solution was filtered and the solvent was removed by evaporation at room temperature. The infrared spectrum of the residue in chloroform was indistinguishable from that of pure Ia. Since as little as 1% of IIa in Ia can be detected by infrared analysis it is clear that the recovered acid phthalate contained less than 1% of the *trans* isomer, IIa.

When this experiment was repeated with *trans*-5-methyl-2-cyclohexenyl acid phthalate (IIa) the recovered acid phthalate was IIa containing less than 1% of the *cis* isomer Ia.

Isolation of Products from the Solvolysis of *cis*-(Ia) and *trans*-5-Methyl-2-cyclohexenyl Acid Phthalate (IIa) and from the Acid-catalyzed Isomerization of *cis*-5-Methyl-2-cyclohexenol (Ib).—The results of these experiments are given in Table IV. The indicated solutions (30 ml.) were sealed in ampules and thermostated at 99.95° for 5.5 hr. (4.4 half-lives for the solvolysis of the *cis*-acid phthalate Ia and 5.5 half-lives[22] for the solvolysis of the *trans*-acid phthalate IIa). The solutions were made alkaline and concentrated at room temperature to remove the acetone, and the resulting solutions were extracted with carbon disulfide. The carbon disulfide solution was filtered and concentrated to about 1 ml. The infrared spectra showed that these solutions contained only the isomeric 5-methyl-2-cyclohexenols and the compositions of the binary mixtures were determined from the infrared spectrum by the previously described method.[20]

In order to determine if the method of isolation results in fractionation, a synthetic mixture of the isomeric 5-methyl-2-cyclohexenols consisting of 48% of the *cis* isomer was dissolved in 60% aqueous acetone and isolated by the above procedure. The mixture of *cis*- and *trans*-5-methyl-2-cyclohexenol isolated was found to consist of 47% of the *cis* isomer by infrared analysis. It is thus clear that fractionation does not occur during the isolation.

TABLE IV

COMPOSITIONS OF THE MIXTURES OF *cis*-(Ib) AND *trans*-5-METHYL-2-CYCLOHEXENOL (IIb) FORMED IN THE ISOMERIZATION OF Ib AND IN THE SOLVOLYSIS OF THE ISOMERIC 5-METHYL-2-CYCLOHEXENYL ACID PHTHALATES IN 60% ACETONE AT 100°

Reactant (*M*)	Reagent (*M*)	Compn. of 5-methyl-2-cyclohexenols (% *cis* isomer)
Ia (0.05)	None	56
IIa (.05)	None	55
Ib (.07)	None	98
Ib (.07)	Phthalic acid (0 05)	53
Ib (.07)	Chloroacetic acid (0.05)	55

The Ethanolysis of *cis*-5-Methyl-2-cyclohexenyl Acid Phthalate (Ia).—A solution of 2.0 g. (0.77 mmole) of Ia in 80 ml. of absolute ethanol[23] was sealed in an ampule and heated at 100° for 68.5 hours.[24] The solution was diluted with an equal volume of water and extracted with two 70-ml. portions of hexane. After shaking with two 100-ml. portions of 5% sodium hydroxide to remove acidic components, the organic layer was fractionated. The only material obtained after removal of the hexane was a mixture of *cis*- and *trans*-ethyl 5-methyl-2-cyclohexenyl ether and a high boiling residue, presumably diethyl phthalate. The infrared spectrum of the mixture of isomeric ethers was a composite of the spectra of the pure isomers and from the absence of a band at 3.08 μ it is clear that 5-methyl-2-cyclohexenol was not present. The composition of the mixture, 74% of the *trans* isomer and 26% of the *cis* isomer, was determined from the percentage transmission at 9.05 and 9.85 μ, bands present in the spectrum of the *cis* isomer, but not of the *trans* isomer.

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[22] This value was estimated by assuming that the rate constant (k_t) which is known for IIa in 90% acetone responds to a change in solvent composition in the same way that k_t for Ia does.

[23] L. F. Fieser, "Experiments in Organic Chemistry," D. C. Heath and Co., New York, N. Y., 1941, p. 359.

[24] The rate constant for the ethanolysis could not be determined because phthalic acid is esterified under the conditions of the reaction. A rate constant of 0.0181 hr.$^{-1}$ for the ethanolysis of Ia at 100° can be estimated from the rate constants in 80% and 90% acetone by the *mY* equation (E. Grunwald and S. Winstein, THIS JOURNAL, **70**, 846 (1948)). The half-period for the ethanolysis of Ia at 100° is thus estimated to be 38 hours.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MARYLAND]

Pyrolysis of Esters. III. Synthesis of 2-Vinylbutadiene[1,2]

BY WILLIAM J. BAILEY AND JAMES ECONOMY[3]

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2-Vinyl-1,3-butadiene was synthesized in three steps from aconitic ester in an over-all yield of 40%. The crucial steps in the synthesis were the reductive acetylation with lithium aluminum hydride and acetic anhydride in a 94% yield and the pyrolysis of a triacetate in a 43% yield. The structure of the triene was proved by analysis, ultraviolet and infrared absorption and conversion to a known derivative through an intermediate Diels–Alder adduct.

The pyrolysis of esters has been shown to be an excellent method for the synthesis of strained dienes, such as 1,2-dimethylenecyclohexane[4] and 1,2-dimethylene-4-cyclohexene,[5] an isomer of *o*-xylene. It seemed likely that this excellent method could be applied to the synthesis of other highly unsaturated compounds that are difficult or impossible to prepare by other more conventional procedures. One such compound is 2-vinylbutadiene (I). This triene is of particular interest since it contains the simplest possible cross-conjugated system. Since it possesses two conjugated diene systems, it will form polymeric Diels–Alder adducts with bifunctional dienophiles. The triene I, for the same reason, should be of interest as a cross-linking agent for vinyl polymers. The Diels–Alder adducts of I with cyclic dienophiles appear to be excellent starting materials for the synthesis of condensed polynuclear aromatic

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[1] Previous paper in this series, THIS JOURNAL, **77**, 357 (1955).

[2] Presented at the 126th National Meeting of the American Chemical Society, New York, N. Y., September, 1954.

[3] Office of Naval Research Fellow, 1953–1954.

[4] W. J. Bailey and H. R. Golden, THIS JOURNAL, **75**, 4780 (1953).

[5] W. J. Bailey and J. Rosenberg, *ibid.*, **77**, 73 (1955).