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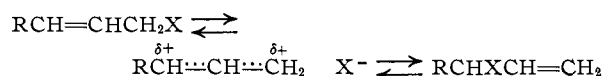
Stereochemistry of Allylic Rearrangements. II. The Kinetics and Stereochemistry of the Rearrangement of *cis*- and *trans*-5-Methyl-2-cyclohexenyl Acid Phthalate¹BY HARLAN L. GOERING, JEAN P. BLANCHARD² AND ERNEST F. SILVERSMITH

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The anionotropic rearrangements of *cis*- (I) and *trans*-5-methyl-2-cyclohexenyl acid phthalate (II) have been investigated in acetonitrile and in the fused state. In every case geometric isomerization and decomposition to 5-methyl-1,3-cyclohexadiene are associated with the rearrangement. In acetonitrile the rearrangement of optically active I or II results in the simultaneous formation of *dl*-I, *dl*-II and *dl*-5-methyl-1,3-cyclohexadiene together with phthalic acid. The geometric isomerization is reversible and the decomposition to methylcyclohexadiene and phthalic acid is irreversible. The rates of formation of each of these products have been measured. The equilibrium constant for the *cis*-*trans* equilibrium (I \rightleftharpoons II) has been determined at 80° and 100° in acetonitrile and the *trans* isomer (II) has been found to be the thermodynamically more stable one under these conditions. When I is rearranged in acetonitrile in the presence of 3-nitro acid phthalate ion exchange occurs. The exchange experiment and the geometric isomerization indicates that free ionic intermediates are involved in the rearrangement. The kinetic experiments show that the rate of loss of optical activity exceeds the rate of ionic dissociation and this is interpreted in terms of ion pair intermediates.

Introduction

Rearrangements and replacement reactions in allylic systems are of interest from both a theoretical and synthetic viewpoint and have received considerable attention in the past.³ In general the main features of the anionotropic (allylic) rearrangement indicate an ionization recombination (carbonium ion) mechanism as illustrated below.^{3a,c,d,4} Certain details of the mechanism are



obscure, however, and there are cases where the carbonium ion mechanism evidently does not operate or requires serious modification. For example, the above mechanism in its simplest form does not provide for (a) the intramolecular nature of the rearrangement of α,α -dimethylallyl chloride in acetic acid⁵ and certain oxotropic rearrangements⁶ and (b) retention of optical activity during the rearrangement of 1-phenyl-3-methylallyl acid phthalate.⁷

The anionotropic rearrangement has been studied in a number of systems³; however, cyclic systems with the migrating group attached directly to the ring before and after rearrangement have not been investigated.⁸ In order to obtain information concerning the nature of the intermediates, and in particular the freedom of the migrating group, we have investigated the kinetics and stereochemistry of the rearrangement in such a cyclic system.

(1) This work was supported in part by the Office of Ordnance Research and in part by the Research Committee of the Graduate School with funds given by the Wisconsin Alumni Research Foundation.

(2) Allied Chemical and Dye Company Fellow, 1952-1953; du Pont summer research assistant 1953.

(3) (a) W. G. Young, *et al.*, *THIS JOURNAL*, **74**, 608 (1952); (b) E. A. Braude and C. J. Timmons, *J. Chem. Soc.*, 3138 (1953); (c) R. S. Airs, M. P. Balfe and J. Kenyon, *ibid.*, 18 (1942); (d) A. G. Catchpole, E. D. Hughes and C. K. Ingold, *ibid.*, 8 (1948), and previous papers in these four series.

(4) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, pp. 586-601.

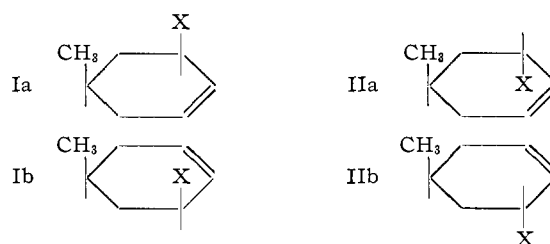
(5) W. G. Young, S. Winstein and H. L. Goering, *THIS JOURNAL*, **73**, 1958 (1951).

(6) E. A. Braude and E. R. H. Jones, *J. Chem. Soc.*, 436 (1944).

(7) J. Kenyon, S. M. Partridge and H. Phillips, *ibid.*, 207 (1937).

(8) Rearrangements have been observed in natural products containing cyclic allylic systems of this type. J. Read and G. Swann, *J. Chem. Soc.*, 239 (1937), observed an acid-catalyzed racemization of *d*-carvotanacetol, *l*-*trans*-carveol and 1- Δ^4 -menthen-3-ol and suggested that an anionotropic rearrangement might be involved.

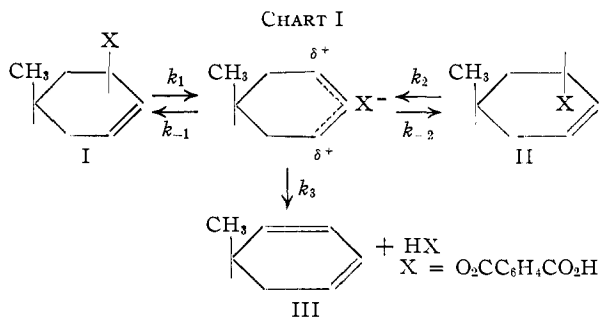
This paper describes a stereochemical kinetic study of the anionotropic rearrangement of *cis*-(I) and *trans*-5-methyl-2-cyclohexenyl acid phthalate (II). The preparation of these compounds and the assignment of configurations are described in the preceding paper.⁹ Four isomers (two racemic modifications) are possible in this system: *cis* (Ia and Ib) and *trans* (IIa and IIb). Because of the symmetry of this system, if the migrating group remains on the same side of the ring, the only structural change accompanying the anionotropic rearrangement is the conversion of one enantiomorph (a) into the other (b). A rearrangement of this type would thus result in the racemization (without geometric isomerization) of optically active isomers. If the migrating group becomes free enough so that it can recombine with the opposite side of the ring geometric isomerization (I \rightleftharpoons II) will be associated with the anionotropic rearrangement. In this system the rate of geometric isomerization (followed spectrophotometrically) and the total rate of rearrangement (followed polarimetrically) can be compared and the tendency of the migrating group to remain on the original side during rearrangement can be determined.



The rearrangement of *cis*- and *trans*-5-methyl-2-cyclohexenyl acid phthalate has been studied in acetonitrile at 80° and 100°. In addition the rearrangement of the *cis* isomer has been examined without solvent (fused state). The rearrangement in each case is accompanied by decomposition of the acid phthalate into phthalic acid and methylcyclohexadiene (III) and in each case geometric isomerization is involved. The products resulting from the rearrangement are consistent with the carbonium ion mechanism shown in Chart I; however, as

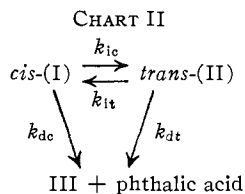
(9) H. L. Goering and J. P. Blanchard, *THIS JOURNAL*, **76**, 5405 (1954).

will be shown later the kinetic experiments require modification of this scheme.



Results

Rearrangement of *cis*-5-Methyl-2-cyclohexenyl Acid Phthalate (I) in Acetonitrile.—The thermal rearrangement of optically active I in acetonitrile results in the simultaneous formation of *dl*-I, *dl*-II and phthalic acid together with inactive 5-methyl-1,3-cyclohexadiene (III). The geometric isomerization is reversible and the decomposition of acid phthalate by elimination of phthalic acid with formation of III is irreversible. These simultaneous reactions are the ones indicated by Chart I and are more simply summarized by Chart II which is independent of any assumed mechanism. These two formulations differ only in that the carbonium ion intermediate, which is assumed to be common for all the reactions in Chart I, is neglected in Chart II. The specific rate constants for the isomerization (k_{ic}) and destruction (k_{dc}) of the *cis*-acid phthalate have been determined in acetonitrile at 80 and 100°. The first-order rate constant (k_1') for the loss of activity during the rearrangement of (–)-I has also been determined under the same conditions.



The equations connecting the various concentrations, rates and specific rate constants summarized in Chart II are shown below where equation 1 is the rate of disappearance of *cis* acid phthalate, 2 is the net rate of formation of the *trans* isomer and 3 is the rate of destruction of acid phthalate. In equation 3 (P acid) is the phthalic acid concentration and (total AP) is the concentration of remaining acid phthalate [*cis* + *trans*].

$$-d(cis)/dt = (k_{dc} + k_{it})(cis) - k_{it}(trans) \quad (1)$$

$$d(trans)/dt = k_{ic}(cis) - (k_{dt} + k_{it})(trans) \quad (2)$$

$$-d(\text{total AP})/dt = d(\text{P acid})/dt = k_{dc}(cis) + k_{dt}(trans) \quad (3)$$

During the early stages of the rearrangement the concentration of *trans*-acid phthalate is very low and equation 1 can be approximated by 4 which upon integration gives 5. The variables in the latter equation can be experimentally determined and the

$$-d(cis)/dt = (k_{dc} + k_{ic})(cis) \quad (4)$$

$$(k_{dc} + k_{ic}) = (1/t) \ln [(cis)_0/(cis)_t] \quad (5)$$

sum ($k_{ic} + k_{dc}$) can be evaluated. In the same way equation 3 can be approximated by 6 during the first part of the reaction. The latter upon integration gives equation 7 with variables that can be measured and thus by use of equations 7 and 5 k_{ic} and k_{dc} can be determined.

$$-d(\text{total AP})/dt = k_{dc}(\text{total AP}) \quad (6)$$

$$k_{dc} = (1/t) \ln [(\text{total AP})_0/(\text{total AP})_t] \quad (7)$$

In acetonitrile at 100° the rate constants k_{dc} and k_{dt} are indistinguishable and consequently the rate of phthalic acid formation or the disappearance of total acid phthalate is first order and independent of the composition of the acid phthalate. Because of the equality of k_{dc} and k_{dt} , equation 7 applies throughout the entire reaction instead of just for the earlier stages as is the case when k_{dc} and k_{dt} differ. The reversible isomerization is also simplified by the equality of k_{dc} and k_{dt} . Under these conditions (100° in acetonitrile) it can be shown that the relationship between time and composition of the remaining acid phthalate is independent of the decomposition which both isomers are undergoing. By neglecting the simultaneous decomposition, the isomerization becomes a typical first-order reversible reaction as is indicated by equation 8 where (f) is the mole fraction of the *cis* isomer in the remaining acid phthalate. It should be pointed out that unlike ordinary reversible reactions equilibrium conditions cannot be established from a pure isomer as the acid phthalate is decomposed before equilibrium is reached. During the early part of the rearrangement the mole fraction of the *trans* isomer

$$-d(f)/dt = k_{ic}(f) - k_{it}(1-f) \quad (8)$$

(1– f) is very low and the last term of equation 8 can be neglected (equation 9). Upon integration, equation 10 is obtained which makes possible the determination of k_{ic} from periodic measurements of the remaining acid phthalate composition.

$$-d(f)/dt = k_{ic}(f) \quad (9)$$

$$k_{ic} = (1/t) \ln (1/f) \quad (10)$$

The complete loss of optical activity that accompanies the rearrangement in acetonitrile is clearly first order. The specific first-order rate constant k_1' was determined from

$$k_1' = [1/t] \ln (\alpha_0/\alpha_t) \quad (11)$$

At first it was thought that the loss of activity would correspond to k_1 in Chart I; however, as will be shown later, the rate of loss of activity is evidently greater than the rate of ionic dissociation. Inasmuch as all of the products resulting from the rearrangement of optically active acid phthalate are racemic, k_1' is the sum of the constants for isomerization (k_{ic}), decomposition (k_{dc}) and racemization (k_{re}).¹⁰ The latter constant can be evaluated from the relationship

$$k_{re} = k_1' - (k_{dc} + k_{ic}) \quad (12)$$

The kinetic experiments were carried out in the following manner: Solutions of *dl*- or (–)*cis*-5-methyl-2-cyclohexenyl acid phthalate in acetonitrile were distributed into ampoules which were

(10) This is the first-order constant for the conversion of (–)*cis*-acid phthalate into *dl-cis*-acid phthalate and is not to be confused with the total first-order loss of activity (k_1').

sealed and placed in a thermostat. At measured time intervals ampules were withdrawn and aliquots analyzed. Inactive acid phthalate was used to determine the rates of decomposition (k_{dc}) and isomerization (k_{ic}).

The decomposition of the acid phthalate involves the formation of a carboxyl group (acid phthalate is converted to phthalic acid) and consequently can be followed by titration.¹¹ At 100° the formation of phthalic acid is first order in acid phthalate concentration during the period that the reaction was followed (55% decomposition). In view of the simultaneous geometric isomerization this first-order behavior requires that $k_{dc} = k_{dt}$ and this has indeed been demonstrated by showing that the rate of decomposition is independent of the composition of the acid phthalate. A typical experiment showing the first-order decomposition associated with the rearrangement of I is summarized in Table I. The values of k_{dc} shown in Table I were determined from equation 7. Under conditions where k_{dc} and k_{dt} are not equal (e.g., acetonitrile at 80°), the first-order constants obtained from equation 7 showed the expected drift and k_{dc} was determined by extrapolation to zero time.

In order to identify the products of decomposition, phthalic acid was isolated and identified by neutral equivalent and conversion to the anhydride. 5-Methyl-1,3-cyclohexadiene was identified by the characteristic absorption at 258–260 $\mu\mu$ ¹² and by isolation of the maleic anhydride adduct which was identified by its chemical composition.

Aliquots of the same samples used to determine the rate of decomposition were used to measure the rate of *cis*- (I) to *trans*- (II) isomerization (k_{ic}). The unreacted acid phthalate was isolated in such a way as to avoid fractionation and the composition of the binary mixture was determined spectrophotometrically. *cis*-5-Methyl-2-cyclohexenyl acid phthalate (I) has a band at 10.63 μ not present in the spectrum of II and the *trans*-acid phthalate (II) has a band at 11.03 μ not present in the spectrum of I. The compositions of the mixture were determined from the transmission at these wave lengths.

From the composition, together with the concentration of remaining total acid phthalate (available directly from titration for phthalic acid) the concentration of I and II can be determined for any time. With this data the sum ($k_{dc} + k_{ic}$) can be determined by use of equation 5 and, since k_{dc} can be obtained by separate measurement (equation 7), k_{ic} can be obtained by difference.

A typical kinetic experiment, in which k_{dc} and ($k_{dc} + k_{ic}$) were determined by equations 7 and 5, respectively, is summarized in Table I. Under the conditions of this experiment $k_{dc} = k_{dt}$ and equation 7 holds throughout the reaction. Equation 5, however, applies only during the early stages of the reaction and consequently ($k_{dc} + k_{ic}$) was determined by extrapolating the series of constants back

(11) Phthalic anhydride was isolated together with phthalic acid from the reaction mixture indicating that phthalic acid is partly dehydrated in acetonitrile at 80 to 100°. This does not complicate the kinetic studies as the analytical method which was used does not distinguish between the free acid and the anhydride.

(12) H. Booker, L. K. Evans and A. E. Gillam, *J. Chem. Soc.*, 1453 (1940).

to zero time. In the present case equation 10 provides an alternate method for the direct evaluation of k_{ic} . When the data are treated in this way a value of 0.014 hr.⁻¹ is obtained for k_{ic} , which is identical with the value obtained from the data in Table I.

TABLE I

THE RATE OF DECOMPOSITION (k_{dc}) AND THE RATE OF CONVERSION OF I TO II (k_{ic}) DURING THE REARRANGEMENT OF 0.2 M *cis*-5-METHYL-2-CYCLOHEXENYL ACID PHTHALATE (I) IN ACETONITRILE AT 100°

| Time, hr. | [I + II] ^a 10 ² M | 10 ² k_{dc} , hr. ⁻¹ | % I ^b | [I] 10 ² M | ($k_{dc} + k_{ic}$), hr. ⁻¹ |
|-----------|--|---|------------------|--------------------------|---|
| 0.0 | 19.98 | | 100 | 19.98 | 3.3 ^c |
| 2.5 | 19.16 | 1.7 | 96 | 18.39 | 3.3 |
| 5.0 | 18.18 | 1.9 | 94 | 17.09 | 3.1 |
| 7.5 | 17.28 | 1.9 | 90 | 15.55 | 3.3 |
| 10.0 | 16.44 | 2.0 | 89 | 14.63 | 3.1 |
| 12.5 | 15.77 | 1.9 | 86 | 13.56 | 3.1 |
| 17.5 | 14.34 | 1.9 | 82 | 11.76 | 3.0 |
| 25.0 | 12.60 | 1.9 | 79 | 9.95 | 2.8 |
| 35.0 | 10.59 | 1.8 | 73 | 7.73 | 2.7 |
| 45.0 | 9.22 | 1.7 | 66 | 6.09 | 2.6 |

Average 1.9 ± 0.07

^a Concentration of total acid phthalate. ^b Percentage of total acid phthalate that is *cis*. ^c This value obtained by extrapolation.

(-)*cis*-5-Methyl-2-cyclohexenyl acid phthalate was used to determine the rate of loss of optical activity during the rearrangement. In these experiments the contents of the ampules were analyzed polarimetrically and k_1' was determined from equation 11. The experiment summarized by Table II illustrates that the constants do not show any trends during the first 70% of the reaction and it seems doubtful that the indicated trend during the later stages of the reaction is significant in view of the small magnitude of the observed rotations.

TABLE II

THE RATE OF LOSS OF OPTICAL ACTIVITY OF 0.2 M (-)*cis*-5-METHYLCYCLOHEXEN-3-YL ACID PHTHALATE IN ACETONITRILE AT 100°

| Time, hr. | α^a | [Acid phthalate] ^b 10 ² M | 10 ² k_1 , hr. ⁻¹ |
|--------------------|------------|--|---|
| 0.00 | 1.071 | 20.0 | |
| 2.50 | 0.832 | 15.5 | 10.1 |
| 5.00 | .622 | 11.6 | 10.9 |
| 7.50 | .494 | 9.2 | 10.3 |
| 10.00 | .384 | 7.1 | 10.3 |
| 12.50 | .311 | 5.8 | 9.9 |
| 17.50 | .205 | 3.8 | 9.4 |
| 35.00 ^c | .044 | 0.8 | 9.1 |

10.0 ± 0.5

^a Observed rotation. ^b This is the concentration of (-)*cis*-acid phthalate and is not to be confused with total acid phthalate concentration. ^c Beyond this time solution became too colored (yellow) to measure the rotation.

The least square plots in Fig. 1 illustrate how well the kinetic data for the loss of optical activity are fit by equation 11. The complete loss of activity,¹³

(13) A. Mousseron and F. Winternitz, *Bull. soc. chim.*, **12**, 67 (1945), report a high rotation for active 5-methyl-1,3-cyclohexadiene. Thus the complete loss of activity indicates that the diene formed by decomposition is racemic.

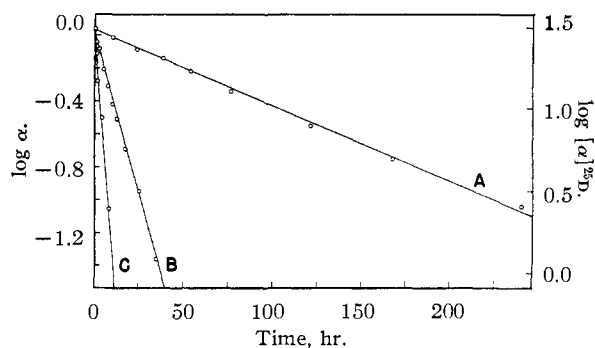


Fig. 1.—First-order rate of loss of optical activity during the rearrangement of $(-)$ *cis*-5-methyl-2-cyclohexenyl acid phthalate: A, in acetonitrile at 80° (left hand scale); B, in acetonitrile at 100° (left hand scale); C, without solvent at 100° (right hand scale).

together with the first-order behavior clearly shows that all of the products are racemic and evidently are formed by way of a symmetrical intermediate.

The rearrangement of *cis*-5-methyl-2-cyclohexenyl acid phthalate in acetonitrile at 100° is summarized in Fig. 2 by concentration-time curves for all of the components involved. The necessary data for these curves were obtained by the analytical methods indicated above and each curve was reproducible. The method of computing concentrations requires that the sum of the concentrations of I, II and phthalic acid be constant and equal to the original concentration.¹⁴ Comparison of curves B and D (or Tables I and II) shows that the rate of loss of optical activity is about three times as great as the rate of disappearance of *cis*-acid phthalate. After ten hours, for example, about half of the remaining *cis*-acid phthalate is racemic and after 50 hours all of the remaining *cis*-acid phthalate is inactive.

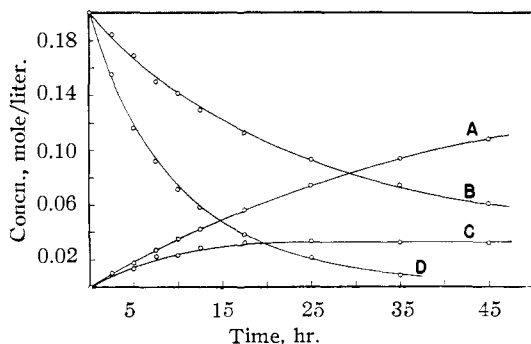


Fig. 2.—Concentration-time curves for all of the components involved in the rearrangement of *cis*-5-methyl-2-cyclohexenyl acid phthalate in acetonitrile at 100° : A, phthalic acid; B, *dl*-*cis*-acid phthalate; C, *dl*-*trans*-acid phthalate; D, $(-)$ *cis*-acid phthalate.

The rearrangement of I in acetonitrile at 80° is very similar to the rearrangement at 100° and the simultaneous reactions have been studied in the same way. At 80° the rate of phthalic acid formation is not first order and the constants obtained by

(14) The concentration of acid phthalate (I + II) is obtained by subtracting the concentration of phthalic acid from the original concentration of I.

equation 7 drift downward because under these conditions $k_{dc} > k_{dt}$. The value of k_{dc} was determined by extrapolating the values obtained from equation 7 back to zero time. With this exception all of the rate constants at 80° were determined as illustrated above. The specific first-order constants for the rearrangement of I in acetonitrile at 80 and 100° are collected in Table III.

TABLE III

SPECIFIC RATE CONSTANTS (HR.⁻¹) FOR RACEMIZATION (k_{ro}), ISOMERIZATION (k_{ic}), DECOMPOSITION (k_{dc}) AND LOSS OF OPTICAL ACTIVITY (k'_1) DURING THE REARRANGEMENT OF *cis*-5-METHYL-2-CYCLOHEXENYL ACID PHTHALATE IN ACETONITRILE

| | $80.05 \pm 0.05^\circ$ | $100.00 \pm 0.05^\circ$ |
|---------------|------------------------|-------------------------|
| $10^3 k'_1$ | 11.3 | 100 |
| $10^3 k_{ro}$ | 6.5 | 67 |
| $10^3 k_{ic}$ | 2.3 | 14 |
| $10^3 k_{dc}$ | 2.5 | 19 |

Rearrangement of *trans*-5-Methyl-2-cyclohexenyl Acid Phthalate II in Acetonitrile.—The rearrangement of II in acetonitrile was studied in the same way and at the same temperatures as the *cis* isomer. The specific rate constant for the decomposition of II (k_{dt}) and the constant for the *trans* to *cis* isomerization (k_{it}) were determined by fitting the data to equations 5' and 7'. A typical experiment is shown in Table IV.

$$(k_{it} + k_{dt}) = (1/t) \ln [(trans)_0 / (trans)_t] \quad (5')$$

$$k_{dt} = (1/t) \ln [(total AP)_0 / (total AP)_t] \quad (7')$$

TABLE IV

THE RATE OF DECOMPOSITION (k_{dt}) AND THE RATE OF CONVERSION OF II TO I (k_{it}) DURING THE REARRANGEMENT OF 0.2 M *trans*-5-METHYL-2-CYCLOHEXENYL ACID PHTHALATE (II) IN ACETONITRILE AT 100°

| Time, hr. | $[I + II]^a$ $10^2 M$ | $10^3 k_{dt}$ hr. ⁻¹ | % II ^b | $[II]$ $10^2 M$ | $10^3 (k_{it} + k_{dt})$ hr. ⁻¹ |
|-----------|--------------------------|------------------------------------|-------------------|--------------------|---|
| 0 | 20.00 | | 100 | 20.00 | 2.8 ^c |
| 2.5 | 19.05 | 2.0 | 98 | 18.67 | 2.7 |
| 5.0 | 18.23 | 1.9 | 96 | 17.50 | 2.7 |
| 7.5 | 17.45 | 1.8 | 95 | 16.58 | 2.5 |
| 10.0 | 16.58 | 1.9 | 93 | 15.42 | 2.6 |
| 12.5 | 15.90 | 1.8 | 92 | 14.63 | 2.5 |
| 17.5 | 14.57 | 1.8 | 91 | 13.26 | 2.4 |
| 25.0 | 12.80 | 1.8 | 87 | 11.12 | 2.4 |
| | | 1.9 ± 0.1 | | | |

^a Concentration of total acid phthalate. ^b Percentage of total acid phthalate that is *trans*. ^c This value obtained by extrapolation.

The loss of optical activity of $(-)$ *trans*-5-methyl-2-cyclohexenyl acid phthalate is first order as indicated by the least square plots in Fig. 3 which illustrate how well the data are fit by equation 11. The rate constants for the loss of activity (k'_2) were determined from the slopes of the least square fits.

A complete kinetic experiment is summarized in Fig. 4 by concentration-time curves for all of the components. The specific first-order constants for all of the simultaneous reactions occurring during the rearrangement of II in acetonitrile at 80 and 100° are shown in Table V.

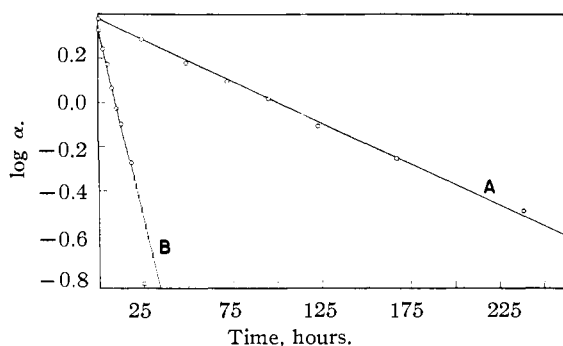


Fig. 3.—First-order rate of loss of optical activity during the rearrangement of (—) *trans*-5-methyl-2-cyclohexenyl acid phthalate in acetonitrile: A, at 80°; B, at 100°.

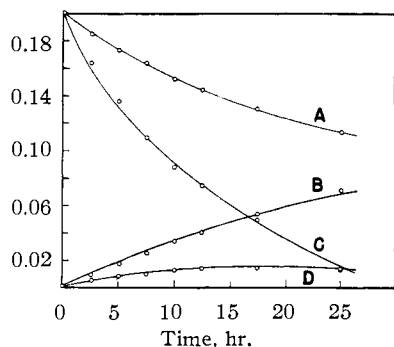


Fig. 4.—Concentration-time curves for all of the components involved in the rearrangement of *trans*-5-methyl-2-cyclohexenyl acid phthalate in acetonitrile at 100°: A, *dl-trans*-acid phthalate; B, phthalic acid; C, (—) *trans*-acid phthalate; D, *dl-cis*-acid phthalate.

| | 80.05 ± 0.05° | 100.00 ± 0.05° |
|---------------|---------------|----------------|
| $10^3 k_2'$ | 8.9 | 78 |
| $10^3 k_{rt}$ | 6.0 | 51 |
| $10^3 k_{it}$ | 0.7 | 8 |
| $10^3 k_{dt}$ | 2.2 | 19 |

The equilibrium constant (K_e) for the *cis-trans* isomerization of the 5-methyl-2-cyclohexenyl acid phthalates can be determined from the specific rate constants for isomerization (k_{ic} and k_{it}).

$$k_{ic}/k_{it} = K_e = [\text{II}]_e/[\text{I}]_e \quad (13)$$

At 80°, $K_e = 2.3/0.7 = 3.3$ corresponding to a mixture consisting of 77% of the *trans* isomer; at 100° the equilibrium mixture consists of 64% of the *trans* isomer (K_e 1.8). At 100° where the rate constants for the decomposition are the same for each isomer ($k_{dc} = k_{dt}$) the equilibrium constant determined by equation 13 readily can be checked independently by direct measurement of the equilibrium composition. In order to reach equilibrium conditions it is necessary to start with a mixture of acid phthalates that is close to or preferably at equilibrium because either I or II is decomposed to

methylcyclohexadiene (III) and phthalic acid before equilibrium is established.

When a 0.2 *M* solution of the equilibrium mixture, determined by equation 13 (65% II, 35% I) was heated in acetonitrile at 100° the composition remained constant as the acid phthalate was decomposed to III and phthalic acid. As $k_{dc} = k_{dt}$ under these conditions it is clear that the constant composition corresponds to the equilibrium composition. During the 55 hours that the equilibrium was observed, 66% of the acid phthalate was decomposed by a first-order process ($k = 0.019$ hr.⁻¹). The data for this experiment are shown in Fig. 5 (line B) where the composition is plotted against time. The least square fit of the experimental points has a slope of zero. The agreement between the measured and calculated equilibrium composition indeed indicates that the rearrangement is described accurately by Chart II.

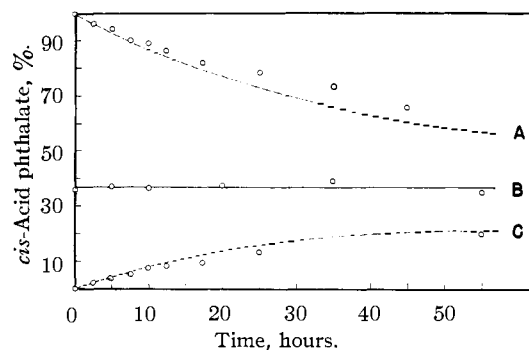


Fig. 5.—Comparison of calculated and experimental composition during the rearrangement of *cis*- and *trans*-5-methyl-2-cyclohexenyl acid phthalate in acetonitrile at 100°: A, starting with *cis*-acid phthalate; B, starting with the calculated equilibrium mixture (35% *cis*); C, starting with *trans*-acid phthalate.

The values for k_{ic} and k_{it} are consistent with the rate of change in composition of the 5-methyl-2-cyclohexenyl acid phthalates throughout the rearrangement starting with either I or II. By substituting the values of these constants from Tables III and V into equation 14, which is obtained by integrating equation 8, the composition can be calculated for any time during the rearrangement of I.

$$[1/(k_{ic} + k_{it})] \ln [k_{ic}/(k_{ic} + k_{it})f - k_{it}] = t \quad (14)$$

In Fig. 5 the calculated composition (curve A) is compared with the experimental values for the rearrangement of I in acetonitrile at 100°. In a similar way the time-composition curve can be calculated for the rearrangement of II from the values of k_{ic} and k_{it} by use of equation 14'. This curve also is shown in Fig. 5 (curve C) together [1/($k_{ic} + k_{it}$)] $\ln [k_{it}/(k_{ic} + k_{it})(1 - f) - k_{ic}] = t$ (14') with the experimental measurements. The satisfactory fit of the experimental data by equations 14 and 14' illustrate the consistency of all of the kinetic data. This fit requires that (a) the decomposition is irreversible, (b) the geometric isomerization is reversible and (c) the rate constants are essentially correct.

By using equation 14' it can be calculated that at

100° in acetonitrile about 160 hours are required to convert pure II to a mixture having a composition within 1% of the equilibrium value. From the value of k_{dt} it can be shown that over 95% of the acid phthalate would decompose during this time. A similar calculation (equation 14) shows that when starting with pure I over 97% of the acid phthalate will be decomposed before that which remains has a composition within 1% of the equilibrium value.

There is another way in which the consistency of the kinetic data can be checked. From the integrated expression for a reversible first-order reaction (equation 15)¹⁵ it is apparent that when starting

$$\ln [(1 - f_e)/(f - f_e)] = (k_{ic} + k_{it})t \quad (15)$$

with the *cis*-acid phthalate (I) a plot of $-\log(f - f_e)$ against time should result in a straight line with a slope of $(k_{ic} + k_{it})/2.3$ and when starting with the *trans*-acid phthalate (II), $-\log(f_e - f)$ should be linear with time with the same slope (equation 15').¹⁶ The mole fraction of I and II at equilibrium,

$$\ln f_e/(f_e - f) = (k_{ic} + k_{it})t \quad (15')$$

f_e and $(1 - f_e)$, respectively, can be calculated from the equilibrium constant (eq. 13). As illustrated by Fig. 6 the data are fit well by equation 15. The slope of the least square fit (A) corresponds to a value of 0.019 for $(k_{ic} + k_{it})$ as compared to the value of 0.022 determined from the values in Table III and V and which were in fact used to successfully determine f_e . The lower line (B) corresponds to a value of 0.016 for $(k_{ic} + k_{it})$.

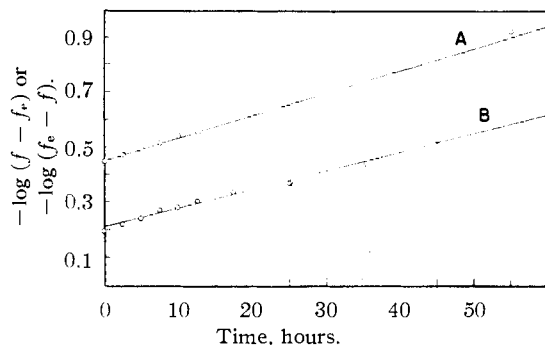


Fig. 6.—First-order behavior of reversible interconversion of *cis*- and *trans*-5-methyl-2-cyclohexenyl acid phthalate in acetonitrile at 100°: A, $-\log(f_e - f)$; B, $-\log(f - f_e)$.

Rearrangement of *cis*-5-Methyl-2-cyclohexenyl Acid Phthalate in the Presence of a Foreign Anion.—The geometric isomerization associated with the rearrangement in acetonitrile indicates that ionic dissociation is involved. In order to obtain additional information concerning the freedom of intermediate ions the rearrangement was carried out in acetonitrile containing diphenylguanidinium 3-nitro acid phthalate (DPG salt). After 25 hours¹⁷ at 100° the product was isolated in such

(15) Derived from equation 14 by letting $f_e = k_{it}/(k_{ic} + k_{it})$. See also A. Frost and R. Pearson, "Kinetics and Mechanism," John Wiley and Sons, Inc., New York, N. Y., 1953, p. 173.

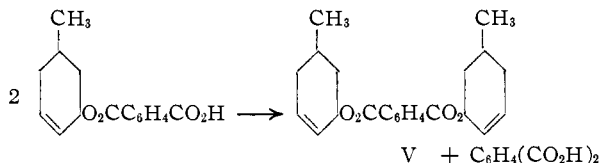
(16) The linear relationship only holds where $k_{do} = k_{dt}$ as is the case in acetonitrile at 100°.

(17) During this period 37% of the acid phthalate is decomposed to 111 and phthalic acid (Table I and Fig. 2). It also is significant that 25 hr. corresponds to 3.6 half-periods for the loss of optical activity (Table II).

a way as to avoid fractionation and the amount of exchange product, 5-methyl-2-cyclohexenyl 3-nitro acid phthalate (IV), determined spectrophotometrically. In these experiments the isomeric rearrangement was diverted readily by the foreign anion in such a way as to indicate a carbonium ion intermediate. The amount of exchange was dependent upon the foreign anion concentration. With an acid phthalate concentration of 0.200 *M* and a DPG salt concentration of 0.0947 *M* the isolated product consisted of 28% of the exchange product IV and 72% of 5-methyl-2-cyclohexenyl acid phthalate. When the salt concentration was raised to 0.189 *M* the product contained 48% of the exchange product.

The Rearrangement of *cis*-5-Methyl-2-cyclohexenyl Acid Phthalate without Solvent.—Fused I rearranges at a measurable rate at 100°. The general picture under these conditions is similar to that in acetonitrile in that the loss of optical activity is first order and geometric isomerization and phthalic acid formation accompany the rearrangement.

The titrimetric method for following the decomposition is not applicable under these conditions because phthalic acid formation does not correspond to the formation of a carboxyl group. A 28% yield of phthalic acid was isolated from a reaction mixture which showed only an 11% increase in acidity (carboxyl groups). Evidently in addition to being formed by elimination, phthalic acid is formed by



The latter process which is actually a solvolysis (acid phthalate is the solvent), does not involve an increase in the number of carboxyl groups. Because of this complication the rearrangement could not be studied in detail; however, the rates of isomerization and loss of optical activity were measured. The data for the rearrangement in the fused state are presented in Fig. 7, which shows the rate as percentage-time curves for the loss of optical activity and for isomerization at 100°.

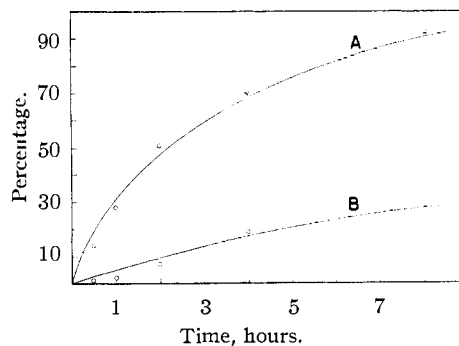


Fig. 7.—The rearrangement of fused *cis*-5-methyl-2-cyclohexenyl acid phthalate at 100°: A, rate of loss of optical activity; B, rate of isomerization expressed as percentage *trans* isomer.

The loss of optical activity is first order (curve C, Fig. 1) and the rate ($k = 0.32 \pm 0.02 \text{ hr.}^{-1}$) is greater, as would be expected, than it is in acetonitrile.

Discussion

The geometric isomerization associated with the rearrangement and the diversion of the isomeric rearrangement by a foreign anion suggests that a carbonium ion mechanism is involved and that the migrating acid phthalate ion becomes free from the allylic cation at some stage of the rearrangement. From these observations it appears that S_{Ni}' ¹⁸ mechanisms of the type which have been proposed^{7,18} for the intramolecular rearrangement of 1-phenyl-3-methylallyl acid phthalate are not important in the present case as such cyclic processes would lead to rearrangement (racemization) without geometric isomerization.

A carbonium ion mechanism also is indicated by the fact that the rearrangements of optically active I and II result in the formation of the same three initial products: (1) *dl-cis*-acid phthalate (I), (2) *dl-trans*-acid phthalate (II), (3) *dl*-methylcyclohexadiene (III) together with phthalic acid. The relative rates of formation of these three products during the rearrangement of optically active I corresponds to the relative magnitudes of k_{rc} , k_{ic} and k_{dc} (Table III) and are shown in the first two columns of Table VI. The relative rates of formation of the same products from optically active II—relative magnitudes of k_{it} , k_{rt} and k_{dt} (Table V)—also are included in Table VI. Both I and II show a somewhat greater tendency to racemize than to undergo geometric isomerization and consequently the relative rates of formation of the three products are considerably different for the two isomers. This difference is particularly informative from a mechanistic viewpoint. For the carbonium ion mechanism shown in Chart I the relative rates of product formation would represent the manner in which the carbonium ion is partitioned or in other words would correspond to the relative magnitudes of k_{-1} , k_{-2} and k_3 . For this mechanism the relative rates of formation of the products would be the same for both isomers since the same intermediate is partitioned in each case.

TABLE VI

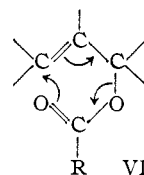
RELATIVE RATES OF FORMATION OF THE PRODUCTS DURING THE REARRANGEMENT OF OPTICALLY ACTIVE I AND II IN ACETONITRILE

| Product | Rel. rates of form. from active I at temperatures ^a | | Rel. rates of form. from active II at temperatures ^b | |
|--------------------------------|--|------|---|------|
| | 80° | 100° | 80° | 100° |
| <i>dl</i> -I (<i>cis</i>) | 2.6 | 3.5 | 0.3 | 0.4 |
| <i>dl</i> -II (<i>trans</i>) | 0.9 | 0.7 | 2.7 | 2.7 |
| III + phthalic acid | 1.0 | 1.0 | 1.0 | 1.0 |

^a The values of the first 2 columns are the relative magnitudes of k_{rc} , k_{ic} and k_{dc} (Table III). ^b These values are the relative magnitudes of k_{it} , k_{rt} and k_{dt} (Table V).

There is another obvious discrepancy between the kinetic results and the carbonium ion mechanism in its simplest form (Chart I). As pointed out earlier k_{dc} is fortuitously indistinguishable from k_{dt} at 100° in acetonitrile, or in other words both I and II are converted into methylcyclohexadiene and phthalic acid at the same rate. According to Chart I this would require that both isomers also form the single symmetrical intermediate at the same rate, which is clearly not the case as is shown by the different rates of loss of optical activity (compare k_1' and k_2' in Tables III and V).

The kinetic analysis shows that the instantaneous fate of optically active I is such as to favor formation of racemic I, whereas active II is partitioned in such a way as to favor formation of racemic II (see Table VI). This could be due possibly to the fact that an S_{Ni}' process VI,⁷ in which the carbon-oxygen bonds are broken and formed simultaneously, is superimposed on the carbonium ion mechanism.¹⁹ From the available information this explanation seems unlikely as it would require that the relative importance of the two independent simultaneous processes be essentially independent of temperature. The fact that change in temperature has only a slight effect on the relative rates of formation of the three products suggests that the temperature is affecting the rate of formation of a common intermediate which is subsequently partitioned.



The formulation shown in Chart I can be expanded in such a way as to accommodate the kinetic data. In this connection there are two possibilities that merit consideration. If the position or location of the departing anion with respect to the symmetrical allylic cation can influence the partitioning of the cation, then the carbonium ion formed from I could be partitioned differently than when formed from II. According to this possibility a different intermediate would result from the geometric isomers, the difference being in the location of the dissociating anion. This interpretation is analogous to the "shielding effect"²⁰ which has been proposed to account for the formation of different products from carbonium ion intermediates derived from enantiomers.

Another interpretation of the carbonium ion mechanism which is consistent with the experimental results is shown in Chart III ($\text{X} = -\text{O}_2\text{C}_6\text{H}_4\text{CO}_2\text{H}$). This scheme differs from the simpler one in Chart I by ion pair intermediates which are involved in the ionic dissociation of I and II. This interpretation receives considerable support from the recent evidence^{21,22} that ion pair intermediates precede dissociated carbonium ion interme-

(19) An alternate S_{Ni}' mechanism involving the free carboxyl group has been suggested for the intramolecular rearrangement of allylic acid phthalates by Catchpole, Hughes and Ingold (ref. 18).

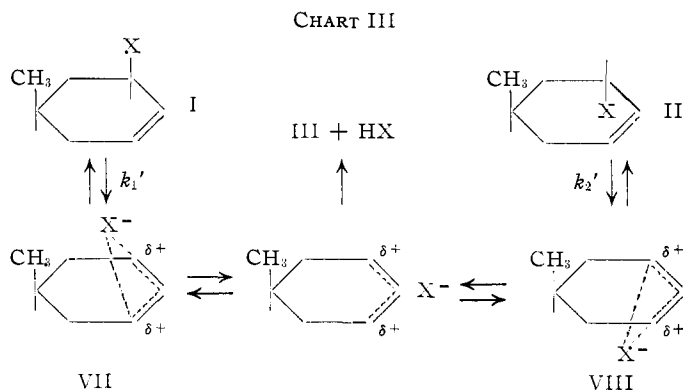
(20) E. D. Hughes and C. K. Ingold, *J. Chem. Soc.*, 244 (1935).

(21) D. J. Cram and F. A. Abd Elhafez, *THIS JOURNAL*, **75**, 3189 (1953), and preceding papers in this series.

(22) S. Winstein and R. Heck, *ibid.*, **74**, 5584 (1952), and preceding papers in this series.

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

diates in similar ionizations.²³ It also is significant that an ion pair intermediate involving an allylic cation has been suggested^{5,22} for the intramolecular rearrangement of α,α -dimethylallyl chloride in acetic acid.⁵



According to this picture the "cis" ion pair VII is involved as an intermediate in the ionic dissociation of I and the "trans" ion pair VIII is involved similarly in the ionization of II. The conversion of optically active I and II into the corresponding ion pair intermediates results in the loss of activity since these intermediates are symmetrical. Thus the rates of loss of optical activity, k_1' and k_2' , correspond to the rates of formation of the intermediates. As shown in the scheme, the ion pairs either can dissociate to the common carbonium ion intermediate or they can reform the reactants by a process which has been designated "internal return."^{5,22} The data in Table VI show that for each geometric isomer the ion pair has a somewhat greater tendency to return to reactant than to dissociate. This mechanism also is consistent with the observed geometric isomerization and intervention of a foreign anion. The geometric isomerization involves "external return"²² and the intervention of a foreign anion results from successful competition for the dissociated free carbonium ion.

It seems likely that this modification of the original ionization recombination mechanism applies to the anionotropic rearrangement in general. It has been pointed out previously²² that internal return of an ion pair is indicated by the intramolecular conversion of α,α -dimethylallyl chloride to γ,γ -dimethylallyl chloride.

One other point of interest in connection with the present work concerns the fact that *trans*-5-methyl-2-cyclohexenyl acid phthalate is thermodynamically more stable in acetonitrile than the *cis* isomer. The equilibrium mixture in acetonitrile at 100° consists of 64% of the *trans* isomer. At 80° the equilibrium composition (determined from k_{1c} and k_{2c}) is 77% *trans*, 23% *cis*. We also have observed that the acid-catalyzed equilibrations of the 5-methyl-2-cyclohexenols in aqueous acetone give equilibrium mixtures consisting of about equal

amounts of the two isomers.²⁴ These results show that there is a considerable difference between the relative stabilities of geometric isomers in 3,5-disubstituted cyclohexenes and in 1,3-disubstituted cyclohexanes. For 1,3-disubstituted cyclohexanes the *cis* isomer is the more stable one.²⁵ The conformation of the cyclohexene ring recently has been considered²⁶ and it has been suggested^{26a} that the *cis* isomer is probably the more stable one for 3,5-disubstituted cyclohexenes. In the present case it is clear that the *trans* isomer is more stable than the *cis* isomer.

Experimental

Materials.—*cis*- (m.p. 78.4–79.3°) and *trans*-5-methyl-2-cyclohexenyl acid phthalate, m.p. 90–90.2°, were prepared, purified and resolved as described in the previous paper.⁹

Optically pure (–)*cis*-5-methyl-2-cyclohexenyl acid phthalate crystallizes with considerable difficulty⁹ and for this reason partially resolved material was used in this work. This material melted at 75.2–76.4° and had a rotation of $[\alpha]_{D}^{27} -29.4^\circ$ (*c* 1.0, chloroform), which corresponds to about 50% optical purity.

The (–)*trans*-5-methyl-2-cyclohexenyl acid phthalate, m.p. 90–90.2°, was presumably optically pure⁹ and had a rotation of $[\alpha]_{D}^{25} -130.4^\circ$ (*c* 1.0, chloroform).

cis-5-Methyl-2-cyclohexenyl 3-nitro acid phthalate was prepared from the alcohol and 3-nitrophthalic anhydride by the same procedure⁹ used for preparing the acid phthalates. After recrystallization from ether–petroleum ether mixture this material melted at 133–134°.

Anal. Calcd. for $C_{15}H_{15}O_6N$: C, 59.01; H, 4.95; neut. equiv., 305.3. Found: C, 59.20; H, 4.89; neut. equiv., 309.5.

Acetonitrile was purified by fractionation. All solutions were standardized at 25° and all reported concentrations are for this temperature.

Polarimetric Measurements.—Optical rotations were determined with an O. C. Rudolph and Sons high precision model 80 polarimeter. The series of readings taken for each determination usually were well within 0.008° of each other.

Infrared Analysis.—The compositions of mixtures of *cis* (I) and *trans*-5-methyl-2-cyclohexenyl acid phthalate (II) were determined with a Baird Associates recording spectrophotometer. The samples to be analyzed were dissolved in chloroform saturated with sodium chloride (approximately 0.4 M solutions were prepared) and the spectra of the resulting solutions were taken in 0.1-mm. sodium chloride cells. The *cis*-acid phthalate I has a band at 10.63 μ not present in the spectrum of the *trans* isomer and the *trans* isomer has a band at 11.03 μ not present in the spectrum of the *cis* isomer. The composition of a mixture of the two isomers can be determined from the relative transmissions at these wave lengths. Although Beer's law was found to apply fairly well over the entire range from pure I to pure II it was found necessary to correct for the slight deviations. These deviations, which at the most amounted to 3 or 4% in the composition of a mixture, were determined by measuring the relative transmissions at 10.63 and 11.03 μ for synthetic mixtures. The complete infrared spectrum of the binary mixtures of I and II isolated in the kinetic experiments showed that the mixtures did not contain an interfering third component.

Rearrangement of *cis*- and *trans*-5-Methyl-2-cyclohexenyl Acid Phthalate in Acetonitrile.—The rates of (a) loss of optical activity, (b) geometric isomerization and (c) decomposition into methylcyclohexadiene and phthalic acid were determined as follows: Standard solutions ($0.2000 \pm 0.0004 M$) of optically active and inactive phthalates were prepared and distributed into ampules (2-ml. portions of active solution and 16-ml. portions of inactive solutions),

(23) This interpretation of carbonium ion reactions (S_N1 reactions) was discussed by S. Winstein at the Thirteenth National Organic Chemistry Symposium, Ann Arbor, Mich., June, 1953; see also S. Winstein, E. Clippinger, A. Fainberg and G. Robinson, THIS JOURNAL, **76**, 2597 (1954).

(24) E. F. Silversmith and H. L. Goering, unpublished results.

(25) D. H. R. Barton, *J. Chem. Soc.*, 1027 (1953).

(26) (a) D. H. R. Barton, R. C. Cookson, W. Klyne and C. W. Shoppee, *Chem. and Ind.*, 21 (1954); (b) R. A. Raphael and J. B. Stenlake, *ibid.*, 1286 (1953).

which were sealed and placed in a thermostat. Zero time was recorded at the time that the solutions were placed in the thermostat. Whenever it was necessary to correct for the reaction occurring during the temperature equilibration, a sample was analyzed as soon as constant temperature was reached and zero time was recorded.

The rate of loss of optical activity was determined as follows: At appropriate time intervals ampules containing the active samples were opened and exactly 1.994-ml. aliquots were diluted with acetonitrile to 13.00 ml. and the rotations measured. The first-order rate constants for the loss of activity (k_1' and k_2') were determined by use of equation 11. Typical data are shown in Table II and Fig. 1.

The rates of decomposition of the acid phthalates into 5-methyl-1,3-cyclohexadiene were determined as follows: Aliquots (4.99 ml.) of the inactive samples were dissolved in 10 ml. of acetone and diluted with 25 ml. of water. After standing for 5 minutes at room temperature the solutions were titrated to the phenolphthalein end-point with standard 0.1 N sodium hydroxide solution. This method of analysis was shown by analysis of known samples to determine phthalic anhydride together with free phthalic acid and acid phthalate. The rates of decomposition (k_{dc} and k_{dt}) were determined from the increase in acidity (carboxyl groups) by use of equations 7 or 7'.

The rates of geometric isomerization were determined from the unused portion of the contents of the ampules used to determine the rate of decomposition.

The solvent was evaporated from 10.00-ml. aliquots (larger aliquots were required when the decomposition exceeded 30%) at room temperature under a stream of filtered air. The residue was dried at reduced pressure overnight. The residue was dissolved in chloroform and the insoluble phthalic acid separated by filtration. The insoluble material was shown to be phthalic acid by melting point and neutral equivalent. The acid phthalate was separated from phthalic anhydride by quantitatively extracting it from the organic layer with three 10-ml. portions of ice-cold 5% sodium hydroxide. The combined aqueous layers were filtered through a cotton plug to remove all of the droplets of chloroform and the clear aqueous extracts were acidified with an equal volume of cold 5% hydrochloric acid. The oily acid phthalate that separated was taken up in 15 ml. of freshly distilled chloroform. The organic layer was washed with water, dried, filtered and evaporated under a stream of filtered air. After drying overnight at reduced pressure over calcium chloride the composition of the residual mixture of I and II was determined by infrared analysis. In every case the infrared spectrum showed the residue obtained by this procedure to be a binary mixture of I and II. The rates of isomerization, k_{ic} and k_{it} , were determined from the composition of the binary mixture by use of equations 5 and 5'. The concentrations of *cis*- and *trans*-acid phthalates can be determined at any time during the rearrangement from the composition of the remaining acid phthalate together with the amount of acid phthalate that has decomposed. Data for typical experiments are shown in Tables I and IV.

Synthetic mixtures of I and II consisting of 54, 78 and 93% of II were isolated from simulated reaction mixtures by this method to show that this procedure does not result in fractionation. In each case the infrared spectrum of the isolated sample was indistinguishable from that of the freshly prepared binary mixture. This demonstrates that the composition of the mixture of I and II produced in the reaction is not altered by over 1% by the method of isolation.

Isolation of the Decomposition Products from *cis*-5-Methyl-2-cyclohexenyl Acid Phthalate.—A solution of 13 g. of *dl*-I in 186 g. of acetonitrile (0.200 M solution) was sealed in ampules and placed in a 100° thermostat for 400 hours (more than ten half-periods for the decomposition: $k_{dc} = 0.019 \text{ hr.}^{-1}$). The solution was diluted with about one liter of water, made strongly alkaline with 5% sodium hydroxide and extracted with three 50-ml. portions of ether. After washing with water the combined ether extracts were dried over calcium chloride. The ether solution was distilled under purified nitrogen. The fractions obtained after removal of ether are given in Table VII.

The maleic anhydride adduct of 5-methyl-1,3-cyclohexadiene was prepared from the second fraction (b.p. 41–78°) as follows. To 4.0 ml. of the second fraction was added 0.30 g. (17% excess) of maleic anhydride. After standing overnight the solvent was evaporated at room temperature

TABLE VII

THE DISTILLATION OF THE NON-ACIDIC VOLATILE PRODUCTS OF THE REARRANGEMENT OF *dl-cis*-5-METHYL-2-CYCLOHEXYL ACID PHTHALATE (I) IN ACETONITRILE AT 100°

| B.p., 740 mm. | Wt., g. | λ_{max} , Å. ^a | MCHD, ^b mg./ml. |
|---------------|-------------------|--|----------------------------|
| 34–41 | ca. 30 ml. | 2630 | 2.7 |
| 41–78 | ca. 5 ml. | 2590 | 61.2 |
| 78–80.5 | 2.06 ^c | 2580 | 27.2 |
| 80.5–80.5 | 0.66 | 2590 | 5.4 |
| 80.5 | 0.42 | 2600 | 36.4 |

^a Ultraviolet spectra of samples dissolved in 95% ethanol were determined with a Cary recording ultraviolet spectrophotometer and a 1-cm. cell. ^b Concentrations of 5-methyl-1,3-cyclohexadiene (MCHD) were calculated from the observed optical densities at the wave lengths of the maxima according to the formula $\text{mg./ml.} = \text{opt. dens.} [\text{m.w./}\epsilon \times l]$, using $\epsilon = 4910$.¹² The concentration calculated in this way is in excellent agreement with the amount of maleic anhydride adduct obtained from a sample of the distillate. ^c Almost completely soluble in water, $n_D^{25} 1.3462$ (acetonitrile, $n_D^{16.5} 1.3460$).

and 0.51 g. (102% yield based on analysis in Table VII) of solid adduct was obtained. After recrystallization from petroleum ether this compound melted at 77.2–79.0°.

Anal. Calcd. for $\text{C}_{11}\text{H}_{12}\text{O}_3$: C, 68.73; H, 6.30. Found: C, 68.90; H, 6.43.

The isolation and separation of phthalic acid from the remaining acid phthalate is described above.

The Rearrangement of *cis*-5-Methyl-2-cyclohexenyl Acid Phthalate in the Presence of 3-Nitro Acid Phthalate Ion.—To a solution of 1.301 g. (5.0 mmoles) of I in 25 ml. of acetonitrile was added 1.000 g. (4.74 mmoles) of 3-nitrophthalic acid and 1.001 g. (4.74 mmoles) of diphenylguanidine.²⁷ The solution was sealed in an ampule and heated at 100° for 25.2 hours.²⁸ The solution was evaporated to dryness at room temperature and the dried solid residue was treated with two 25-ml. portions of water to remove most of the diphenylguanidinium salts. After drying the water-insoluble material the acid phthalates were separated from the phthalic acids by the method described above for the isomerization studies (the acid phthalates are soluble in chloroform whereas 3-nitrophthalic acid and phthalic acid are insoluble in this solvent). This method was shown to remove all of the acids without fractionating the mixture of acid phthalates²⁹ and 3-nitro acid phthalates.²⁹

The content of 5-methyl-2-cyclohexenyl 3-nitro acid phthalate²⁹ in the mixture of acid phthalates was determined by infrared analysis. The 3-nitro acid phthalates have an absorption band at 6.50 μ (due to the nitro group)³⁰ where neither I nor II absorbs. Because of deviations from Beer's law the composition of the mixture was determined by comparing the transmission at 6.50 μ with that of synthetic mixtures. The comparison of these spectra indicated the complete absence of interfering impurities.

The experiment using one-half as much foreign anion was carried out in the same way.

Determination of Equilibrium Composition of *cis*- and *trans*-5-Methyl-2-cyclohexenyl Acid Phthalates in Acetonitrile at 100°.—An equilibrium composition consisting of 65% *trans* and 35% *cis* is indicated by the values of k_{ic} and k_{it} (Tables III and V). In order to test this computation a solution of 1.822 g. (7.00 mmoles) of I and 3.384 g. (13.00 mmoles) of II in 100 ml. of acetonitrile was distributed in

(27) Diphenylguanidinium 3-nitro acid phthalate, prepared by the method of S. Winstein, *et al.*, THIS JOURNAL, **70**, 812 (1948), was found to be extremely hygroscopic and for this reason the salt was prepared in the reaction mixture.

(28) From the value of k_{dt} (0.019 hr.^{-1}) it can be shown that about 27% of the acid phthalate is decomposed during this period. Actually this value for the decomposition is a lower limit because of the probable positive salt effect of the diphenylguanidinium salt.

(29) A mixture of *cis* and *trans* isomers is undoubtedly formed. The isomeric composition was not determined.

(30) H. M. Randell, R. G. Fowler, N. Finson and J. R. Dangl, "Infrared Determination of Organic Structures," D. Van Nostrand Co., Inc., New York, N. Y., 1943, pp. 33–34.

ampules and placed in the 100° thermostat. Samples were withdrawn periodically and the amount of decomposition and the composition of the remaining acid phthalate were determined as described above. The data for this experiment (Fig. 5, curve B) show that the composition of the acid phthalate mixture (65% *trans*, 35% *cis*) remained constant for the 55 hours that the reaction was observed.

Rearrangement of Fused *cis*-5-Methyl-2-cyclohexenyl Acid Phthalate.—Carefully weighed samples (*ca.* 0.23 g.) of solid (–)I were sealed in ampules and immersed in the 100° bath. At measured time intervals samples were quantitatively transferred to 25.00-ml. volumetric flasks and diluted with chloroform to exactly 25 ml. at 25°. The rate of loss of optical activity was determined from the rotations of the chloroform solutions.

Samples of isomer *dl*-I were used to study the decomposition and the isomerization. The acidity (decomposition) of the heated samples (*ca.* 0.3 g.) was determined by ti-

tration of aqueous acetone solutions to the phenolphthalein end-point. The increase in acidity (carboxyl groups) did not correspond to the formation of phthalic acid. For example, in 8 hours the number of carboxyl groups increased only 11.5%; however, a 28% yield of phthalic acid was isolated as follows. The contents of an ampule were extracted with chloroform and the insoluble phthalic acid collected on a filter and air-dried. This material was water insoluble and had a neutral equivalent of 78 (calcd. for phthalic acid 83).

Large samples (*ca.* 1 g.) of *dl*-I were used to study the rate of *cis-trans* isomerization. The remaining acid phthalate was separated from the phthalic acid and the composition of the binary mixture determined spectrophotometrically by the procedure described above for the rearrangement in acetonitrile. Typical data showing the change in composition with time are presented in Fig. 7.

MADISON, WISCONSIN

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, WAYNE UNIVERSITY]

Polymers. I. Synthesis of an All-*cis* Diene Polymer¹

BY WILLIAM J. BAILEY² AND HAROLD R. GOLDEN³

RECEIVED APRIL 29, 1954

The cyclic diene, 1,2-dimethylenecyclohexane, was polymerized to a high molecular weight, all-1,4-, all-*cis* diene polymer. This polymer was a white crystalline solid, melting at 165° and possessing no rubber-like properties, even though it is very similar in structure to natural rubber.

Although much work has been published on the correlation of the structure and properties of condensation polymers,⁴ no such comprehensive study has been reported for hydrocarbon polymers. Hydrocarbon polymers appeared to be an attractive field to study the effect of structure on properties since two complicating factors, hydrogen bonding and strong dipole interactions, are absent. Also, addition polymers of high molecular weight could be studied to eliminate further the additional complicating effect of molecular weight on the properties. With the number of variables thus reduced, it would appear much easier to develop a systematic correlation with hydrocarbon polymers than was possible with condensation polymers.

Natural rubber I appeared to be a logical starting point for this investigation, since its structure has been determined and found to be fairly simple. It is of further interest because natural rubber I is probably still the best available all-purpose rubber, even though many excellent special purpose elastomers have been developed. If other special purpose elastomers are to be discovered, knowledge of which structural features of natural rubber I are responsible for its excellent rubbery properties would be indeed helpful.

Natural rubber has been assigned a very regular structure composed of repeating isoprenoid units in which all the units are connected in a 1,4-, head-

to-tail manner with the methyl groups always on the same side of the double bond.⁵ All the double bonds have the *cis* structure; that is, the polymer chain enters and leaves from the same side of the double bond. Since there are relatively few structural features in this polymer, it should be possible to determine the relative importance of each in producing rubbery characteristics. The first clue to which feature was most important was available from a comparison of the structure of balata II (or gutta percha) with that of rubber. Balata II has been assigned a structure very similar to natural rubber, with the exception that the double bonds have the *trans* structure⁶; that is, the polymer chain enters and leaves from opposite sides of the double bond. Balata II is not a rubber at room temperature but is a hard, horny substance with a softening point at 60°,⁶ while natural rubber maintains its rubbery properties to extremely low temperatures but will retain crystallites up to 25°. This striking difference in the properties of these two polymers led to the widespread belief that any all-*cis* diene polymer would be a good rubber. It was considered of extreme importance, therefore, to synthesize an all-*cis* diene polymer in order to test this hypothesis.

Much energy has been spent in an effort to find experimental conditions that would permit simple dienes, such as 1,3-butadiene, to polymerize to an all-*cis* polymer or to a polymer with at least a high content of 1,4-*cis* units. However, the problem is extremely complex since butadiene can produce a polymer III consisting theoretically of a mixture of six structural units, as indicated in the diagram. Although experimental conditions will change the

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(2) Department of Chemistry, University of Maryland, College Park, Md.

(3) Atomic Energy Commission Fellow, 1949-1950.

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