present at low concentration and in a solvent that does not produce anomalous changes in shielding.[33,34] These estimates are compared in Table III with theoretical values from other sources.

The experimental charge distributions in Table III show all the features that are expected from the relative reactivities of the different positions. They also closely resemble the type of charge distribution predicted by the molecular orbital and resonance theories of aromatic molecules. Since the theoretical calculations are based on highly simplified assumptions and are not intended to provide accurate electron densities, it is not surprising that there are, at times, fairly large discrepancies between the calculated and "experimental" values. In particular, they involved assigning an "electronegativity parameter" to nitrogen and oxygen. A recent theoretical discussion[35] suggests that some of the work quoted here is based on too large a value for this parameter and may exaggerate the non-uniformity of the charge distribution.

TABLE III

CHARGE DENSITIES IN AROMATIC COMPOUNDS ESTIMATED FROM PROTON CHEMICAL SHIFTS

Compound	Excess electron density, q *ortho*	*meta*	*para*	Origin
Nitrobenzene	−0.097	−0.030	−0.042	Chemical shifts[a] and eq. 1
	− .15	.00	− .17	[b]
Aniline	.077	.013	.040	Chemical shifts and eq. 1
	.02	.00	.02	[b]
Pyridine	− .13	.00	− .037	Chemical shifts[d,e] and eq. 1
	− .151	− .053	− .178	[c]

[a] P. C. Corio and B. P. Dailey, THIS JOURNAL, **78**, 3043 (1956). [b] Molecular orbital calculations by G. W. Wheland and L. Pauling, *ibid.*, **57**, 2086 (1935). [c] Molecular orbital calculations by H. C. Longuet-Higgins and C. A. Coulson, *Trans. Faraday Soc.*, **43**, 87 (1947). [d] Spectrum of 3% pyridine in CCl_4 taken in these laboratories. [e] Chemical shifts analyzed by W. G. Schneider, H. J. Bernstein and J. H. Pople, *Can. J. Chem.*, **35**, 1487 (1957).

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(33) A. A. Bothner-By and R. E. Glick, *J. Chem. Phys.*, **26**, 1651 (1957).

(34) A. A. Bothner-By and R. E. Glick, THIS JOURNAL, **78**, 1071 (1956).

(35) A. Lofthus, *Mol. Phys.*, **2**, 367 (1959).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF WISCONSIN, MADISON 6, WIS.]

Stereochemistry of Allylic Rearrangements. XI. The Isomeric Rearrangement of *trans*-5-Methyl-2-cyclohexenyl *p*-Nitrobenzoate-carbonyl-O^{18} in Aqueous Acetone[1]

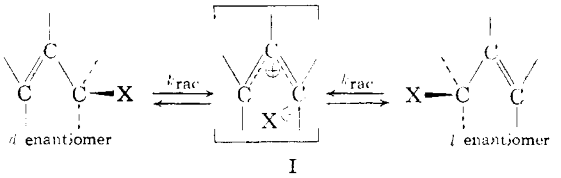
BY HARLAN L. GOERING AND JOYCE TAKAHASHI DOI

RECEIVED APRIL 8, 1960

Optically active *trans*-5-methyl-2-cyclohexenyl *p*-nitrobenzoate undergoes simultaneous racemization and solvolysis in 80% acetone. The racemization is a stereospecific intramolecular isomeric allylic rearrangement—racemization is not accompanied by geometric isomerization or exchange with added *p*-nitrobenzoate ion. Carbonyl-O^{18} ester undergoes equilibration of the label between the two positions about twice as fast as it racemizes. Thus there is a path whereby the oxygen atoms become equivalent without loss of optical configuration. Presumably oxygen scrambling and racemization involve internal return. However, there must be more than one intermediate of this type: one which is common to the two enantiomers (involved in racemization and scrambling) and one which is not common to both enantiomers (involved in oxygen scrambling without racemization).

Introduction

Symmetrical allylic chlorides,[2] acid phthalates[3] and *p*-nitrobenzoates[4,5] undergo simultaneous racemization and solvolysis in hydroxylic solvents. The racemization, which accompanies solvolysis, results from an intramolecular stereospecific allylic rearrangement.[2-5] Presumably this process involves return from an internal ion pair intermediate I as



I

(1)

The solvolysis, which does not disturb the rearrangement (racemization), is not included in this scheme.

The preceding paper in this series describes an investigation of the relative positions of the oxygen atoms in the reactant and product for the rearrangement (racemization) of *trans*-α,γ-dimethylallyl *p*-nitrobenzoate in aqueous acetone.[5a] In that system it was found that carbonyl-O^{18} ester undergoes first-order equilibration of the label between the two positions at the same rate as active ester racemizes; *i.e.*, k_{eq} (eq. 2) is the same as k_{rac} (eq. 3).[5a,6]

$$dl\text{-}ROCO^{18}C_6H_4NO_2 \xrightarrow{k_{eq}} dl\text{-}RO^{18}CO^{18}C_6H_4NO_2 \quad (2)$$

$$\text{(active) } ROCOC_6H_4NO_2 \xrightarrow{k_{rac}} \text{(racemic) } ROCOC_6H_4NO_2 \quad (3)$$

With carbonyl-O^{18} optically pure (+)-ester it was shown that there is a tendency for the carbonyl-oxygen atom in the reactant (one enantiomer) to become the ether-oxygen atom in the product (the other enantiomer). If the reaction proceeded exclusively as summarized by II, k_{eq} would equal

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[1] This work was supported in part by the National Science Foundation and in part by the Research Committee of the Graduate School with funds given by the Wisconsin Alumni Research Foundation.

(2) H. L. Goering, T. D. Nevitt and E. F. Silversmith, THIS JOURNAL, **77**, 5026 (1955).

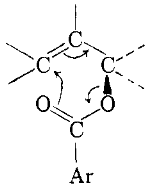
(3) (a) H. L. Goering and E. F. Silversmith, *ibid.*, **77**, 1129 (1955); (b) H. L. Goering and R. W. Greiner, *ibid.*, **79**, 3464 (1957).

(4) H. L. Goering and E. F. Silversmith, *ibid.*, **77**, 6249 (1955).

(5) (a) H. L. Goering and M. M. Pombo, *ibid.*, **82**, 2515 (1960); (b) H. L. Goering, *Rec. Chem. Prog.*, 109 (1960).

(6) M. M. Pombo, unpublished results.

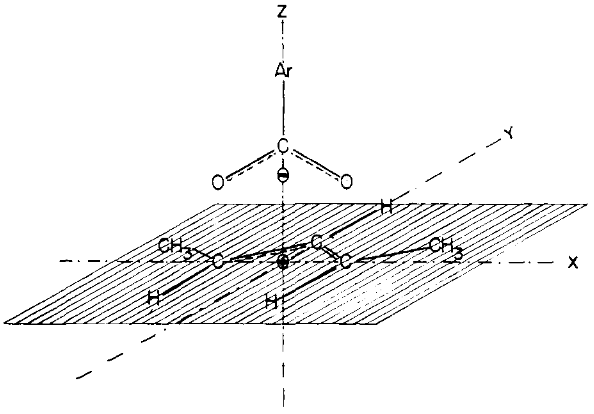
k_{rac} but the enantiomers would remain discretely labeled throughout the reaction, the (+)-enantiomer in the carbonyl position and the (−)-enantiomer in the ether-oxygen position (*e.g.* (+)-$ROCO^{18}$ Ar $\rightleftarrows$ (−)-$RO^{18}COAr$). However, this is not the case. At 100° in 90% aqueous acetone the oxygen atoms become scrambled in the enantiomers by a first-order process at a rate 1/2.9 times that of racemization; *i.e.*, k_S (eq. 4)/k_{rac} (eq. 3) = 1/2.9. In eq. 2-4, R = *trans*-α,γ-dimethylallyl and in eq. 2 and 4, *dl*-RO^{18}-$CO^{18}C_6H_4NO_2$ represents racemic ester with the label equally distributed between the two positions in each enantiomer.



II

$$\left.\begin{array}{l}(+)\text{-ROCO}^{18}\text{C}_6\text{H}_4\text{NO}_2\\(-)\text{-RO}^{18}\text{COC}_6\text{HNO}_2\end{array}\right\}\xrightarrow{k_S} dl\text{-RO}^{18}\text{CO}^{18}\text{C}_6\text{H}_4\text{NO}_2 \quad (4)$$

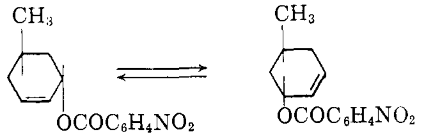
These observations suggest that in this case the ion pair intermediate I involved in the racemization has the geometry illustrated by III.[5] In this structure the plane of the carboxylate ion is nearly or completely perpendicular to and intersects the plane of the cation (x, y-plane) at the allylic carbon atoms.[5] There is equal chance that the intermediate will be converted to either enantiomer (reaction of the anion with the two equivalent allylic carbon atoms produces the two enantiomers) and there is also the same probability that either oxygen will become the ether-oxygen atom. In other words, this structure requires that k_{eq} (eq. 2) = k_{rac} (eq. 3).



III

The observation that k_S (eq. 4)< k_{rac} suggests that the indicated orientation of the carboxylate ion in III represents an energy minimum which is separated by a small barrier from the equivalent structure derived by rotating the carboxylate ion 180° about the *Z*-axis. Thus there is not an equal chance that either oxygen atom will become attached to a specific carbon atom. Rather, there is a greater than even chance that the oxygen atoms will become connected to the nearest carbon atom. In fact, under the above-mentioned conditions the oxygen atoms in III react with the nearest carbon atom (the one directly below) about 4 times faster than with the other carbon atom. In other words, rotation of the carboxylate ion (about the *Z*-axis) with respect to the cation (which results in scrambling of the oxygen atoms in the enantiomers) is a little slower than the conversion of III to racemic allylic ester.

In the present work a similar investigation in the *trans*-5-methyl-2-cyclohexenyl system (IV) has brought a new phenomenon to light. Unlike with the *trans*-α,γ-dimethylallyl system, in aqueous acetone equilibration of the oxygen atoms in IV occurs faster than racemization; *i.e.*, $k_{eq} > k_{rac}$. This means that there is a path whereby the oxygen atoms become equilibrated with retention of the optical configuration.



IVa

As shown in the illustration, in this system the intramolecular rearrangement which accompanies solvolysis results only in the interconversion of enantiomers (racemization). The rate constant for the first-order racemization (k_{rac}) is the difference between the rate constants for loss of optical activity (k_α) and solvolysis (k_t); *i.e.*, $k_{rac} = k_\alpha - k_t$,[5] and thus can be determined readily. That the racemization in hydroxylic solvents is stereospecific and intramolecular (racemization of *cis*- and *trans*-5-methyl-2-cyclohexenyl *p*-nitrobenzoate is not accompanied by geometric isomerization[4]) had been shown earlier and this has been reconfirmed in the present work.

Results

Optically pure (−)-*trans*-5-methyl-2-cyclohexenyl acid phthalate, $[\alpha]^{25}D$ −266° ($CHCl_3$), was obtained by recrystallization of the brucine salt[7] followed by recrystallization of the acid phthalate to constant rotation. This material, which had a rotation twice as large as that reported previously,[7] was shown to be optically pure by an isotope dilution method.[8] The active acid phthalate was converted to active *trans*-5-methyl-2-cyclohexenyl *p*-nitrobenzoate (IV) which was used to determine the polarimetric rate constants.

The polarimetric (k_α) and titrimetric (k_t) first-order rate constants for the solvolysis of IV in aqueous acetone are shown in Table I. These constants were determined by the methods used earlier.[4,5a] The reactions were followed to about 80% reaction and in all cases good first-order behavior was observed. Each value of k_α and k_t is the average (and mean deviation) of 6 to 8 values determined at appropriate time intervals during the reaction.

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

(8) J. A. Berson and D. A. Ben-Efraim, *ibid.*, **81**, 4083 (1959).

TABLE I

POLARIMETRIC (k_α) AND TITRIMETRIC (k_t) FIRST-ORDER RATE CONSTANTS FOR SOLVOLYSIS OF *trans*-5-METHYL-2-CYCLOHEXENYL *p*-NITROBENZOATE IN AQUEOUS ACETONE

Expt.	*T*, °C.	Ester, 10^2M	10^2k_α, hr.$^{-1}$	10^2k_t, hr.$^{-1}$	10^2k_{rac},[b] hr.$^{-1}$
		80% aqueous acetone[a]			
1[c]	99.83	5		1.33 ± 0.02	0.71
2[c]	99.83	5	2.04 ± 0.01		
3	99.72	4.56		1.30 ± .04	.69
4	99.72	5.00	1.99 ± .07		
5	99.65	4.61		1.28 ± .02	.66
6	99.65	4.55	1.94 ± .04		
		60% aqueous acetone[a]			
7	99.72	1.66		16.7 ± 0.2	6.9
8	99.72	1.5	23.6 ± 1.0		
9	99.72	1.37		16.5 ± .4	7.3
10	99.72	1.9	23.8 ± 0.6		

[a] Solvent composition based on volumes of pure components at 25° prior to mixing. [b] First-order constant for racemization which accompanies solvolysis ($k\alpha - k_t$). [c] Taken from ref. 4.

Since both k_α and k_t show *no* trends, it is clear that racemization (k_{rac}) is a first-order process. It was shown in an earlier paper[4] that solvolysis involves alkyl-oxygen rather than acyl-oxygen cleavage. The rate constants determined in the present study agree well with those reported previously[4] (*cf.* expts. 1 and 2 with 3–6).

The rate of equilibration of the oxygen atoms (eq. 2) associated with the racemization and solvolysis in aqueous acetone at 100° was determined using carbonyl-O^{18} *dl*-IV. In the present system the difference between k_α and k_t is not as large as for *trans*-α,γ-dimethylallyl *p*-nitrobenzoate.[4] Thus samples of unsolvolyzed ester IV cannot be isolated after as many interconversions between enantiomers as was possible with the acyclic system.[5a] The value of k_{rac}/k_t is 0.53 for 80% acetone and 0.43 for 60% acetone. Thus, during a period corresponding to 50% racemization of the unsolvolyzed ester, in 80% acetone 73% of the original ester is solvolyzed and in 60% acetone 80% of the ester is solvolyzed.

In control experiments 0.04 *M* *dl*-*trans*-5-methyl-2-cyclohexenyl *p*-nitrobenzoate-carbonyl-O^{18} (2.45 ± 0.02 atom % excess O^{18}) in (a) 80% acetone, (b) 80% acetone containing 0.02 *M* *p*-nitrobenzoic acid and (c) 80% acetone containing 0.02 *M* sodium *p*-nitrobenzoate was heated at 100° for 92.5 hours. This corresponds to about 47% racemization and 70% solvolysis. The O^{18} contents of the recovered unsolvolyzed samples were 2.52 ± 0.02, 2.54 ± 0.05 and 2.46 ± 0.02, respectively. The fact that no exchange occurred demonstrates that the rearrangement (racemization) is intramolecular and that the oxygen atoms in IV do not exchange with the solvent. Comparison of the infrared spectra of the isolated samples with those of authentic *cis*- and *trans*-5-methyl-2-cyclohexenyl *p*-nitrobenzoate[4,7] confirmed that geometric integrity is maintained throughout the solvolysis.

The extent of oxygen equilibration was determined by isolation of the unsolvolyzed labeled ester at appropriate time intervals and determining the distribution of the label between the two positions. This was accomplished by hydrolysis in a manner which involves exclusive acyl-oxygen cleavage (methanolic potassium hydroxide) followed by determination of the O^{18} content of the resulting *trans*-5-methyl-2-cyclohexenol (as the *p*-nitrobenzoate derivative). The O^{18} abundance in the alcohol corresponds to that of the ether-oxygen position of the ester.

The following results were obtained from control experiments. (a) Isolation of optically active IV by the method used in the kinetic experiments did not result in loss of optical activity. This proves that racemization (rearrangement) does not occur during isolation. (b) Saponification of carbonyl-O^{18} IV gave alcohol containing no excess O^{18}. (c) Conversion of partially active *trans*-5-methyl-2-cyclohexenol to the *p*-nitrobenzoate followed by saponification of the latter gave alcohol having the original rotation. This demonstrates that saponification involves exclusive acyl-oxygen cleavage. These experiments show that the oxygen atom in the alcohol obtained by saponification is the ether-oxygen atom in the ester.

First-order rate constants for the equilibration of oxygen atoms in ester (k_{eq}, eq. 2) were determined by use of eq. 5 in which a is the O^{18} content of the carboxyl group at zero time and x is the O^{18} content of the ether oxygen at time t. In this equation a corresponds to amount of unequilibrated ester at zero time and $(a - 2x)$ corresponds to the remaining unequilibrated ester at time t.

$$k_{eq} = (1/t) \ln a/(a - 2x) \qquad (5)$$

Data for two kinetic experiments for the racemization in 80% acetone and one experiment for the racemization in 60% acetone are presented in Table II. This table includes the extent of solvolysis at the time of isolation of the unsolvolyzed ester (column 2) and the extent of oxygen equilibration of the unsolvolyzed ester (column 4) as well as the rate constants.

TABLE II

KINETIC DATA FOR O^{18} EQUILIBRATION DURING RACEMIZATION OF *dl-trans*-5-METHYL-2-CYCLOHEXENYL *p*-NITROBENZOATE

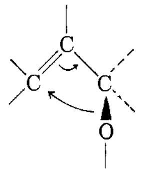
Time, hr.	Solvolysis, %	x[a] [b]	Equilibrated,[c] %	k_{eq}, 10^2 hr.$^{-1}$
	Expt. 11, 99.72°, 80% acetone, a = 3.82[a]			
0	0	0	0	
23.2	25.9	0.462 ± 0.002	24.2	1.19
51.2	48.5	0.876 ± 0.004	45.8	1.20
	Expt. 12, 99.65°, 80% acetone, a = 2.93[a]			
0	0	0	0	
41.8	41.9	0.56 ± 0.01	38.2	1.16
80.3	64.8	0.87 ± 0.02	59.4	1.12
	Expt. 13, 99.72°, 60% acetone, a = 3.00[a]			
0	0	0		
2.0	28.1	0.304 ± 0.006	20.3	11.3
4.0	48.5	.480 ± .006	32.0	9.6
6.5	66.0	.744 ± .016	49.6	10.5

[a] Atom % excess O^{18}. [b] Oxygen-18 abundance of ether-oxygen atom in unsolvolyzed ester. [c] Percentage of unsolvolyzed ester which has equal amounts of O^{18} at two positions; *i.e.*, $(2x/a)100$.

Discussion

Comparison of the first-order rate constants for equilibration of the oxygen atoms in IV (k_{eq}, Table II) with those for racemization (k_{rac}, Table I) for the corresponding conditions shows that $k_{eq} > k_{rac}$. Evidently the racemization under these conditions involves internal return from an ion pair intermediate as illustrated by eq. 1. This process in its simplest form, however, cannot account for all of the oxygen scrambling observed in the present case.

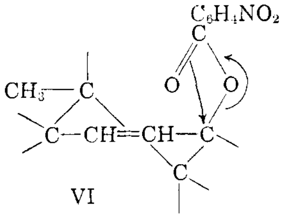
For internal return of the type illustrated by eq. 1 it is possible to visualize a situation where $k_{rac} > k_{eq}$. The structure of I might be such that the rearrangement could be summarized by V. In this case the rearrangement would result in racemization but not in equilibration of the oxygen atoms. Regardless of the structure of I, k_{eq} cannot exceed k_{rac} for eq. 1. If the structure of I is such that racemization is summarized by II (*i.e.*, no rotation of the anion with respect to the cation in III) or if both oxygen atoms become equivalent in I, $k_{rac} = k_{eq}$.



V

Presumably racemization involves an intermediate of the type illustrated by I and III. In symmetrical allylic systems this intermediate has a plane of symmetry and thus is inactive. Moreover the oxygen atoms are equivalent. This is indicated by the fact that for the racemization of *trans*-α,γ-dimethylallyl *p*-nitrobenzoate[5a] and *cis*-5-methyl-2-cyclohexenyl *p*-nitrobenzoate[9] $k_{eq} = k_{rac}$. In other words, in these systems rearrangements of the type illustrated by V do not contribute to the racemization and there is no reason for suspecting contributions of this type in the present case. Thus formation of the intermediate involved in the racemization of IV (measured by k_{rac}) involves complete equilibration of the oxygen atoms.

The excess scrambling which does not result in racemization (rearrangement) is summarized by VI and eq. 6. The first-order rate constant for equilibration by this process (k_{eq}') is the difference between k_{eq} and k_{rac} (*i.e.*, $k_{eq}' = k_{eq} - k_{rac}$). The value of $10^2\ k_{eq}'$ for 100° is 0.48 hr.^{-1} for 80% acetone and 3.4 hr.^{-1} for 60% acetone. Evidently this process also involves internal return from an ion pair intermediate which unlike I or III (the intermediate involved in racemization) is not common to the two enantiomers but rather is asymmetric. Internal return from an ion pair is indicated by the fact that k_{eq}' shows essentially the same dependence on the ionizing power of the solvent as k_α, k_t and k_{rac}. The rate constants are about tenfold larger for 60% acetone than for 80% acetone; however, the values of k_{eq}'/k_{rac} are similar for the two solvents (0.7 for 80% acetone and 0.5 for 60% acetone).



VI

$$d\text{-ROCO}^{18}\text{C}_6\text{H}_4\text{NO}_2 \xrightarrow{k_{eq}'} d\text{-RO}^{18}\text{CO}^{18}\text{C}_6\text{H}_4\text{NO}_2 \quad (6)$$

Why there is excess oxygen equilibration in the present case but not in the *trans*-α,γ-dimethylallyl[5a,6] or *cis*-5-methyl-2-cyclohexenyl[9] systems is not clear. Evidently in the latter two cases the substrate reacts completely *via* a conformation which corresponds to III. In other words, the bonds in the substrate are rotated so that the carbonyl-oxygen atom is located perpendicular to the plane of the double bond and as close as possible to the γ-carbon atom. This rotational conformation permits a gradual transition to III. Thus in these cases the only intermediate formed is common to both enantiomers.

On the other hand, in IV there is evidently more than one conformation eligible for ionization. One of these is the one discussed above which gives rise to the intermediate corresponding to III (this results in racemization and equilibration). In the other(s) the rotation about the carbon–oxygen bonds is such that the carbonyl-oxygen is closer to $C\alpha$ than $C\gamma$. Ionization gives rise to an ion pair intermediate in which both oxygen atoms are closer to $C\alpha$ than $C\gamma$. This portion of the ionization results in oxygen equilibration but not in racemization (the intermediate is not common to the enantiomers).

From examination of scale models it is not apparent why different conformations should be involved in these systems.

Experimental

Materials.—Pure *dl-trans*-5-methyl-2-cyclohexenyl *p*-nitrobenzoate (IV), m.p. 85.6–87.0°, was obtained by recrystallization (95% ethanol) of a mixture of *cis*- and *trans*-5-methyl-2-cyclohexenyl *p*-nitrobenzoate[7] consisting of about 95% of the *trans* isomer. The mixture was prepared[7] from alcohol having the same composition which in turn was obtained by hydrolysis of 5-methyl-2-cyclohexenyl chloride.[10]

A solution of 65 g. (0.50 mole) of 5-methyl-2-cyclohexenyl chloride[11] (the configurational composition of the chloride is unimportant)[10] and 100 g. (0.94 mole) of anhydrous sodium carbonate in 2.75 l. of 27% aqueous acetone was refluxed for 30 minutes. The solution was concentrated to about 2 l. under reduced pressure and saturated with sodium chloride. Extraction with ether followed by distillation of the dried extract (K_2CO_3) gave 42 g. of 5-methyl-2-cyclohexenol (*ca.* 95% *trans* isomer), b.p. 67–70° (13 mm.).

Pure *dl-trans*-5-methyl-2-cyclohexenol was obtained by saponification of the pure *p*-nitrobenzoate.[7] The preparation and resolution of *dl-trans*-5-methyl-2-cyclohexenyl acid phthalate have been described previously.[7] The brucine salt of the acid phthalate was recrystallized ten times from acetone and had $[\alpha]^{25}\text{D}$ 108–113° ($CHCl_3$), m.p. 140.4–

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[9] Unpublished observation by J. T. Doi.

[10] E. F. Silversmith, Ph.D. Dissertation, University of Wisconsin, Madison, Wisc., 1956.

[11] H. L. Goering, T. D. Nevitt and E. F. Silversmith, THIS JOURNAL, **77**, 4042 (1955).

142.0°. The acid phthalate obtained from this salt was recrystallized to constant rotation from ether–pentane mixtures. This material had $[\alpha]^{25}D$ −266 ± 2° ($CHCl_3$), lit.[7] $[\alpha]^{25}D$ −130.4° ($CHCl_3$), and was shown to be optically pure (see below).

Anal. Calcd. for $C_{15}H_{16}O_4$: C, 69.21; H, 6.20; neut. equiv., 260.3. Found: C, 69.14; H, 6.20; neut. equiv., 260.7.

Saponification of the acid phthalate with 2.5 *M* sodium hydroxide[7] gave optically pure (−)-*trans*-5-methyl-2-cyclohexenol, $[\alpha]^{23}D$ −265° (neat). This alcohol was converted to optically pure (−)-*trans*-5-methyl-2-cyclohexenyl *p*-nitrobenzoate, m.p. 70–71°, $[\alpha]^{25}D$ −295.3° (*c* 0.98, acetone).

Carbonyl-O^{18} IV was prepared from the pure alcohol and carbonyl-O^{18} *p*-nitrobenzoyl chloride.[5a]

Determination of Optical Purity of (−)-*trans*-5-Methyl-2-cyclohexenyl Acid Phthalate.—The optical purity of the acid phthalate described above was established by a modification of the isotope dilution method described by Berson and Ben-Efraim.[8]

dl-trans-5-Methyl-2-cyclohexenyl acid phthalate-7-C^{14} was prepared from pure *trans*-alcohol and phthalic anhydride-7-C^{14} (Tracerlab Inc.). After purification by recrystallization (ether–pentane mixtures) this material gave a correct carbon and hydrogen analysis, melted at 89–91° and had 68,200 ± 300 d.p.m.[12]

A mixture of 1.4954 g. of (−)-acid phthalate, $[\alpha]^{25}D$ −265.2°($CHCl_3$), and 0.7004 g. of radioactive *dl*-acid phthalate was dissolved in 15 ml. of acetone containing 3.368 g. of brucine. The brucine salt was recrystallized five times and the recovered acid phthalate was then recrystallized from ether–pentane until optically pure; *i.e.*, $[\alpha]^{25}D$ −265.9° ($CHCl_3$). The radioactivity of the optically pure sample was 12,980 ± 90 d.p.m. From these data it can be determined[8] that optically pure (−)-acid phthalate has $[\alpha]^{25}D$ −265 ± 2° ($CHCl_3$).

Polarimetric and Titrimetric Rates.—The ampule technique[3,4] was used to obtain k_α and k_t. For the polarimetric runs aliquots (in ampules) were stored at 10° and then rotations on successive aliquots were determined at 25 ± 1°. A 4-dm. polarimeter tube equipped with central tubulation for filling was used to determine the rotations and the end-plates of the polarimeter tube were not removed during a kinetic experiment. The total change in optical rotation during a run was about 2–3°.

Determination of O^{18} Equilibration in *dl-trans*-5-Methyl-2-cyclohexenyl *p*-Nitrobenzoate-carbonyl-O^{18}.—Solutions (0.05 *M*) of *dl-trans*-5-methyl-2-cyclohexenyl *p*-nitrobenzoate in 60 or 80% aqueous acetone were sealed in glass bombs of 200-ml. capacity and placed in a constant temperature oil-bath at 100°. The progress of the reaction was followed polarimetrically and titrimetrically.

In experiment 12, Table II, the solution of the ester (6.723 g.) dissolved in 500 cc. of 80% aqueous acetone (0.0519 *M*) was distributed in three sealed glass bombs and heated at 99.65 ± 0.02°. One bomb was removed from the bath after 41.8 hours and the remaining two after 80.3 hours. Each point was treated as follows: The *p*-nitrobenzoic acid produced by solvolysis was neutralized with sodium hydroxide and the acetone was evaporated from the cold solution at *ca.* 15 mm. pressure. The ester and solvolysis products were extracted with diethyl ether and dried over magnesium sulfate. The ether was evaporated and the ester was purified by extensive evacuation over calcium chloride (sometimes including 30-min. to 2-hour heating at 50° or treatment of an ethereal solution with calcium chloride) and recrystallization from ether–pentane. In all cases the infrared spectra corresponded to that of pure *trans* *p*-nitrobenzoate and showed that the samples were not contaminated with alcohol.

The ester was saponified by refluxing 2 hours in methanolic potassium hydroxide (18 ml. of methanol containing 1 g. of KOH per gram of ester). The methanolic solution was diluted with an equal volume of water and the resulting solution was extracted continuously with pentane for 40 hours. The resulting alcohol was converted to its *p*-nitrobenzoate derivative for O^{18} analysis.[5a] The results of three experiments are shown in Table II.

Control experiments which demonstrate that isolation, saponification and derivatization are not accompanied by rearrangement or exchange or in other words that the O^{18} content of the *p*-nitrobenzoate derivative corresponds to that of the ether-oxygen atom of the unsolvolyzed IV in the reaction mixture have been outlined in a preceding section.

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(12) The d.p.m. reported is per millimole of compound and has been corrected for background and efficiency of the counting. The C^{14} contents were determined with a Packard Tri-Carb liquid scintillation spectrometer model 314-DC (toluene–2,5-diphenyloxazole solution). We are indebted to Professor C. Heidelberger, University of Wisconsin, for making these facilities available to us.

[Contribution from the Research Laboratories of the Dow Corning Corporation, Midland, Mich.]

Inductive Effects in the Chlorosilane Hydrolysis Equilibrium[1]

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A detailed study of a series of nine triorganosubstituted chlorosilanes has shown that their hydrolysis involves a readily reversible equilibrium which intimately relates chlorosilane and siloxane chemistry. Free energy changes and heat of reaction values which are important to basic understanding of organosilicon chemistry have been derived. Marked changes in the equilibrium constants are brought about by changes in the substituent organic groups. These differences arise from inductive effects transmitted through the central silicon atom to modify the chemical reactivity of the electron-rich chlorine atom. Supporting this interpretation is the good correlation obtained between the equilibrium constants and the infrared frequency shift of the SiH vibration for the corresponding silane, which is also determined by the inductive effect of the organic substituents. This direct correlation of the chemical reactivity with precise infrared measurements offers a new approach to equilibrium studies and to the calculation of important thermodynamic data not previously available.

Introduction

The organochlorosilanes constitute one of the most important classes of compounds in the organosilicon field since they are intermediates from which industrial silicones are made.

One of the most striking and characteristic reactions of chlorosilanes is their rapid hydrolysis to produce hydrogen chloride and silanols, siloxanes, or both, depending upon the conditions imposed during the hydrolysis reaction.

It is generally recognized on a qualitative basis that the readiness with which hydrolysis occurs, under comparable conditions, is noticeably influenced by the degree of organic substitution, as shown by the series in decreasing order: $SiCl_4 > RSiCl_3 > R_2SiCl_2 > R_3SiCl$.

A basic understanding of such hydrolysis phenomena is of great interest and importance from an academic as well as industrial point of view.

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