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

The Iodide Ion-promoted Dehalogenation of *cis*- and *trans*-1,2-Dihalocyclohexanes[1]

BY HARLAN L. GOERING AND HERBERT H. ESPY[2]

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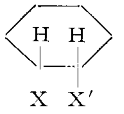
The relative rates of iodide ion-promoted dehalogenations of *cis*- and *trans*-dihalocyclohexanes in methanol at 80 and 100° have been determined. At both temperatures *trans*-1,2-dibromocyclohexane is debrominated about 11.5 times as fast as the *cis* isomer and *trans*-1-bromo-2-chlorocyclohexane is dehalogenated at about the same rate as the *cis* isomer. From (a) the relative rates of elimination, (b) the rate of the SN2 reaction of iodide ion with cyclohexyl bromide and (c) numerous previous observations it is concluded that *trans*-1,2-dibromo- and bromochlorocyclohexane undergo a concerted *trans*-dehalogenation (E_2 elimination), whereas the *cis* isomers are converted to *trans*-1-halo-2-iodocyclohexanes, by a rate-limiting displacement reaction, prior to dehalogenation.

The iodide ion-promoted elimination of halogen from vicinal dihalides is an E_2-type reaction (first-order in iodide ion and dihalide) and the stoichiometric equation involved is[3]

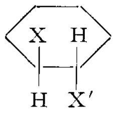
$$\mathrm{RCHXCHXR} + 3\mathrm{I}^{\ominus} \longrightarrow \mathrm{RCH{=}CHR} + 2\mathrm{X}^{\ominus} + \mathrm{I_3}^{\ominus} \quad (1)$$

This reaction is general for 1,2-dihaloalkanes[4] and has been observed with *trans*-1,2-diiodoethylene[5] and *trans*-1,2-dihalocyclohexane derivatives[6,7]; however, there do not appear to be any reports of this reaction with *cis*-1,2-dihalocyclohexane derivatives. In connection with other work[8] in this Laboratory pure samples of *cis*-(I) and *trans*-1,2-dihalocyclohexanes (II) were obtained and we now have examined the relative rates of dehalogenation of these compounds.

This information was of interest in view of the compelling evidence[7,9] that iodide ion-promoted dehalogenations involve concerted *trans*-eliminations. The *trans*-1,2-dihalocyclohexanes (II) can assume the required[7] geometry for the concerted elimination (*i.e.*, halogen atoms in axial positions); however, the *cis*-isomers (I) cannot.



Ia, X = Cl; X' = Br
b, X = X' = Br
c, X = X' = Cl



IIa, X = Cl; X' = Br
b, X = X' = Br
c, X = X' = Cl

Results.—The specific second-order rate constants (k_2) and activation parameters for the dehalogenation of *cis*-(I) and *trans*-1,2-dihalocyclohexanes (II) in 99% (by weight) methanol at 80 and 99.8° are shown in Table I, together with the second-order rate constants (and activation parameters) for the SN2 reaction of iodide ion with cyclohexyl bromide. Concentrations are reported for 25° and all rate constants are corrected for thermal expansion of the solvent.

The dehalogenation reactions were followed by titration methods developed by Dillon.[3] In all of the elimination experiments the apparent second-order rate constants, calculated by use of the appropriate equation,[3] showed consistent downward trends during the reactions, similar to those that have been observed previously.[4,10] For all of the experiments plots of k_2 against time were linear up to about 30% reaction after which the downward trend in k_2 became more pronounced. Because of the downward trends in k_2—4% decrease for the *trans*-dibromide and 12–25% decrease for the *cis*-dibromide Ib and the isomeric chlorobromides Ia and IIa during the first 25% reaction—initial rate constants were evaluated by extrapolating (least squares) the linear portions of plots of k_2 against time to zero time. The values of k_2 reported in the various tables are initial rate constants obtained in this way. The average deviation of the four to six values of k_2 from the least square fits are included in Table I.

The rate of reaction of the isomeric dichlorides Ic and IIc with iodide ion at 100° was too slow for accurate measurement and the upper limits for k_2 shown in Table I (expts. 5 and 6) were estimated from the time required for 1% reaction.

The SN2 reaction of iodide ion with cyclohexyl bromide in 99% methanol (expt. 7) was followed potentiometrically and was first order in iodide ion and cyclohexyl bromide. The second-order rate constants were steady up to about 50% reaction after which a downward trend was observed because of the reversible nature of the reaction.

There are several possible causes for the downward trend in the second-order constants for the elimination reactions. A greater than first-order dependence in iodide ion would result in such a trend and for this reason the dependence in iodide ion was investigated by varying initial concentrations. The results of these experiments are presented in Table II and clearly show that under the conditions of our experiments the debromination of *trans*-1,2-dibromocyclohexane is first order in iodide ion.

A downward trend in k_2 also could result from a competing solvolytic reaction. The first-order rate constants for the methanolysis of the dihalides in 99% methanol can be estimated from the value for *trans*-1,2-dibromocyclohexane by assuming that

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[2] du Pont Summer Research Assistant, 1953, 1954.

[3] R. T. Dillon, THIS JOURNAL, **54**, 952 (1932).

[4] See W. G. Young, S. J. Cristol and T. Skei, *ibid.*, **65**, 2099 (1943), and references therein.

[5] S. I. Miller and R. M. Noyes, *ibid.*, **74**, 3403 (1952).

[6] S. Winstein, *ibid.*, **64**, 2792 (1942); J. Weinstock, R. G. Pearson and F. G. Bordwell, *ibid.*, **76**, 4748 (1954).

[7] D. H. R. Barton and W. J. Rosenfelder, *J. Chem. Soc.*, 1048 (1951); D. H. R. Barton and E. Miller, THIS JOURNAL, **72**, 1066 (1950).

[8] (a) H. L. Goering and L. L. Sims, *ibid.*, **77**, 3465 (1955); (b) P. Bender, D. L. Flowers and H. L. Goering, *ibid.*, **77**, 3463(1955).

[9] S. Winstein, D. Pressman and W. G. Young, *ibid.*, **61**, 1645 (1939).

[10] T. L. Davis and R. Heggie, *J. Org. Chem.*, **2**, 470 (1937).

TABLE I

RATES OF REACTION OF 1,2-DIHALOCYCLOHEXANES AND CYCLOHEXYL BROMIDE WITH IODIDE ION IN 99% METHANOL

Expt.	Compd.	[Halide], 10^2 M	[KI], 10^2 M	$10^6 k_2$, l. mole^{-1} sec.$^{-1}$		$\Delta H^{\ddagger}$,[a] kcal.	$\Delta S^{\ddagger}$,[a] e.u.
				79.99 ± 0.02°	99.80 ± 0.02°		
1	Ia	2.62	26.0	0.380 ± 0.0008	2.75 ± 0.002	25.4	−16.3
2	IIa	2.63	25.7	.305 ± .0002	2.48 ± .002	26.9	−12.3
3	Ib	2.64	25.8	.951 ± .002	6.85 ± .02	25.4	−14.6
4a	IIb	2.49	25.8	11.0 ± .01	78.0 ± .2	25.1	−10.3
4b	IIb	2.52	25.8	11.0 ± .05	80.1 ± .9	25.5	− 9.2
5	Ic	2.52	25.8		<0.2		
6	IIc	3.36	26.1		<0.2		
7	Cyc-Hex Br	12.2	12.2	25.1 ± .9	193 ± 9	26.9	− 5.7

[a] The error in $\Delta H^{\ddagger}$ is estimated to be less than ±0.3 kcal. and in $\Delta S^{\ddagger}$ less than ±0.7 e.u. except for cyclohexyl bromide, for which the corresponding values are estimated to be ±1.3 kcal. and ±3.5 e.u. These errors were estimated by calculating the parameters using the high and low limits of k_2 at both temperatures.

TABLE II

RATE OF REACTION OF *trans*-1,2-DIBROMOCYCLOHEXANE WITH IODIDE ION IN 99% METHANOL AT 100.00 ± 0.02°

Expt.	[$C_6H_{10}Br_2$], 10^2 M	[NaI], 10^2 M	[$LiClO_4$], 10^2 M	$10^6 k_2$, l. mole^{-1} sec.$^{-1}$
8	2.54	25.0	..	83.5 ± 0.1
9	2.58	13.0	..	85.3 ± .3
10	2.54	12.5	12.5	84.8 ± .2

the relative solvolytic reactivities are the same in this solvent as in 80% ethanol.[11] These estimated constants are shown in Table III together with the ratio of the solvolysis constant (k_1) to the pseudo first-order rate constant for elimination ($k_2[I^-]$), which corresponds to the ratio of solvolysis to elimination.

These data show that the second-order eliminations are isolated essentially from solvolysis in reactions involving the dibromides Ib and IIb, and solvolysis is of only minor importance in elimination reactions of the chlorobromides Ia and IIa. It appears that the downward trend in the second-order rate constants is at most only partly due to competing solvolysis and that this trend is due primarily to a side reaction in which triiodide ion, or its equivalent, is consumed. This is consistent with our observation that the slower reactions show the greater downward trend.

TABLE III

RATIO OF SOLVOLYSIS TO ELIMINATION IN 99% METHANOL AT 100.00 + 0.02°

Compound	$10^6 k_1$[a]	Solvolysis[b] / elimination
Ia	0.07[c]	0.11
IIa	.13[c]	.22
Ib	.12[c]	.08
IIb	.113	.006

[a] Specific first-order rate constants for solvolysis. [b] This corresponds to the ratio $k_1/(k_2\,[I^-])$ and is corrected for solvent expansion. [c] This value was estimated by assuming that the ratio $k_{80\%\ \mathrm{EtOH}}/k_{\mathrm{MeOH}}$ is the same for this compound as for IIb.

It has been pointed out[4] that the rate constants for dehalogenations in 99% methanol vary with different batches of solvent. Since different batches of solvent were used for the experiments in Table I and those in Table II it was of interest to determine the effect of small variations in water concentration on the rate of reaction. The rate of debromination of *trans*-1,2-dibromocyclohexane was determined at 100° in absolute methanol and in methanol containing small amounts of water. These results are summarized in Table IV and show that the rate of reaction is not very sensitive to small variations in the amount of water present.

These data are of interest in connection with some of the earlier work in which it is not specified whether the composition of the solvent (99% methanol) corresponds to a weight or volume percentage. Since the difference in rate in 99% methanol by weight and 99% methanol by volume (98.61% by weight) is only about 2%, previous data can be used for comparison purposes even though it is not known whether the solvent composition corresponds to a weight or volume percentage.

TABLE IV

RATES OF REACTION OF *trans*-1,2-DIBROMOCYCLOHEXANE WITH IODIDE ION IN METHANOL AND AQUEOUS METHANOL AT 100.00 ± 0.02°

% H_2O (wt.)	[$C_6H_{10}Br_2$], 10^2 M	[KI], 10^2 M	$10^6 k_2$, l. mole^{-1} sec.$^{-1}$
0.0	2.44	25.0	77.7 ± 0.5
0.50	2.52	24.8	79.0 ± .5
1.00	2.44	24.9	81.6 ± .5
2.00	2.39	24.8	85.6 ± .5

Discussion.—As shown in Table I, *trans*-1,2-dibromocyclohexane is debrominated more readily than the *cis* isomer by a factor of about 11.5 and *trans*-1-bromo-2-chlorocyclohexane is slightly less reactive than the *cis* isomer. It appears that the isomeric chlorides also react at about the same rate. For each pair of isomers the ratio of the rate constants varies only slightly with a 20° change in temperature indicating that the activation energies are about the same for the isomers. The small difference in reactivities and activation parameters of the geometric isomers is surprising since presumably the isomers are dehalogenated by different processes. The only consistent difference between isomers is in the entropies of activation; in both cases this parameter is larger for the *trans* isomer. It is interesting to note that iodide ion reacts about twice as fast with cyclohexyl bromide as with the most reactive dihalide, *trans*-1,2-dibromocyclohexane, at 80 and 100°.

It seems likely that the *trans*-dihalocyclohexanes are dehalogenated by the process

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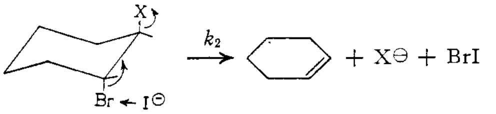
[11] Details of the relative solvolytic reactivities of *cis*- and *trans* 1,2-dihalocyclohexanes will be included in a future paper.

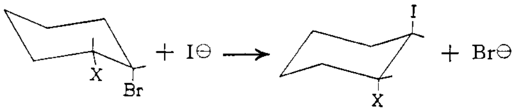


(2)

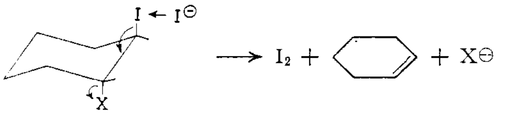
$$\mathrm{BrI} + 2\,\mathrm{I}^{\ominus} \longrightarrow \mathrm{Br}^{\ominus} + \mathrm{I}_3^{\ominus} \qquad (3)$$

since these isomers, in the axial conformation, have the required geometry[7] for a concerted dehalogenation. The concerted mechanism illustrated in reaction 2 was first suggested by Winstein, Pressman and Young[9] on the basis of stereochemical observations, and the present work provides evidence of a different type that the reaction is indeed concerted. This is indicated by the fact that *trans*-1,2-dibromocyclohexane is dehalogenated more readily than *trans*-1-bromo-2-chlorocyclohexane by a factor of 36 at 80°, a factor of the expected magnitude for a concerted elimination.[12]

Conformational requirements for a concerted elimination[7,13] preclude dehalogenation of *cis*-1,2-dihalocyclohexanes by the above process. The present data indicate that these compounds are dehalogenated by the following process which involves an initial SN2 displacement of halogen by iodide ion to give the *trans*-haloiodide which is subsequently dehalogenated by iodide ion.



(4)



(5)

$$\mathrm{I}_2 + \mathrm{I}^{\ominus} \longrightarrow \mathrm{I}_3^{\ominus} \qquad (6)$$

This process is consistent with the observed second-order kinetics providing the displacement reaction is rate-determining. If this interpretation is correct, the data in Table I show that reaction 5 is indeed faster than reaction 4 as required by the kinetics. The rate of reaction 4 corresponds to the rate of dehalogenation of the *cis* isomers; the rate of reaction 5 can be estimated from the rate of dehalogenation of the *trans* isomers. In the case of *cis*-1,2-dibromocyclohexane reaction 5 is over 1000 times (bromoiodides are dehalogenated about 100 times as fast as dibromides[14]) as fast as reaction 4.

The relative rates of dehalogenation of *cis*-1,2-dibromocyclohexane (Ib) and *cis*-1-bromo-2-chlorocyclohexane (Ia) also indicate that a rate-determining displacement is involved. The factor of 2.5, which is smaller than that observed for the corresponding *trans* isomers (and smaller than would be expected for a concerted elimination), is about what would be expected for an SN2 displacement of bromine (reaction 4). For a displacement reaction in a cyclohexyl system the axial conformation (*i.e.*, the leaving group in an axial position) undoubtedly is preferred and may be required. In Ib, one of the bromine atoms is necessarily in a reactive axial position, whereas in Ia there is a somewhat less than 50% chance of the bromine atom being axial (steric factors should slightly favor the equatorial bromine conformation). Since a β-chlorine has about the same effect as a β-bromine on the rate of an SN2 reaction,[15] the dibromide Ib would be expected to undergo a displacement reaction a little over twice as fast as the chlorobromide Ia.

The data for cyclohexyl bromide included in Table I show that dehalogenations of the *cis*-dihalides are not too fast to be consistent with a rate-determining displacement by iodide ion. The present data show that an equatorial β-halogen decreases the rate of displacement by at least a factor of 66 at 80° and 70 at 100° (compare cyclohexyl bromide with Ia). This factor is a conservative lower limit since the *cis*-dihalide is more likely than cyclohexyl bromide to be in the reactive conformation (*i.e.*, bromine in an axial position).[16] It is likely that displacement would be much slower in the case of a *trans*-1,2-dihalide than with the *cis* isomer since nucleophilic attack by iodide ion would be more hindered by an adjacent axial halogen (*trans* isomer) than by an adjacent equatorial halogen (*cis* isomer).[17] Thus it appears that the reaction of the *trans*-dihalides with iodide ion involves a clean concerted elimination without interference from a competing displacement reaction.

Experimental

Materials.[18]—The dihalocyclohexanes were prepared and purified by previously described methods. The physical properties of the compounds used in this work are shown in Table V together with references for the preparation of the compounds.

TABLE V

PHYSICAL PROPERTIES OF 1,2-DIHALOCYCLOHEXANES

Dihalocyclohexane	B.p., °C.	Mm.	$n^{25}\mathrm{D}$	$d^{25}{}_4$	Ref.
cis-1-Bromo-2-chloro (Ia)	90–91	8	1.5238	1.508	[a]
trans-1-Bromo-2-chloro (11a)	76	9	1.5173	1.479	[a]
cis-1,2-Dibromo (1b)	100–104	8	1.5514	1.803	[a]
trans-1,2-Dibromo (11b)	80	5	1.5507	1.784	[b]
cis-1,2-Dichloro (1c)	100–100.5	30	1.4953	1.199	[c]
trans-1,2-Dichlorocyclohexane	87.5–88	30	1.4888	1.180	[d]

[a] Ref. 8a. [b] H. R. Snyder and L. A. Brooks, "Organic Syntheses," Coll. Vol. II, p. 173. [c] H. C. Stevens and O. Grummitt, THIS JOURNAL, **74**, 4876 (1952). [d] B. Carroll, D. G. Kubler, H. W. Davis and A. M. Whaley, *ibid.*, **73**, 5382 (1951).

Cyclohexyl bromide, Eastman White Label, was purified by fractionation and had b.p. 83.0–83.5° (57 mm.).

The solvents used in the kinetic experiments were prepared from absolute methanol[19] and distilled water. Reagent grade potassium iodide was dried 2 days at 105° and U.S.P. sodium iodide was dried 3 hr. at 105°.

Kinetic Experiments.—All concentrations are reported for 25°. Elimination (dehalogenation) reactions were followed by adding 5-ml. aliquots of reaction solution to 2.5 g. of potassium iodide and 0.05 ml. of glacial acetic acid in 50 ml. of distilled water, and titrating triiodide ion to the

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[12] E. D. Hughes and U. G. Shapiro, *J. Chem. Soc.*, 1177 (1937); H. C. Brown and I. Moritani, THIS JOURNAL, **76**, 455 (1954).

[13] C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p. 468.

[14] S. J. Cristol, M. Brindell and J. Q. Weber, THIS JOURNAL, in press.

[15] J. Hine and W. H. Brader, Jr., *ibid.*, **75**, 3964 (1953).

[16] It is interesting to note that the retarding effect of a β-halogen atom on an Sn2 reaction appears to be much greater in cyclohexyl systems than in acyclic systems (ref. 15).

[17] See ref. 13, pp. 404–406.

[18] We are indebted to Mr. L. L. Sims of this Laboratory for providing us with pure samples of *cis*-1,2-dibromocyclohexane and *cis*- and *trans*-1-bromo-2-chlorocyclohexane.

[19] L. F. Fieser, "Experiments in Organic Chemistry," 2nd ed. D. C. Heath and Co., Boston, Mass., 1941, p. 360.

starch end-point with 0.05 N sodium thiosulfate. The sealed ampule technique was used and reactions were quenched by placing ampules containing aliquots in an ice-bath. Aliquots were measured at 25° with calibrated pipets and 5-ml. calibrated microburets were used for titrations. The titer changed about 1.5 ml. during the 35–40% of completion to which the reactions were carefully followed and individual titrations were reproducible to ±0.004 ml.

The rate of reaction of cyclohexyl bromide with iodide ion was followed by potentiometric (Beckman model G potentiometer) titration of 5-ml. aliquots in 50 ml. of water with 0.15 N silver nitrate.

Second-order elimination rate constants, k_2, were calculated from the equation

$$k_2 = \frac{1}{t(a - 3b)} \ln[(1 - 3b\phi/a)/(1 - \phi)]$$

where a is the initial concentration of iodide ion, b the initial dihalide concentration, t the elapsed time, and ϕ the fraction of dihalide that has reacted (*i.e.*, $\phi = [I_3^-]/b$) at time t. The values of k_2 were corrected for solvent expansion by multiplying by the ratio $d^{25}{}_4/d^t{}_4$. The values used were: $d^{25}{}_4$ 0.7870 (by interpolation), $d^{80}{}_4$ 0.7355, $d^{100}{}_4$ 0.714.[20]

The values of k_2 obtained in this way decreased as the reactions progressed. The rate constants were linear with time to about 30% reaction and initial rate constants were determined by extrapolation to zero time by the method of least squares. Data for typical runs are presented in Tables VI and VII.

The second-order constants for the S$_N$2 reaction of cyclohexyl bromide with iodide ion were determined from the relationship

$$k_2 = 1/t\left[1/(a - x) - \frac{1}{a}\right]$$

where a is the initial concentration of iodide ion and of cyclohexyl bromide. Correction was made for solvent expansion as described above.

TABLE VI

THE REACTION OF *cis*-1,2-DIBROMOCYCLOHEXANE (Ib) WITH POTASSIUM IODIDE IN 99% METHANOL AT 79.99° (EXPERIMENT 3)

Time, $10^{-5}t$, sec.	ϕ	10^6k_2,[a] l. mole^{-1} sec.$^{-1}$
0	(0)	(0.951)[b]
3.600	0.075	.914
5.400	.108	.893
7.992	.149	.861
9.972	.178	.843
12.096	.207	.823
14.202	.232	.803[c]

[a] Corrected for solvent expansion. [b] Extrapolated value at zero time. [c] Omitted in extrapolation.

TABLE VII

THE REACTION OF *trans*-1-BROMO-2-CHLOROCYCLOHEXANE (IIa) WITH POTASSIUM IODIDE IN 99% METHANOL AT 99.80° (EXPERIMENT 2)

Time $10^{-5}t$, sec.	ϕ	10^6k_2,[a] l. mole^{-1} sec.$^{-1}$
0	(0)	(2.48)[b]
2.592	0.123	2.02
3.888	.168	1.90
4.788	.194	1.81
6.264	.229	1.68
7.200	.254	1.65[c]
8.820	.287	1.56[c]

[a] Corrected for solvent expansion. [b] Extrapolated value at zero time. [c] Omitted in extrapolation.

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[20] Landolt–Börnstein "Tabellen," J. Springer Verlag, Berlin, 1923, Vol. I, p. 278.

[CONTRIBUTION FROM DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WISCONSIN]

Stereochemistry of Allylic Rearrangements. VI. The Ethanolysis and Acetolysis of *cis*- and *trans*-5-Methyl-2-cyclohexenyl Chloride[1]

BY HARLAN L. GOERING, THOMAS D. NEVITT AND ERNEST F. SILVERSMITH[2]

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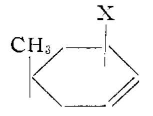
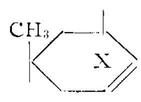
The kinetics and products of ethanolysis and acetolysis of *cis*- and *trans*-5-methyl-2-cyclohexenyl chloride have been examined. For both geometric iosmers the polarimetric rate constants (k_α) and titrimetric constants (k_t) are steady during the solvolysis and $k_\alpha > k_t$. Ethanolysis of the isomeric chlorides gives binary mixtures of *cis*- and *trans*-ethyl 5-methyl-2-cyclohexenyl ether of the same composition. Mixtures of *cis*- and *trans*-5-methyl-2-cyclohexenyl acetate of the same composition result from the acetolysis of the isomeric chlorides. Since in each case the products are stable under the conditions of the product-isolation experiment, it appears that a common intermediate is involved in the solvolysis of the isomeric chlorides. The kinetic and product-isolation experiments suggest that under the present conditions solvolysis involves the reversible formation of an ion-pair intermediate which dissociates irreversibly to give 5-methyl-2-cyclohexenylcarbonium ion—the common intermediate for the isomeric chlorides—which is irreversibly converted to product.

The isomeric anionotropic rearrangement of *cis*-(Ia) and *trans*-5-methyl-2-cyclohexenyl acid phthalate (IIa) in acetonitrile and the solvolysis of the isomeric acid phthalates in aqueous acetone have been described in previous papers in this series.[3,4] We have now extended our studies to the chlorides and this paper describes the products and kinetics of the solvolysis of *cis*-(Ib) and *trans*-5-methyl-2-cyclohexenyl chloride (IIb) in acetic acid and ethanol. The preparation (and assignment of configurations) of the isomeric chlorides used in the present work has been described in a previous paper.[5]



Ia, X = $O_2CC_6H_4CO_2H$
b, X = Cl
c, X = OH
d, X = OAc
e, X = OEt



IIa, X = $O_2CC_6H_4CO_2H$
b, X = Cl
c, X = OH
d, X = OAc
e, X = OEt

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[1] This work was supported by the Office of Ordnance Research.

[2] National Science Foundation Fellow, 1954–1955.

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

[4] H. L. Goering and E. F. Silversmith, *ibid.*, **77**, 1129 (1955).

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