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

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

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	$10^6 k_2$,[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	$10^6 k_2$,[a] l. mole^{-1} sec.$^{-}$
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.

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

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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]

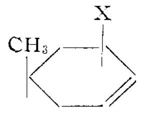
Stereochemistry of Allylic Rearrangements. VI. The Ethanolysis and Acetolysis of *cis*- and *trans*-5-Methyl-2-cyclohexenyl Chloride[1]

By Harlan L. Goering, Thomas D. Nevitt and Ernest F. Silversmith[2]

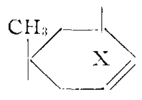
Received March 30, 1955

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).

TABLE I

SOLVOLYSIS RATES OF *cis*-5-METHYL-2-CYCLOHEXENYL CHLORIDE[a]

Expt.	[RCl] 10^2 *M*	Solvent	Temp.,[b] °C.	Added salt	Method[c]	10^5k, sec.$^{-1}$	Initial rotation	Final rotation
1	4.23	EtOH	30	None	T	2.12 ± 0.02		
2	4.62	EtOH	30	None	T	2.15 ± .03		
3	7.88	EtOH	30	None	P	2.35 ± .01	0.575	−0.086
4	4.73	EtOH	30	0.1004 *M* $LiClO_4$	T	3.25 ± .07		
5	4.87	EtOH	30	0.0836 *M* NaOEt	T	2.57 ± .1		
6	4.65	EtOH	50	None	T	20.2 ± .7		
7	9.44	EtOH	50	None	P	25.1 ± 1.2	.750	− .082
8	4.52	AcOH	30	0.0518 *M* NaOAc	T	0.88 ± 0.02		
9	4.73	AcOH	30	.0518 *M* NaOAc	T	0.89 ± .02		
10	7.55	AcOH	30	.0518 *M* NaOAc	P	2.67 ± .06	.541	.010
11[d]	11.5	AcOH	30	.0479 *M* NaOAc	P	2.67 ± .05	−1.386	.001
12	73.7	AcOH	30	.527 *M* NaOAc	T	1.29 ± .02		
13	4.96	AcOH	50	.0518 *M* NaOAc	T	8.9 ± .2		
14	8.32	AcOH	50	.0518 *M* NaOAc	P	28.1 ± 2.2	0.650	.002
15	3.76	AcOH	30	.0521 *M* LiOAc; 0.0516 *M* LiCl	T	0.97 ± 0.04		
16	8.18	AcOH	30	.0521 *M* LiOAc; .0525 *M* LiCl	P	3.12 ± .06	.860	.022
17	7.38	AcOH	30	.0521 *M* LiOAc; .0517 *M* $LiClO_4$	P	4.42 ± .12	.935	.018
18	3.76	AcOH	30	.0518 *M* NaOAc; .0081 *M* $LiClO_4$	T	1.00 [illegible] .04		
19	2.82	AcOH	30	.0518 *M* NaOAc; .0164 *M* $LiClO_4$	T	1.11 ± .02		
20	5.00	AcOH	30	.0518 *M* NaOAc; .0256 *M* $LiClO_4$	T	1.33 ± .02		
21	4.32	AcOH	30	.0481 *M* LiOAc; .0481 *M* $LiClO_4$	T	1.67 ± .08		
22	4.26	AcOH	30	.0518 *M* NaOAc; .0797 *M* $LiClO_4$	T	2.60 ± .06		
23	3.00	AcOH	30	.0518 *M* NaOAc; .1005 *M* $LiClO_4$	T	3.03 ± .04		
24	3.72	AcOH	30	.0518 *M* NaOAc; .1551 *M* $LiClO_4$	T	4.35 ± .12		
25	5.10	AcOH	30	.0518 *M* NaOAc; .0517 *M* LiBr	T	1.26 ± .04		

[a] The chloride used in all runs except experiment 11 was 100% *cis*-5-methyl-2-cyclohexenyl chloride. [b] The titrimetric rates denoted 30° were determined at 29.99 ± 0.01°; the polarimetric rates at 30.12 ± 0.02°. The titrimetric and polarimetric rates denoted 50° were determined at 50.02 ± 0.01°. [c] P = polarimetric; T = titrimetric. [d] The chloride used in this run was prepared from (+)*trans*-5-methyl-2-cyclohexenol with phosphorus trichloride in hexane (ref. 5) and consisted of 35% of *cis*- and 65% of *trans*-5-methyl-2-cyclohexenyl chloride.

TABLE II

SOLVOLYSIS RATES OF *trans*-5-METHYL-2-CYCLOHEXENYL CHLORIDE[a]

Expt.	[RCl] 10^2 *M*	Solvent	Temp.,[b] °C.	Added salt	Method[c]	10^5k, sec.$^{-1}$	Initial rotation	Final rotation
26	4.86	EtOH	30	None	T	1.56 ± 0.01		
27	2.91	EtOH	30	None	T	1.58 ± .02		
28	8.51	EtOH	30	None	P	2.55 ± .05	−0.751	0.135
29	3.14	EtOH	30	0.1004 *M* $LiClO_4$	T	2.70 ± .02		
30	2.24	EtOH	30	0.0638 *M* NaOEt	T	1.73 ± .03		
31	4.79	EtOH	50	None	T	16.4 ± .2		
32	8.60	EtOH	50	None	P	24.6 ± .6	− .367	.041
33	5.03	AcOH	30	0.0518 *M* NaOAc	T	0.59 ± .01		
34	2.56	AcOH	30	.0518 *M* NaOAc	T	0.58 ± .01		
35[d]	5.44	AcOH	30	.0518 *M* NaOAc	P	2.85 ± .05	.751	− .005
36	8.88	AcOH	30	.0479 *M* NaOAc	P	2.94 ± .05	1.502	.000
37	4.53	AcOH	50	.0518 *M* NaOAc	T	6.48 ± .06		
38	7.91	AcOH	50	.0479 *M* NaOAc	P	27.8 ± .8	−0.368	.010
39[d]	4.24	AcOH	50	.0518 *M* NaOAc	P	29.3 ± 1.0	0.556	− .023

[a] The chloride used in all runs except experiments 35 and 39 was 100% *trans*-5-methyl-2-cyclohexenyl chloride. [b] See footnote *b*, Table I. [c] T = titrimetric; P = polarimetric. [d] The chloride used in this run was prepared from (−)*cis*-5-methyl-2-cyclohexenol with phosphorus trichloride in hexane and consisted of 32% *cis*- and 68% *trans*-5-methyl-2-cyclohexenyl chloride (ref. 5).

Results of Kinetic Experiments.—Polarimetric (k_α) and titrimetric (k_t) first-order rate constants for ethanolysis and acetolysis of *cis*-5-methyl-2-cyclohexenyl chloride (Ib) are shown in Table I; similar data for *trans*-5-methyl-2-cyclohexenyl chloride (IIb) are presented in Table II. The titrimetric first-order rate constants (k_t) (calculated by use of the integrated equation for a first-order reaction) were steady over the ranges that the reactions were followed (50 to 90% completion). Each value of k_t in Tables I and II is the average value (and mean deviation) of 7 to 12 determinations during the reaction.

The polarimetric constants (k_α) were determined from the rate of loss of optical activity of solutions of active Ib and IIb. In all cases these first-order constants were steady over the ranges (50 to 80% completion) that the reactions were followed. Kinetic experiments that show the magnitude of the positive salt effect are included in Table I.

The isomeric chlorides were prepared from the corresponding alcohols by reaction of the latter with thionyl chloride in ether.[5] Freshly prepared samples were used for the kinetic experiments and with the exception of experiments 11, 35 and 39, infrared spectra indicated that the samples were configurationally homogeneous. The homogeneity of the samples also is indicated by the fact that titrimetric rate constants, which differ by factors of 1.23 to 1.49 for the geometric isomers, were reproducible (values of k_t for independent experiments varied less than 3%) and did not show significant trends in reactions that were carefully followed to over 80% completion. Typical experiments illustrating the first-order behavior of the titrimetric rates for the isomeric chlorides are shown in Fig. 1.

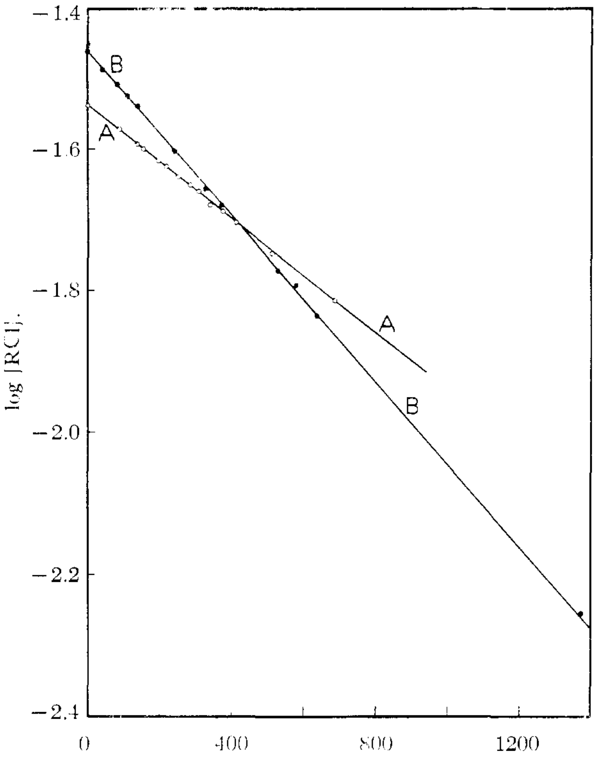

Fig. 1.—First-order ethanolyses of the isomeric 5-methyl-2-cyclohexenyl chlorides at 30°: A, *trans*-isomer (IIb); B, *cis*-isomer (Ib).

Polarimetric solvolysis rate constants for optically active chlorides prepared by the reaction of active alcohol with phosphorus trichloride in hexane[5] are included in Tables I and II. As shown by Table I, expt. 11, the polarimetric rate constant for the (−)chloride (35% *cis* isomer and 65% *trans* isomer[5]), derived from (+)*trans*-5-methyl-2-cyclohexenol (IIc), is the same as that for (+)Ib (100% *cis* isomer; expt. 10). The polarimetric constants for (+)chloride (68% *trans* isomer and 32% *cis* isomer[5]) derived from (−)*cis*-5-methyl-2-cyclohexenol (Ic) (Table II, expts. 35 and 39) are similar to those for active IIb (100% *trans* isomer). As has been pointed out previously[5] these data indicate that the reaction of optically active Ic or IIc with phosphorus trichloride in hexane gives optically active chloride with the opposite geometric configuration together with racemic chloride having the same geometric configuration as the alcohol.

In order to confirm the allylic structure of Ib and IIb, their rates of ethanolysis were compared with those of other α,γ-dialkylallylic chlorides. These data, which indeed demonstrate the allylic structure of Ib and IIb, are presented in Table III. The values of k_t shown in this table are average values (and mean deviations) of 3 or 4 independent kinetic experiments (followed to from 70 to 90% completion) and illustrate the precision with which these constants were determined. It is interesting to note that 2-cyclopentenyl chloride is more reactive than 2-cyclohexenyl chloride by a factor of *ca.* 600 and more reactive than the acyclic analog, α,γ-dimethylallyl chloride, by a factor of 150. These results are similar to the observation by Brown and co-workers[6] that 1-methylcyclopentyl chloride solvolyzes *ca.* 120 times as fast as 1-methylcyclohexyl chloride and 13 times as fast as 3-chloro-3-methylpentane in 80% ethanol at 25°.

TABLE III

THE SOLVOLYSIS OF α,γ-DIALKYLALLYL CHLORIDES IN ETHANOL AT 30°

Chloride	[RCl], *M*	$10^5 k_t$,[a] sec.$^{-1}$
cis-5-Methyl-2-cyclohexenyl	0.04	2.15 ± 0.02
trans-5-Methyl-2-cyclohexenyl	.05	1.57 ± .01
2-Cyclohexenyl	.03	1.86 ± .003
α,γ-Dimethylallyl	.04	7.59 ± .07
2-Cyclopentenyl	.05	1130 ± 33

[a] Average values and mean deviations of three or four independent kinetic experiments followed to from 70 to 90% completion.

As shown in Tables I and II, $k_\alpha > k_t$ under all conditions where the two were compared. The effect of varying solvent and temperature on the ratio, k_α/k_t, is illustrated by Table IV. These data appear to be consistent with previous observations that in cases where internal return is involved, k_α/k_t is quite insensitive to change in

TABLE IV

RATIOS OF POLARIMETRIC (k_α) TO TITRIMETRIC (k_t) RATES OF SOLVOLYSIS OF 0.05 *M* *cis*-(Ib) AND *trans*-5-METHYL-2-CYCLOHEXENYL CHLORIDE (IIb)

Compd.	Solvent[a]	Temp., °C.	k_α/k_t[b]
Ib	EtOH	30	1.11 ± 0.07
IIb	EtOH	30	1.63 ± .04
Ib	EtOH	50	1.24 ± .10
IIb	EtOH	50	1.50 ± .06
Ib	HOAc(NaOAc)	30	3.03 ± .10
IIb	HOAc(NaOAc)	30	5.07 ± .13
Ib	HOAc(NaOAc)	50	3.16 ± .26
IIb	HOAc(NaOAc)	50	4.27 ± .16
Ib	HOAc(LiOAc, LiCl)	30	3.22 ± .20
Ib	HOAc(NaOAc, $LiClO_4$)	30	2.51 ± .20[c]

[a] The initial concentration of indicated salt was 0.05 *M*

[b] Indicated error calculated from limiting values of k_α and k_t using values from independent experiments where available.

[c] Value for k_t (1.76×10^{-5} sec.$^{-1}$) estimated by interpolation of data given in Table I.

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(6) H. C. Brown, R. Fletcher and R. Johnson, THIS JOURNAL, **73**, 212 (1951).

temperature[4,7] and larger for acetolysis than for ethanolysis.[7] The activation parameters, calculated from the values of k_t in Tables I and II, are presented in Table V. As indicated by the small variation of k_α/k_t with a 20° change in temperature, the activation parameters for the polarimetric processes are in every case within the combined experimental errors of the values given in Table V. The indicated errors of the parameters were calculated from the limiting values of k_t (from independent experiments) at both temperatures.

TABLE V

ACTIVATION PARAMETERS FOR THE SOLVOLYSIS (TITRIMETRIC) OF *cis*-(Ib) AND *trans*-5-METHYL-2-CYCLOHEXENYL CHLORIDE (IIb)

Compd.	Solvent	$\Delta H^{\ddagger}$, kcal.[a]	$\Delta S^{\ddagger}$, e.u.[a]
Ib	EtOH	21.1 ± 0.5	−10.3 ± 1.7
IIb	EtOH	22.1 ± .2	− 7.7 ± 0.6
Ib	HOAc(NaOAc)[b]	21.7 ± .3	−10.1 ± 1.1
IIb	HOAc(NaOAc)	22.7 ± .3	− 7.7 ± 0.8

[a] Errors calculated from limiting values of k_t (independent experiments) at 30 and 50°. [b] NaOAc concentration = 0.05 *M*.

Results of Product-Isolation Experiments.—Since $k_\alpha > k_t$ it is clear that solvolysis of active Ib or IIb results in the simultaneous formation of two initial products: racemic 5-methyl-2-cyclohexenyl chloride (product of internal return) and solvolysis product. The configurational composition of each of these products has been investigated for the acetolysis of Ib and IIb. For ethanolysis the small difference in k_α and k_t precludes isolation and examination of the product of internal return and in this case only the composition of the solvolysis product, a binary mixture of *cis*-(Ie) and *trans*-ethyl 5-methyl-2-cyclohexenyl ether (IIe), was determined.

Unsolvolyzed chloride was recovered from partly acetolyzed solutions of Ib and IIb to determine the configuration of the product resulting from internal return. The first-order behavior of the titrimetric rates indicates that geometric isomerization does not occur during solvolysis; however, the difference in k_t for Ib and IIb is not great (Ib is more reactive than IIb by a factor of 1.49 at 30° and 1.37 at 50°) and appreciable isomerization would be required to cause a detectable kinetic disturbance. The chloride recovered from a 0.5 *M* solution of *dl*-Ib in acetic acid (0.5 *M* NaOAc) after 10.5 hr. (0.7 titrimetric half-life) at 30° was found to be >95% *cis*-chloride (Ib) by infrared analysis. This value is a conservative lower limit and indeed there was no evidence for the presence of the *trans* isomer, IIb.[8] As indicated by expt. 12 (Table I) the solvolysis is first-order under the conditions of this experiment and k_t is somewhat larger than at lower ionic strength (*e.g.*, expt. 9) as would be expected. Since the data in Table IV show that k_α/k_t is not greatly affected by varying ionic strength, it appears that the value of this ratio under the conditions of this experiment is at least 2.5.[9] This value corresponds to a value of 1.94×10^{-5} sec.$^{-1}$ for $(k_\alpha - k_t)$ which is the specific first-order rate constant for the excess loss of optical activity.[7] From the latter value it readily can be determined that at the time of isolation, optically active chloride would retain <48% of its original activity. In other words >26% of the isolated chloride was converted to its enantiomer without detectable geometric isomerization. When the isolation experiment was carried out with the *trans*-chloride, IIb, using the conditions described above for the *cis* isomer, the recovered chloride was found to be >95% IIb.[8] From these experiments it is clear that the product of internal return has the same geometric configuration as the reactant. These results are similar to the previous observation[4] that internal return does not result in geometric isomerization of the isomeric 5-methyl-2-cyclohexenyl acid phthalates.

The solvolysis product isolated from a 0.058 *M* solution of the *cis*-chloride, Ib, in acetic acid (0.10 *M* NaOAc) after 7 days at 30° (*ca.* 7 titrimetric half-lives) was a binary mixture of the isomeric acetates, Id and IId, consisting of 97 ± 2% of the *trans* isomer, IId (infrared analysis[5]). When this experiment was repeated with the *trans*-chloride, IIb, the composition of the mixture of isomeric acetates was 94 ± 2% *trans* isomer. The data in Tables I and II (expt. 8 and 33) show that the reactions are first order and an independent control experiment showed that: (a) the isomeric 5-methyl-2-cyclohexenyl acetates are stable under the conditions of the solvolysis and (b) the product is isolated without fractionation of the binary mixture.

The products resulting from the ethanolysis of the isomeric chlorides were investigated in a similar manner. These solvolyses were carried out in the presence of sodium ethoxide (initial concentration 0.075 *M*) to avoid acid-catalyzed isomerization of the initially formed products. As shown by comparison of expt. 2, 4 and 5 in Table I and 27, 29 and 30 in Table II, the inclusion of 0.08 *M* sodium ethoxide results in a small positive salt effect and the reaction is first order. The binary mixtures of the isomeric ethyl 5-methyl-2-cyclohexenyl ethers (Ie and IIe) isolated from 0.06 *M* solutions of the isomeric chlorides in ethanol (0.075 *M* NaOEt) after 6 days at 30° (>10 titrimetric half-lives) were indistinguishable and consisted of 85 ± 2% *trans* isomer (infrared analysis). That the isomeric ethyl ethers are stable under the conditions of the experiment, and isolated without fractionation of the geometric isomers, was demonstrated by an independent experiment. The ultraviolet spectrum of a completely ethanolyzed solution of Ib at 30° had a band at 257 mμ, which is characteristic of 5-methyl-1,3-cyclohexadiene,[10] and indicated that about 2% of the reactant is converted to diene.

Discussion of Results.—The kinetic experiments and product studies indicate that the solvolysis

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[7] S. Winstein and K. C. Schreiber, THIS JOURNAL, **74**, 2165 (1952).

[8] In this experiment the isolated chloride could not be separated completely from the acetates and the isomeric composition of the chlorides was determined in the presence of acetate. Under these conditions less than 5% of one of the isomeric chlorides in the other cannot be detected with certainty by the analytical method used.

[9] It appears that this is a conservative lower limit and that the value is probably over 3 since it has been shown (ref. 7) that for the acetolysis of 3-phenyl-2-butyl *p*-toluenesulfonate k_α/k_t is increased slightly by the addition of 0.1 *M* sodium acetate.

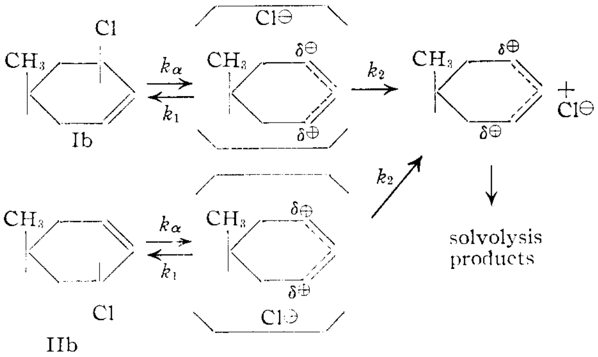
[10] H. Booker, L. K. Evans and A. E. Gillam, *J. Chem. Soc.*, 1453 (1940).

of the isomeric chlorides is an S_N1-type reaction, *i.e.*, nucleophilic participation of the solvent is not involved to any appreciable extent. This is indicated by the similar rates of acetolysis and ethanolysis,[11] the slightly larger positive salt effect of "non common-ion" salts than of salts of the conjugate base of the solvent,[12] and evidence that intermediates are involved (see below).

It is clear that the discrepancy between k_α and k_t is due to internal return.[13a] That the greater polarimetric rate is not due to external return[13] (mass law effect[14]) is indicated by: (a) the excess loss of optical activity, measured by $k_\alpha - k_t$, does not involve geometric isomerization of the isomeric chlorides[4]; (b) both k_α and k_t are steady throughout the reaction[7]; (c) addition of 0.05 *M* lithium chloride, a "common-ion"[14] salt, does not result in a large increase in k_α/k_t (see Table IV) as would be the case if the difference between k_α and k_t were due to external return.[7]

The results of the kinetic and product-isolation experiments appear to be consistent with the process shown in Chart I in which the ion-pair interpretation[13] of internal return has been applied to the present system. According to this scheme the solvolysis of Ib or IIb involves two intermediates: the common intermediate for internal return and solvolysis (*i.e.*, the ion-pair intermediate) and the common intermediate for the solvolysis of the isomeric chlorides (*i.e.*, the 5-methyl-2-cyclohexenylcarbonium ion). Evidence that internal return and solvolysis involve a common intermediate has been discussed previously[4,13a] and the present results appear to be consistent with this interpretation. The common intermediate for the isomeric chlorides is indicated by the similar configurational compositions of the kinetically controlled solvolysis products. In view of the recent evidence presented by Winstein and co-workers[15] concerning intermediates involved in the ionization processes of S_N1-type reactions it seems likely that additional intermediates may well be involved in the present case.

CHART I



It is interesting to note that although the titrimetric rates for Ib and IIb are greater in ethanol than in acetic acid by factors of 2.3 to 2.6, the polarimetric rates in all cases are slightly larger in acetic acid. According to Chart I the polarimetric rate corresponds to the rate of formation of the symmetrical ion-pair intermediate and a reaction of this type would be expected to be as fast in acetic acid as in ethanol.[11] If the present interpretation is correct, the relative titrimetric rates show that the ratio k_1/k_2 is larger in acetic acid than in ethanol. This is also clearly indicated by the fact that k_α/k_t is larger in acetic acid than in ethanol since $k_\alpha/k_t = 1 + k_1/k_2$.[7] In cases where comparisons have been made, k_α/k_t (and thus k_1/k_2) is larger in acetic acid than in ethanol.[7] The reason for this is obscure since k_1/k_2 would be expected to decrease as ionizing power of the medium increases if the reactions involved are of the types indicated in Chart I.[7] Nucleophilic participation of the solvent in the conversion of the ion-pair intermediate to solvolysis product could account for the present results; however, the product studies show that if there is such participation it does not result in the formation of different products from the isomeric ion-pair intermediates.

The absence of detectable geometric isomerization of either of the isomeric chlorides during solvolysis clearly shows that the dissociation of the ion-pair intermediate is not reversible to any appreciable extent. The kinetic experiments indicate that this reaction may be reversible to a slight extent, however. Comparison of expt. 15, 22 and 25 shows that the positive salt effect of lithium chloride, a "common-ion" salt, is smaller than that of the "non-common-ion" salts, lithium bromide and lithium perchlorate. The smaller salt effect of lithium chloride can be attributed to a mass law effect; however, as has been pointed out[16] such data do not necessarily demonstrate this effect.

As shown in Tables I and II ethanolysis, and in some cases acetolysis, of active Ib or IIb does not result in complete loss of optical activity. The nature of the active products or of the process by which they are formed is not clear. The kinetic and product studies suggest that nucleophilic participation by solvent is not involved and even if such participation is assumed there does not appear to be any single process which can account for the present results. The relative configurations of the active chlorides and ethyl ethers[17] show that an S_N2 displacement by ethanol would convert (−)-*trans*-chloride to (−)*cis*-ethyl ether. An S_N2' displacement with retention of geometric configuration[18] would convert (+)*cis*-chloride to (+)*cis*-ethyl ether. Clearly the present results (*i.e.*, the fact that the sign of the rotation changes in every case) cannot be attributed to either of these processes. As mentioned in the preceding section, ethanolysis results in a 2% conversion to 5-methyl-1,3-cyclohexadiene. This diene is reported[19] to

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[11] S. Winstein, E. Grunwald and H. W. Jones, THIS JOURNAL, **73**, 2700 (1951).

[12] O. T. Benfey, E. D. Hughes and C. K. Ingold, *J. Chem. Soc.*, 2494 (1952).

[13] (a) S. Winstein and R. Heck, THIS JOURNAL, **74**, 5584 (1952), and previous papers in this series; (b) D. J. Cram, *ibid.*, **74**, 2129 (1952).

[14] L. C. Bateman, M. G. Church, E. D. Hughes, C. K. Ingold and N. A. Taher, *J. Chem. Soc.*, 979 (1940); O. T. Benfey, E. D. Hughes and C. K. Ingold, *ibid.*, 2488 (1952).

[15] S. Winstein, E. Clippinger, A. H. Fainberg and G. C. Robinson, THIS JOURNAL, **76**, 2597 (1954); *Chemistry and Industry*, 664 (1954).

[16] W. C. Coburn, E. Grunwald and H. P. Marshall, THIS JOURNAL, **75**, 5735 (1953).

[17] H. L. Goering and E. F. Silversmith, *ibid.*, **77**, 5023 (1955).

[18] G. Stork and W. N. White, *ibid.*, **75**, 4119 (1953).

[19] M. Mousseron and F. Winternitz, *Bull. soc. chim.*, **12**, 67 (1945)

have a high rotation; however, it is not formed in sufficient amounts to account for the residual activities.

Experimental

Materials.—The preparation and physical properties of the isomeric 5-methyl-2-cyclohexenyl chlorides used in the present work have been described in a previous paper.[5]

3-Chlorocyclohexene, b.p. 52° (25 mm.), $d^{25}{}_{25}$ 1.040, $n^{25}\mathrm{D}$ 1.4868, *MR* 32.23 (calcd. 32.12), solvolysis equivalent 117[20] (calcd. 116.5) (lit.[21] b.p. 62° (35 mm.), $n^{26}\mathrm{D}$ 1.4860, d^{28} 1.030), was prepared in 95% yield by the reaction of 2-cyclohexenol with thionyl chloride in ether using the described procedure[5] for the preparation of 5-methyl-2-cyclohexenyl chloride from the corresponding alcohol. 2-Cyclohexenol was prepared from dihydroresorcinol[22] by the same procedure that has been described[23] for the conversion of 5-methyl-1,3-cyclohexanedione to 5-methyl-2-cyclohexenol.

4-Chloro-2-pentene, b.p. 47–48° (25 mm.), $n^{25}\mathrm{D}$ 1.4327, $d^{25}{}_{25}$ 0.8982, *MR* 30.15 (calcd. 29.7), solvolysis equivalent 105[20] (calcd. 104.5) (lit.[24] b.p. 100.5°, $n^{20}\mathrm{D}$ 1.4322, d^{20} 0.9004), was prepared in 90% yield by the reaction of thionyl chloride with 2-penten-4-ol[25] in ether.[5]

3-Chlorocyclopentene, b.p. 38° (25 mm.), $n^{25}\mathrm{D}$ 1.4728, $d^{25}{}_{25}$ 1.039, *MR* 27.68 (calcd. 27.50), solvolysis equivalent 103[20] (calcd. 102.5), lit.[26] b.p. 40° (25 mm.), was prepared by the addition of hydrogen chloride to cyclopentadiene. The adduct was obtained in 75% yield by passing dry hydrogen chloride through freshly distilled cyclopentadiene at room temperature. The product was isolated and purified by fractionation with a short helix-packed column.

Titrations.[27]—Ethanolyses of the allylic chlorides were followed by periodically titrating aliquots of reaction mixtures to the sharp brom thymol blue end-point with a standard solution (0.05 *N*) of sodium methoxide in methanol.[28] The sodium methoxide solution was standardized against aqueous hydrochloric acid.

When the ethanolyses were carried out in the presence of ethoxide ion the concentration of remaining ethoxide ion was determined by titration of aliquots with 0.05 *N* alcoholic perchloric acid (prepared by mixing 60% aqueous perchloric acid with ethanol) to the brom thymol blue end-point.

The titrations involved in the acetolysis in the presence of acetate ion have been described previously.[29] In the present work the remaining acetate ion concentration was determined by titration of aliquots to the brom phenol blue end-point with a standard solution of perchloric acid in acetic acid. The indicator end-point is easier to reproduce if approached from the acid (colorless) side and for this reason a slight excess of perchloric acid was added and the pale yellow or colorless solution was back titrated with standard sodium acetate in acetic acid to the bright yellow equivalence point.[30] The equivalence point is sharp in the absence of the buffering effect of chloride ion. At high chloride ion concentrations (0.05–0.10 *M*) the color change is gradual[29]; however, with practice it is possible to titrate with an accuracy of ±0.0015 meq. with a 0.05 *N* titrant. All concentrations of acetic acid solutions were related to the perchloric acid solution (prepared by mixing 60% aqueous perchloric acid and acetic acid) which was standardized against potassium acid phthalate in acetic acid.

Titrimetric Rate Measurements.[31] (A) **Ethanolysis.**—Reaction solutions were prepared at 30° by dissolving weighed samples of the pure chlorides in absolute[32] ethanol. The rate constants were determined from the relationship

$$k_t = (1/t)\ \ln\ [a/(a - x)]$$

where a is the initial concentration of allylic chloride, and x is the concentration of chloride which has reacted at any time. The initial concentrations (a) were determined from the weight of the chloride used or from the infinity titer. The runs at 30° were carried out in thermostated reaction flasks from which aliquots of reaction mixture were withdrawn during the reaction and analyzed by titration with sodium methoxide in methanol. Several minutes were allowed for temperature equilibration before determining the "zero-point" titer and from 7 to 12 "points" were determined during the reaction. Infinity titers were determined in duplicate by titrating aliquots after ten half-periods. For slow reactions aliquots were sealed in ampules and heated to 100° to obtain the infinity titer. The lithium perchlorate (G. Frederic Smith Co.; reagent grade) used in some of the experiments was dried to constant weight by heating at 120° for 24 hours *in vacuo*.

The solvent containing sodium ethoxide (expt. 5 and 30) was prepared by dissolving clean sodium in ethanol. The reactions carried out in this solvent were followed by periodically determining the remaining ethoxide ion concentration by titration of aliquots with alcoholic perchloric acid.

The rate constant for the ethanolysis of 3-chlorocyclopentene was estimated by intermittent titration[33] of the reaction mixture. For this experiment the chloride and solvent were thermostated (30°) prior to mixing.

The ampule technique was used at 50°. The "zero-point" titers were determined after temperature equilibration (ten minutes) and the reactions were quenched by chilling the ampules in an ice-bath. In the ethanolysis experiments at both 30 and 50°, the average deviation of values of k_t observed in a single run was about 1 or 2%. A typical experiment is shown in Table VI.

TABLE VI

ETHANOLYSIS OF *trans*-5-METHYL-2-CYCLOHEXENYL CHLORIDE AT 50° (EXPT. 31)

t, 10^{-3} sec.	[RCl], 10^2 *M*	10^5k, sec.$^{-1}$
0	4.79	. .
1.86	3.38	16.4
2.82	2.86	16.9
3.60	2.54	16.4
4.50	2.20	16.4
5.40	1.90	16.4
6.48	1.61	16.1
7.20	1.44	16.2
	Average	16.4 ± 0.2

(B) **Acetolysis.**—The solvent containing sodium acetate was prepared by dissolving the calculated amount of sodium carbonate ("Primary standard" grade) in glacial acetic acid. The resulting solution was refluxed overnight with the calculated amount of acetic anhydride required to remove the water produced during the formation of the sodium acetate and that present in the 99.5% acetic acid. All salts (lithium bromide, lithium chloride, lithium acetate and lithium perchlorate) were dried to constant weight by heating *in vacuo*. Because of the fact that sodium chloride is not very soluble in glacial acetic acid, it was necessary to use lithium acetate instead of sodium acetate in experiments involving high initial concentrations of chloride ion. The solvent containing lithium acetate was prepared by dissolving reagent grade lithium acetate in 99.5% acetic acid and refluxing the resulting solution overnight with the calculated amount of acetic anhydride.

The ampule technique was used and from 10 to 12 "points" were taken during a reaction. The "zero-point" titer was determined after temperature equilibration and the reactions were quenched by placing ampules containing the reaction mixture in an ice-bath. The average deviation of values of k_t within a run was generally within 3%. Values obtained in a typical run are shown in Table VII.

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(20) Determined by titration of completely solvolyzed solutions.

(21) A. Berlande, *Bull. soc. chim.*, **9**, 644 (1942).

(22) R. B. Thompson, *Org. Syntheses*, **27**, 21 (1947).

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

(24) J. Baudrenghien, *Bull. acad. belg.*, [5] **15**, 56 (1929).

(25) C. D. Hurd and E. H. Ensor, THIS JOURNAL, **72**, 5135 (1950).

(26) Buu-Hoi and P. Cagniant, *Bull. soc. chim.*, **9**, 99 (1942).

(27) All concentrations are reported for 30°.

(28) H. L. Goering and A. C. Olson, THIS JOURNAL, **75**, 5853 (1953).

(29) W. G. Young, S. Winstein and H. L. Goering, *ibid.*, **73**, 1958 (1951).

(30) S. Winstein, C. Hanson and E. Grunwald, *ibid.*, **70**, 812 (1948).

(31) The temperatures of the two thermostats used in this work were 29.99 ± 0.01° and 50.02 ± 0.01°.

(32) L. F. Fieser, "Experiments in Organic Chemistry," D. C. Heath and Co., New York, N. Y., 1941, p. 359.

(33) P. D. Bartlett and C. G. Swain, THIS JOURNAL, **71**, 1406 (1949).

TABLE VII

SOLVOLYSIS OF *cis*-5-METHYL-2-CYCLOHEXENYL CHLORIDE AT 30° IN ACETIC ACID CONTAINING 0.0518 M SODIUM ACETATE (EXPT. 9)

t, 10^{-3} sec.	[RCl], 10^2 M	10^5k, sec.$^{-1}$
0	4.73	..
2.4	4.63	0.91
6.6	4.50	.83
10.5	4.32	.88
19.6	4.12	.90
24.0	3.70	.87
69.6	2.50	.92
84.6	2.18	.92
94.8	2.04	.90
156.0	1.18	.89
263.4	0.46	.90
	Average	0.89 ± 0.02

Polarimetric Rate Measurements.—Optical rotations were determined with an O. C. Rudolph and Sons high precision model B polarimeter with a precision of ±0.003°. The polarimetric reactions were carried out in a specially constructed (American Instrument Co.) 4.038-dcm. all-glass jacketed polarimeter tube of *ca.* 23-ml. capacity. The reaction solutions were prepared by dissolving a known weight of optically active chloride in solvent. The thermostated mixtures were transferred to the thermostated polarimeter tube through a central filling opening.

The rate constants for the loss in activity were determined from the rotations of the solution during the reaction by use of the relationship

$$k_\alpha = \frac{1}{t} \ln \frac{(\alpha_0 - \alpha_\infty)}{(\alpha_t - \alpha_\infty)}$$

where α_0 is the observed rotation at zero time, α_∞ is the final rotation and α_t is the rotation at time t. A large number of points was taken within a run and the average deviation of the values of k_α for each run are included in Tables I and II. The rate constant (k_α) obtained for an experiment by this method was within 1% of the value obtained from the slope of a least squares plot of ln ($\alpha_t - \alpha_\infty$) against time.

Isolation of Solvolysis Products. (A) Ethanolysis of *cis*- and *trans*-5-Methyl-2-cyclohexenyl Chloride.—Three grams (0.023 mole) of *cis*-5-methyl-2-cyclohexenyl chloride was dissolved in 400 ml. of absolute ethanol containing 0.03 mole of sodium ethoxide (prepared by dissolving 0.7 g. (0.03 mole) of clean sodium in absolute ethanol). As shown by expt. 5 (Table I) the solvolysis of the chloride in this medium is first order. The solution was allowed to stand at room temperature (*ca.* 30°) for six days (*ca.* 16 half-periods) and then diluted with an equal volume of water. The resulting solution was extracted with a 250-ml. and two 100-ml. portions of freshly distilled hexane and the combined hexane extracts were dried. After removal of the hexane by fractionation with a short column the product was flash-distilled under reduced pressure and 85% yield of ethyl 5-methyl-2-cyclohexenyl ether was obtained. The infrared spectrum of this material was a composite of the spectra of *cis*- and *trans*-ethyl-5-methyl-2-cyclohexenyl ethers,[4] and corresponded to a binary mixture consisting of 85 ± 2% of the *trans* isomer. The infrared analysis of binary mixtures of *cis*- and *trans*-ethyl 5-methyl-2-cyclohexenyl ethers has been described previously.[4]

The mixture of ethers resulting from the ethanolysis of *trans*-5-methyl-2-cyclohexenyl chloride under the conditions described above had the same composition (85 ± 2% *trans* isomer and 15 ± 2% *cis* isomer) as the mixture obtained from the *cis*-chloride.

The solvolysis products (*cis*- and *trans*-ethyl 5-methyl-2-cyclohexenyl ether) were shown to be stable under the conditions of the solvolysis by the following experiment. A binary mixture of the isomeric allylic ethers consisting of 34 ± 2% of the *trans* isomer was dissolved in 0.08 M alcoholic sodium ethoxide and the resulting solution was kept at room temperature for 12 days. The allylic ether was recovered as described above and was found to contain 37 ± 2% of the *trans* isomer. This demonstrates that isomerization is not appreciable under the conditions of the solvolysis and that the method of isolation does not result in fractionation of the binary mixture of *cis*- and *trans*-ethyl 5-methyl-2-cyclohexenyl ether.

The ultraviolet spectrum (Cary recording spectrophotometer) of a completely ethanolized (18 half-periods) solution had a peak at 257 mμ, which is characteristic of 5-methyl-1,3-cyclohexadiene.[10] The amount of diene was estimated from the observed optical density and reported extinction coefficient[10] as previously described[3] and corresponded to a 2% yield.

(B) Acetolysis of *cis*- and *trans*-5-Methyl-2-cyclohexenyl Chlorides.—Three grams (0.023 mole) of *cis*-5-methyl-2-cyclohexenyl chloride was dissolved in 400 ml. of glacial acetic acid containing 0.04 mole of sodium acetate. As shown by data in Tables I and II the solvolysis is first order in this medium. The reaction mixture was allowed to stand at room temperature for six days (*ca.* 7 half-periods) and the binary mixture of *cis*- and *trans*-5-methyl-2-cyclohexenyl acetates was isolated in 90% yield by the procedure described above for the isolation of the ethers formed in the ethanolysis. The binary mixture was found to consist of 97 ± 2% of the *trans* isomer by infrared analysis. The method of analysis has been described previously.[4]

The binary mixture of acetates resulting from the acetolysis of *trans*-5-methyl-2-cyclohexenyl chloride under the conditions described above consisted of 94 ± 2% of the *trans* isomer.

The following experiment shows that the methylcyclohexenyl acetates are not isomerized under the conditions of the solvolysis and that the binary mixture is not fractionated during the isolation. To a solution of 0.20 g. (0.024 mole) of fused sodium acetate in 240 ml. of dry acetic acid was added 1.8 g. (0.012 mole) of a binary mixture of the isomeric 5-methyl-2-cyclohexenyl acetates consisting of 41 ± 2% of the *trans* isomer. After keeping the solution at room temperature for 13 days the mixture of acetates was isolated as described above and consisted of 39 ± 2% of the *trans* isomer.

Isolation of Unsolvolyzed *cis*-5-Methyl-2-cyclohexenyl Chloride.—A solution of 6 g. (0.046 mole) of the *cis*-chloride and 4.1 g. (0.05 mole) of sodium acetate in 100 ml. of acetic acid was thermostated at 30° for 10.5 hours (0.7 titrimetric half-life, Table I, expt. 12). An equal volume of water was added and the mixture was extracted with one 100-ml. and two 50-ml. portions of hexane. The extracts were combined, washed twice with 100-ml. portions of 5% sodium hydroxide solution (to remove acetic acid), dried, and fractionally distilled. It was found impossible to remove all the 5-methyl-2-cyclohexenyl acetate from the chloride, because the extended heating required for efficient fractionation isomerizes the chlorides.[5] However, by comparing the optical density of the mixture at 13.0 μ, where the isomeric chlorides absorb to considerably different extents and the acetates absorb only very weakly, with those of synthetic mixtures of pure Ib and *trans*-acetate and pure IIb and *trans*-acetate, it was determined that the chloride fraction contained >95% of the *cis* isomer. When the same experiment was repeated with *trans*-5-methyl-2-cyclohexenyl chloride, the recovered chloride contained >95% of the *trans* isomer. In neither case was there positive evidence for *any cis–trans* isomerization of the chlorides.

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