E. Reaction of the Ester Ylide Ia with Methyl Maleate.—A stirred solution of 9.2 mmol of ester ylide Ia and 1.32 g (9.2 mmol) of methyl maleate was heated under reflux for 17 hr. Concentration and vpc analysis indicated the formation of a 71% yield of cyclopropane XXI. The latter was isolated by evaporation of the solvent and sublimation of the residual oil to afford XXI as a colorless powder, mp 54–56° (lit.[36] mp 56–57°), ν_{CO} 1720 cm^{-1}.

Anal. Calcd for $C_9H_{12}O_6$: C, 50.00; H, 5.59. Found: C, 50.11; H, 5.73.

Registry No.—1, 19023-61-1; 2, 19023-62-2; 3, 19023-63-3; 4, 19023-64-4; 5, 19643-11-9; 6, 5697-33-6; 7, 19643-13-1; 8, 19643-14-2; 9, 19643-15-3; 10, 19643-16-4; 11, 19643-17-5; Ia, 18915-90-7; II, 5633-34-1; VIII, 14679-98-2; IX, 5633-35-2; X, 5633-68-1; XI, 5633-36-3; XIII, 5492-70-6; XIV, 19643-24-4; XV, 4727-41-7; XVI, 10132-50-0; XIX, 19643-27-7; XX, 19643-28-8; phenacyldimethylsulfonium bromide, 5667-47-0; carbomethoxymethyldimethylsulfonium bromide, 19643-31-3; carbomethoxymethyldimethylsulfonium chloride, 19643-32-4.

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(36) C. Grundmann, *Ann.*, **555**, 77 (1943).

Polarity Effects in the Solvolysis of Cyclohexane Derivatives. The Importance of Field Effects in Determining Relative Reactivities[1,2]

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The rates of acetolysis of 4-substituted cyclohexyl methanesulfonates are shown to be dependent upon the polarity and conformation of the substituent as well as the conformation of the leaving methanesulfonate group. Rates of solvolysis for *cis*- and *trans*-4-chlorocyclohexyl methanesulfonate and for *cis*- and *trans*-4-bromocyclohexyl methanesulfonate have been calculated using a field effect model by employing the observed ground-state conformer populations (as determined by infrared spectroscopy) and the appropriate bond dipoles. The good agreement of the kinetic data with rate constants calculated employing a purely field effect model indicates the absence, or at least the very small role, of "through-the-bond" inductive effects.

Some years ago investigations in these laboratories showed that the solvolysis of 4-methoxycyclohexyl tosylate occurs with methoxyl participation.[4,5] In developing a comprehensive interpretation of the nature of the products, one of the questions which was very difficult to answer was the expected rate in the absence of participation. We did not reach a definitive conclusion at this point in our earlier publications. One approach, in order to gain further information at this point, is to examine the rate of solvolysis of substituted cyclohexane derivatives with polar substituents, which should be expected *not* to participate in any transannular sense. Chloro and cyano substituents satisfy this criterion very well. It is therefore the purpose of the present report to examine the solvolysis of such systems. In the course of this study it became apparent that the influence of the polarity of the substituent causes a very substantial perturbation of the conformational equilibria of the starting materials, the cyclohexyl sulfonates, and that in addition field effects are particularly important in determining the relative reactivities of the pairs of isomers.

Results

The preparation of the requisite compounds was in general unexceptional. Treatment of 1,4-epoxycyclohexane with concentrated hydrochloric acid[6] afforded *trans*-4-chlorocyclohexanol (1) in excellent yield. The configuration of 1 is confirmed by the studies of Heine,[7] who demonstrated the formation of 1,4-epoxycyclohexane in the reaction of 1 with base. From 1, tosylate 2 and methanesulfonate 3 were prepared. Treatment of 1 with sodium acetate in dimethylformamide afforded an authentic sample of *cis*-4-chlorocyclohexanol (4), from which tosylate 5 and methanesulfonate 6 were prepared. Solvolysis of 2 and of 5 in acetic acid showed that the *cis* isomer solvolyzes more slowly than the *trans* isomer. Examination of the products from each of these solvolyses showed that they were the normal products; *i.e.*, there was no evidence for any participation. This result shows that the polar influence of the chloro substituent vitiates the general rule that *trans*-4-substituted cyclohexane derivatives will generally react more slowly than *cis* isomers, for the reason that the *cis* isomer will have a higher population of that conformation with the reacting moiety in the axial position.

In order to determine the source of this inversion of relative reactivities, we have examined the conformational population of a number of derivatives of 4-chlorocyclohexanol. During the course of this study, Takeoka[8] reported that 1 is 28% in the diaxial conformation in carbon disulfide solution. It is known that both 1,4-dichlorocyclohexane and 1,4-dibromocyclohexane are predominantly in the diaxial conformation in a variety

(1) Supported in part by grants from the National Science Foundation, G-13125, GP-1572, and GP-6133X.

(2) A portion of this work has been published in a preliminary form: D. S. Noyce, B. N. Bastian, and R. S. Monson, *Tetrahedron Lett.*, 863 (1962).

(3) Dow Chemical Fellow in Chemistry, 1961–1962.

(4) D. S. Noyce, B. R. Thomas, and B. N. Bastian, *J. Amer. Chem. Soc.*, **82**, 885 (1960).

(5) D. S. Noyce and B. N. Bastian, *ibid.*, **82**, 1246 (1960).

(6) E. L. Bennett and C. Niemann, *ibid.*, **74**, 5076 (1952).

(7) H. W. Heine, *ibid.*, **79**, 6268 (1957).

(8) Y. Takeoka, *Bull. Chem. Soc. Jap.*, **35**, 1371 (1962).

of solvents.[9] We find, from an examination of the infrared spectrum, that *trans*-4-chlorocyclohexyl acetate appears to be 73% in the diaxial conformation in carbon disulfide solution, while *cis*-4-chlorocyclohexyl acetate appears to be a 46:54 mixture of two conformations. These results were obtained from measurements using the 752- and 717-cm^{-1} bands representing equatorial and axial carbon–chlorine stretching vibrations, respectively. In the case of **2**, such an examination of the ground-state conformation was precluded by the intense aromatic absorptions in this region of the spectrum. In the hope that the spectrum could be simplified by a change to an aliphatic sulfonate, we turned our attention to the examination of the methanesulfonates. The results of these studies will be elaborated below.

An analogous preparative sequence was used to obtain both *trans*-4-bromocyclohexanol (**7**), trans-4-bromocyclohexyl tosylate (**8**), and *trans*-4-bromocyclohexyl methanesulfonate (**9**). Reduction of 4-bromocyclohexanone afforded a mixture rich in *cis*-4-bromocyclohexanol (**10**) which was largely separated by fractionation. Tosylate **11** and methanesulfonate **12** were prepared.

The synthesis of the cyanocyclohexanols started with the known isomers of the hydroxycyclohexanecarboxylic acids. As each hydroxy acid was converted smoothly into a distinctive cyanocyclohexanol, we consider this method of preparation adequate proof of configuration for the cyanocyclohexanols. *trans*-4-Cyanocyclohexanol (**13**), *cis*-4-cyanocyclohexanol (**14**), *trans*-3-cyanocyclohexanol (**15**), and *cis*-3-cyanocyclohexanol (**16**) were prepared in this fashion, and converted into the respective sulfonate esters.

Conformational Relationships.—The use of the methanesulfonates provided opportunity to examine directly the conformational situation of the reacting systems. We have shown[10] that the methanesulfonate group has an A value of 0.56, and that two bands in the region 900–950 cm^{-1} are characteristic for axial and equatorial methanesulfonates. Using the bands at 936 cm^{-1} (equatorial sulfonate) and the band at 909 ± 3 cm^{-1} (axial sulfonate) which were shown to have nearly identical extinction coefficients,[10] we obtain the results for the conformational populations given in Table I.

TABLE I

OBSERVED CONFORMATIONAL POPULATIONS OF THE 4-HALOCYCLOHEXYL METHANESULFONATES IN CARBON TETRACHLORIDE SOLUTION

Compd	% equatorial OMs	% axial OMs
3	39.8	60.2
6	63.6	36.4
9	37.0	63.0
12	62.9	37.1

It is to be noted that the *trans* isomers are predominantly in the diaxial conformation, similar to the 1,4-dihalocyclohexanes.[9]

(9) K. Kozima and T. Yoshino, *J. Amer. Chem. Soc.*, **75**, 166 (1953).
(10) D. S. Noyce, B. E. Johnston, and B. Weinstein, *J. Org. Chem.*, **34**, 463 (1969).

Kinetic Results

The results of measurement of the rate of acetolysis of the several compounds prepared in this study are given in Table II.

TABLE II

RATES OF ACETOLYSIS OF SUBSTITUTED CYCLOHEXYL SULFONATES

Compd	Concn of sulfonate, M[a]	Temp,[b] °C	10^6k, sec^{-1}
2	0.03	75.00	4.58 ± 0.6
	0.03	90.00	28.5 ± 0.6
5	0.03	75.00	2.07 ± 0.03
	0.03	90.00	12.1 ± 0.2
3	0.05	70.00	3.11 ± 0.05
	0.05	90.00	30.3 ± 0.7
6	0.05	70.00	1.31 ± 0.02
	0.05	90.00	14.5 ± 0.2
8	0.05	89.97	24.2 ± 0.7
11	0.05	89.97	12.1 ± 0.2
9	0.05	70.00	2.56 ± 0.09
	0.05	90.00	27.1 ± 0.08
12	0.05	70.00	1.27 ± 0.01
	0.05	90.00	12.4 ± 0.1
13-OTs	0.05	90.00	9.32 ± 0.05
14-OTs	0.05	90.00	8.14 ± 0.12
15-OTs	0.05	90.00	5.89 ± 0.1
16-OTs	0.05	90.00	3.84 ± 0.1

[a] All solvolyses were carried out in acetic acid with added acetic anhydride and sodium acetate, both at twice the concentration of the sulfonate. [b] Temperatures all ±0.03°.

The rates of solvolysis of the compounds studied in this report are uniformly less than the rates for cyclohexyl itself. This is, of course to be expected for compounds containing electron-withdrawing substituents. It is of interest to examine the rate ratios (k_{trans}/k_{cis}) for each of these pairs. The data are summarized in Table III, along with additional data reported previously from these laboratories[4,11] and by Mori.[12,13]

TABLE III

RATE RATIOS FOR SOLVOLYSIS OF SUBSTITUTED CYCLOHEXYL SULFONATES

Substituted cyclohexyl	Sulfonate group	Temp, °C	k_{trans}/k_{cis}	Ref
4-Chloro	OTs	90	2.34	*a*
	OMs	90	2.09	*a*
4-Bromo	OTs	90	2.02	*a*
	OMs	90	2.19	*a*
4-Cyano	OTs	90	1.13	*a*
4-Methoxy	OTs	75	4.18	*b*
4-Acetoxy	OTs	99.8	2.50	*c*
4-Tosyloxy	OTs	99.8	2.18	*d*
3-Cyano	OTs	90	1.53	*a*
3-Methoxy	OTs	75	1.49	*b*
3-Methoxycarbonyl	OTs	75	4.7	*e*

[a] Present study. [b] Reference 4. [c] Reference 12. [d] Reference 13. [e] Reference 11.

For the 4-substituted cyclohexyl sulfonates the *trans* isomer typically solvolyzes about twice as rapidly as the *cis* isomer. This generalization helps to clarify the ex-

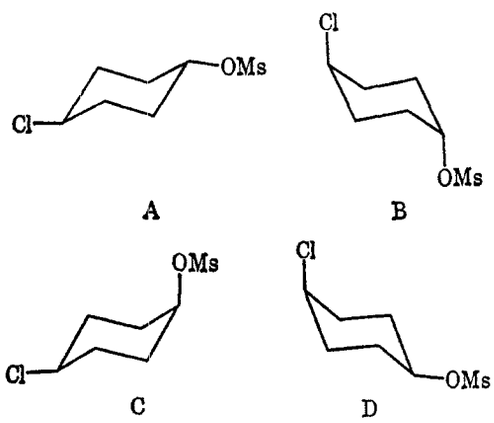
(11) D. S. Noyce and H. I. Weingarten, *J. Amer. Chem. Soc.*, **79**, 3103 (1957).
(12) N. Mori, *Bull. Chem. Soc. Jap.*, **33**, 1332 (1960).
(13) N. Mori, *ibid.*, **34**, 110 (1961).

tent of methoxyl participation in *trans*-4-methoxycyclohexyl tosylate.[5]

In the limited number of cases of 3-substituted cyclohexyl sulfonates, the *trans* isomers solvolyze more rapidly than the *cis* isomers. This is a more "normal" ratio, and shows that a major portion of the inversion in rate for the 4-substituted cyclohexyl sulfonates comes from the reversal of the ground-state conformational populations (see Table I).

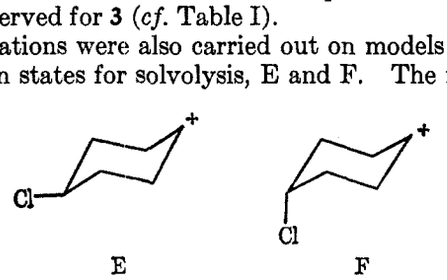
In order to establish more clearly the role of electrostatic interactions in the solvolysis of 4-chlorocyclohexyl methanesulfonate, we have carried out calculations based on a Kirkwood–Westheimer model.

Models for the two conformations of **3** (A and B) and of **6** (C and D) were used. Distances and geometry



were taken from standard sources.[14] Using a relatively high group moment for the methanesulfonoxy group,[15,16] conformation B is slightly more than 1 kcal more stable than conformation A on electrostatic grounds alone. Conformations C and D are of essentially equal energy, in agreement with the experimental observations. For conformations A and B, the addition of this dipole–dipole interaction to the normal steric terms which are encompassed in the *A* values results in a satisfactory explanation of the conformational equilibria which we have observed for **3** (*cf.* Table I).

Calculations were also carried out on models for the transition states for solvolysis, E and F. The method



of calculation followed that used and recently described by Wilcox and Leung.[17,18] The extent to which charge was developed at C-1 was varied in subsequent calculations. The most usual model assumes that *X*, the fractional positive charge, is 0.50.[19] We observe somewhat more satisfactory fit of experimental results with calculation when *X* is set at 0.8.

For models E and F, there is greater electrostatic repulsion in E than in F which amounts to nearly 0.9 kcal/mol. From the calculations of the ground-state energies, and electrostatic interactions in the transition state, one may then predict the rates of acetolysis for the halogen-substituted cyclohexyl methanesulfonates, by using observed rates for *trans*-4-methylcyclohexyl methanesulfonates and *cis*-4-*t*-butylcyclohexyl methanesulfonate[10] as models for pure, unperturbed equatorial and axial rates. Table IV summarizes these comparisons.

TABLE IV
COMPARISON OF CALCULATED AND EXPERIMENTAL ACETOLYSIS RATES AT 70°

Cyclohexyl methanesulfonate	10^6k, sec^{-1} Calcd	Exptl	$k_{calcd}/k_{exp\ tl}$
3	2.14	3.11	0.69
6	1.37	1.31	1.05
9	2.52	2.56	0.98
12	1.60	1.27	1.26

The very satisfactory agreement between the observed rates of acetolysis of **3**, **6**, **9**, and **12** with those calculated using a field effect model indicates the absence, or at least the very small role, of a "through-the-bond" inductive effect. If inductive effects were dominant, then conformers of the same methanesulfonate conformation would be expected to show the same reactivity. The results of the present study show that this is not the case, and that an axial bromine or chlorine is rate enhancing relative to equatorial bromine or chlorine by a factor of 3.2 or 2.04, respectively. Field effect calculations predict ratios of 3.5 and 3.02, respectively.

In making these calculations we were greatly assisted by Professor C. F. Wilcox of Cornell University, who generously made his FIELD computer program available to us.[11] We also wish to thank Professor Wilcox for his counsel in carrying through these calculations.[20]

The composition of solvolysis product mixtures are given in Table V.

TABLE V
COMPOSITION OF SOLVOLYSIS PRODUCT MIXTURES

Compd solvolyzed	Products formed,[a] mol % A	B	C	D	E	F
2	83.8	N.D.[b]	14.9	1.3		
5	70.7	N.D.	<0.5	29.3		
3	87.5	N.D.	11.1	1.4		
6	81.4	N.D.	1.1	17.5		
9	80.5	2.3	15.3	2.0		
12	74.6	4.4	1.1	19.9		
15-OTs	61.4	8.1			23.5	6.9
16-OTs	51.6	12.6			<1.0	35.8

[a] Products formed: A = 4-ene; B = 3-ene; C = *cis*-4-acetate; D = *trans*-4-acetate; E = *cis*-3-acetate; F = *trans*-3-acetate. [b] N.D. = not determined. The isolated chlorocyclohexene had an infrared spectrum essentially identical with that of authentic 4-chlorocyclohexene.

(14) E. L. Eliel, "Conformational Analysis," Interscience Publishers, New York, N. Y., 1965, p 454.

(15) *Cf.* the dipole moment of dimethyl sulfone[16] of 4.44 D.

(16) V. Baliah and Sp. Shanmuganathan, *Trans. Faraday. Soc.*, **55**, 232 (1959).

(17) C. F. Wilcox and C. Leung, *J. Amer. Chem. Soc.*, **90**, 336 (1968).

(18) The energy of interaction between a dipole at C-4 and a charge at C-1 were calculated by computing the energies of an array of charges embedded in a cavity of dielectric constant 2, in turn embedded in a continuous medium of higher dielectric constant (6.62 for acetic acid). Calculations were made using both the molecular volume as calculated by Traube's rules [J. Traube, *Samml. Chem. Chem.-Tech. Vortr.*, **4**, 255 (1899)] and also estimating the radius of the cavity by Tanford's method [C. Tanford, *J. Amer. Chem. Soc.*, **79**, 5348 (1957)].

(19) S. Winstein, E. Grunwald, and L. L. Ingraham, *ibid.*, **70**, 821 (1948).

(20) The calculations were made at the Computer Center, University of California, using an IBM 7094 computer. We wish to thank the center for making computer time available to us.

Experimental Section[21]

trans-**4-Chlorocyclohexanol** (1).—Treatment of 1,4-epoxycyclohexane with concentrated hydrochloric acid at room temperature for 8 days, following the procedure of Bennett and Niemann,[6] afforded *trans*-4-chlorocyclohexanol, mp 84–85°, in 72% yield (lit.[6,22] mp 82–83°).

trans-**4-Chlorocyclohexyl acetate** was prepared from *trans*-4-chlorocyclohexanol in the usual manner: bp 93.5–93.7° (4.5 mm); n^{25}D 1.4644; distinguishing ir bands at 8.97, 9.90, and 13.78 μ.

Anal. Calcd for $C_8H_{13}ClO_2$: C, 54.39; H, 7.42; Cl, 20.07. Found: C, 54.52; H, 7.37; Cl, 20.10.

trans-**4-Chlorocyclohexyl 3,5-dinitrobenzoate**, prepared in the usual manner,[23] crystallized from ethyl acetate in lustrous white plates, mp 158.8–159.8°.

Anal. Calcd for $C_{13}H_{13}ClN_2O_6$: C, 47.58; H, 3.99; Cl, 10.79; N, 8.52. Found: C, 47.75; H, 4.12; Cl, 10.68; N, 8.46.

trans-**4-Chlorocyclohexyl** *p*-**toluenesulfonate** (2) was prepared from *p*-toluenesulfonyl chloride and *trans*-4-chlorocyclohexanol in pyridine. Isolation in the usual manner afforded *trans*-4-chlorocyclohexyl *p*-toluenesulfonate, mp 74.6–76.0°. A sample for analysis and for the kinetic runs was prepared by additional crystallization from hexane–carbon tetrachloride, mp 76.1–76.9°.

Anal. Calcd for $C_{13}H_{17}ClO_3S$: C, 54.06; H, 5.94; Cl, 12.28; S, 11.10. Found: C, 54.06; H, 6.15; Cl, 12.40; S, 10.88.

trans-**4-Chlorocyclohexyl methanesulfonate** (3) was prepared following the procedure of Truce, Campbell, and Norbell[24] in nearly quantitative yield. Crystallization from ligroin (bp 90–120°) gave pure material, mp 88.5–89.0°.

Anal. Calcd for $C_7H_{13}ClO_3S$: C, 39.53; H, 6.16; S, 15.08. Found: C, 39.31; H, 5.94; S, 15.03.

cis-**4-Chlorocyclohexanol** (4).—*trans*-4-Chlorocyclohexyl tosylate was heated with sodium acetate in dimethylformamide (steam bath, 72 hr) to afford *cis*-4-chlorocyclohexyl acetate in 27% yield, after distillation and chromatography on alumina: bp 80–81° (1 mm); n^{25}D 1.4675; distinguishing ir bands at 9.07, 11.53 and 13.92 μ. Vapor phase chromatography on a silicone oil–Chromosorb column revealed that the material is greater than 96% *cis* isomer. The *cis*-4-chlorocyclohexyl acetate was reduced with lithium aluminum hydride to afford *cis*-4-chlorocyclohexanol, which slowly crystallized, mp 23.8–25.6° (from hexane).

Reduction of 4-chlorocyclohexanone with lithium aluminum hydride afforded a mixture of *cis*- and *trans*-4-chlorocyclohexanols (60% *cis*) which was separated by distillation at reduced pressure with a spinning-band column to afford a larger sample of *cis*-4-chlorocyclohexanol, which crystallized slowly and was 97% *cis* by vpc.

cis-**4-Chlorocyclohexyl 3,5-dinitrobenzoate**, prepared in the usual manner,[23] was crystallized from ethyl acetate–hexane, mp 158.2–159.6° (mmp 132–136° with *trans* isomer).

Anal. Calcd for $C_{13}H_{13}ClN_2O_6$: C, 47.58; H, 3.99; Cl, 10.79; N, 8.52. Found: C, 47.47; H, 4.05; Cl, 10.83; N, 8.59.

cis-**4-Chlorocyclohexyl tosylate** (5), prepared in the usual manner, was crystallized from hexane, mp 66.0–67.0°.

Anal. Calcd for $C_{13}H_{17}ClO_3S$: C, 54.06; H, 5.94; Cl, 12.28; S, 11.10. Found: C, 53.88; H, 6.08; Cl, 12.14; S, 10.98.

cis-**4-Chlorocyclohexyl methanesulfonate** (6) was prepared by treating a mixture of *cis*-4-chlorocyclohexanol and methanesulfonyl chloride in benzene, cooled to 0°, with a 10% excess of triethylamine. The precipitated triethylamine hydrochloride was removed by filtration, and the solvent and excess triethylamine were removed under reduced pressure. The residual oil slowly crystallized from anhydrous methanol at −78° and was then crystallized twice from cyclohexane to give *cis*-4-chlorocyclohexyl methanesulfonate, mp 44.2–44.7°.

Anal. Calcd for $C_7H_{13}ClO_3S$: C, 39.53; H, 6.16; S, 15.08. Found: C, 39.37; H, 5.95; S, 14.88.

trans-**4-Bromocyclohexanol** (7).—1,4-Epoxycyclohexane (217 g) was mixed with 48% aqueous hydrobromic acid (391 g), and the solution stirred at 50°. After 3 days, the solution separated into two layers. The reaction was discontinued after 6 days. The mixture was saturated with sodium chloride and extracted with ether. The ethereal solution was washed with sodium bicarbonate solution, then water, then dried over anhydrous sodium sulfate. The ether was evaporated and a small amount of unreacted oxide (*ca.* 10 g) was distilled under reduced pressure from the residue, which then solidified upon standing. Two recrystallizations from hexane gave 233 g (59%) of *trans*-4-bromocyclohexanol as white plates, mp 81–82° (lit.[8] mp 81.0–81.5°).

Anal. Calcd for $C_6H_{11}BrO$: C, 40.24; H, 6.28; Br, 44.67. Found: C, 40.22; H, 6.11; Br, 44.73.

In the case of 4-bromocyclohexanol, the reaction of 1,4-epoxycyclohexane with hydrogen bromide is not so stereospecific as with HCl.

trans-**4-Bromocyclohexyl 3,5-dinitrobenzoate** was prepared in the usual way.[23] Recrystallization from ethanol–ethyl acetate gave white plates, mp 164–165°.

Anal. Calcd for $C_{13}H_{13}BrN_2O_6$: C, 41.82; H, 3.49; Br, 21.44; N, 7.50. Found: C, 42.06; H, 3.72; Br, 21.23; N, 7.34.

trans-**4-Bromocyclohexyl tosylate** (8) was prepared in the usual manner. Six crystallizations from hexane afforded pure material, mp 85–86°.

Anal. Calcd for $C_{13}H_{17}BrO_3S$: C, 46.85; H, 5.14; Br, 23.98; S, 9.62. Found: C, 46.97; H, 5.11; Br, 23.91; S, 9.48.

trans-**4-Bromocyclohexyl Methanesulfonate** (9).—*trans*-4-Bromocyclohexanol (10.00 g) and methanesulfonyl chloride (6.40 g) were cooled to 0° in benzene (50 ml) and a 10% excess of triethylamine in benzene (6.40 g of triethylamine in 25 ml of benzene) was added over 30 min, with stirring. The precipitate of triethylamine hydrochloride (7.85 g, 102%) was filtered off, and the solvent and excess triethylamine were removed by distillation at reduced pressure, leaving a residual white solid (13.5 g, 0.052 mol, 94%). This solid was recrystallized twice from hexane to give pure *trans*-4-bromocyclohexyl methanesulfonate (7.60 g, 52.8%), mp 83.5–84.0°.

Anal. Calcd for $C_7H_{13}BrO_3S$: C, 32.70; H, 5.10; S, 12.47. Found: C, 32.58; H, 5.08; S, 12.32.

cis-**4-Bromocyclohexanol** (10).—*trans*-4-Bromocyclohexanol was oxidized with sodium dichromate in 10% sulfuric acid. After 2 hr at 50° the reaction solution was cooled and extracted with ethyl ether, and the extract was washed with sodium bicarbonate solution and with water. The dried ether solution of 4-bromocyclohexanone was used directly for reduction with lithium aluminum hydride. Addition of this solution to a slurry of lithium aluminum hydride in ethyl at −78° was carried out over 100 min. The reaction mixture was allowed to return to room temperature over 90 min and then heated briefly. After work-up in the usual fashion distillation at reduced pressure afforded a yellow oil (76% over-all yield from *trans*-4-bromocyclohexanol), which proved to be a mixture of 57% *cis*- and 43% *trans*-4-bromocyclohexanol by vpc. Careful refractionation of this material at reduced pressure gave samples of *cis*-4-bromocyclohexanol of up to 97% *cis* content (by vapor phase chromatography), bp 94° (20 mm).

cis-**4-Bromocyclohexyl 3,5-dinitrobenzoate** was prepared in the usual way, and the product recrystallized from ethanol: mp 163–164°; mmp 137–140° with *trans* isomer.

Anal. Calcd for $C_{13}H_{13}BrN_2O_6$: C, 41.82; H, 3.49; Br, 21.44; N, 7.50. Found: C, 41.81; H, 3.65; Br, 21.47; N, 7.56.

cis-**4-Bromocyclohexyl Tosylate** (11).—The oily *cis*-4-bromocyclohexenol was dissolved in pyridine and treated with *p*-toluenesulfonyl chloride in the usual way. The product was recrystallized six times from hexane: mp 79–80°; mmp 57–62° with *trans* isomer.

Anal. Calcd for $C_{13}H_{17}BrO_3S$: C, 46.85; H, 5.14; Br, 23.98; S, 9.62. Found: C, 46.57; H, 5.16; Br, 24.18; S, 9.38.

cis-**4-Bromocyclohexyl Methanesulfonate** (12).—A *cis*-rich mixture of *cis*- and *trans*-4-bromocyclohexanols (containing 85.1% *cis* isomer by vpc) was treated with methanesulfonyl

(21) Melting points are corrected; boiling points are uncorrected. Analyses are by the Microanalytical Laboratory, University of California.

(22) E. A. Fehnel, S. Goodyear, and J. Berkowitz, *J. Amer. Chem. Soc.*, **73**, 4978 (1951).

(23) S. M. McElvain, "The Characterization of Organic Compounds," The MacMillan Co., New York, N. Y., 1956, p 199.

(24) W. E. Truce, R. W. Campbell, and J. R. Norbell, *J. Amer. Chem. Soc.*, **86**, 288 (1964).

chloride and a 10% excess of triethylamine in benzene. After work-up as described above a pale yellow viscous oil was obtained, which did not crystallize. Several drops were dissolved in a minimal amount of methylcyclohexane at 60°, and the solution was seeded with a small crystal of *trans*-4-bromocyclohexyl methanesulfonate and cooled. The main portion of the product was then taken up in minimal methylcyclohexane at 60°, filtered hot, cooled in an ice bath, and seeded with some seed crystals formed above. This process induced crystallization as a partially crystalline mass. The material was allowed to stand for 1 hr in the ice bath, whereupon the mass was broken up with a spatula, filtered cold, and air dried, obtaining crude *cis*-4-bromocyclohexyl methanesulfonate with mp 25–40°, mostly at 37–40°. Three further recrystallizations from methylcyclohexane as above gave pure *cis*-4-bromocyclohexyl methanesulfonate (45% yield), mp 44.5–45.0°.

Anal. Calcd for $C_7H_{13}BrO_3S$: C, 32.70; H, 5.10; S, 12.47. Found: C, 32.89; H, 5.23; S, 12.55.

cis-4-Carboxamidocyclohexanol.—*cis*-4-Hydroxycyclohexanecarboxylic acid lactone[25] (17.1 g) was mixed with concentrated aqueous ammonium hydroxide (200 ml) and stirred at room temperature. Dissolution of the solid lactone occurred after 30 min and stirring was continued for an additional 2.5 hr. Ammonia and water were removed under reduced pressure and the white solid residue was recrystallized from acetonitrile: mp 140–143°; yield 14.6 g (75%).

Anal. Calcd for $C_7H_{13}NO_2$: C, 58.74; H, 9.10; N, 9.80. Found: C, 58.46; H, 8.82; N, 9.62.

cis-4-Carboxamidocyclohexyl Acetate.—*cis*-4-Carboxamidocyclohexanol (13.6 g) was stirred at room temperature with 100 ml of pyridine and 100 ml of acetic anhydride for 24 hr. Volatile materials were removed by vacuum distillation, and the residue was recrystallized from benzene–hexane, giving white plates: mp 137–139°; yield 13.4 g (76%).

Anal. Calcd for $C_9H_{15}NO_3$: C, 58.43; H, 8.11; N, 7.57. Found: C, 58.45; H, 7.93; N, 7.54.

cis-4-Cyanocyclohexyl Tosylate.—*cis*-4-Carboxamidocyclohexyl acetate (13.4 g) was dissolved in thionyl chloride (50 ml) and refluxed for 1 hr. Excess thionyl chloride was removed on an aspirator. The infrared spectrum of the residue showed complete conversion of the amide into *cis*-4-cyanocyclohexyl acetate, as evidenced by the disappearance of the amide band at 6.08 μ and the appearance of the strong nitrile band at 4.46 μ. The oily product was then stirred with aqueous sodium hydroxide (400 ml, 0.2 *N*) for 11 hr at room temperature. The mixture was then continuously extracted with ether overnight. Evaporation of the ether left an oil whose infrared spectrum showed complete conversion of the acetate to *cis*-4-cyanocyclohexanol (**14**), as evidenced by the disappearance of the acetate band at 5.78 μ and the appearance of the hydroxyl band at 2.88 μ. Treatment of this oil with pyridine and *p*-toluenesulfonyl chloride in the usual way gave a solid tosylate which was recrystallized from cyclohexane affording white needles: mp 105–106°; yield 5.4 g (20.7%).

Anal. Calcd for $C_{14}H_{17}NO_3S$: C, 60.21; H, 6.13; N, 5.02; S, 11.47. Found: C, 60.02; H, 5.91; N, 5.36; S, 10.22.

trans-4-Carboxamidocyclohexyl Acetate.—*trans*-4-Acetoxycyclohexanecarboxylic acid (8.1 g), prepared by the method of Campbell and Hunt,[26] was combined wth redistilled thionyl chloride (20 ml) and the mixture refluxed for 1 hr. Excess thionyl chloride was removed and the oily residue poured slowly into 50 ml of concentrated aqueous ammonia. The white solid precipitate was recrystallized from chloroform–cyclohexane giving crystals: mp 198–200°; yield 3.9 g (48%).

Anal. Calcd for $C_9H_{15}NO_3$: C, 58.43; H, 8.11; N, 7.57. Found: C, 58.22; H, 8.19; N, 7.55.

trans-4-Cyanocyclohexyl Tosylate.—*trans*-4-Carboxamidocyclohexyl acetate (10.6 g) was mixed with purified thionyl chloride (40 ml) and the solution refluxed for 1 hr. Excess thionyl chloride was removed on an aspirator and the residual oil stirred with aqueous sodium hydroxide solution (200 ml, 0.4 *N*) for 40 hr at room temperature. The mixture was then continuously extracted with ether and the ether evaporated. The infrared spectrum of the crystalline product showed complete conversion of *trans*-4-acetoxycyclohexanecarboxamide into *trans*-4-cyanocyclohexanol (**13**), as evidenced by the disappearance of the amide and acetate bands at 6.13 and 5.78 μ, respectively, and the appearance of the strong nitrile band and the hydroxyl band at 4.46 and 2.89 μ, respectively. The white solid was dissolved in pyridine and treated with *p*-toluenesulfonyl chloride in the usual way. The product was recrystallized from cyclohexane: mp 95–96°; yield 4.9 g (24%).

Anal. Calcd for $C_{14}H_{17}NO_3S$: C, 60.21; H, 6.13; N, 5.02; S, 11.47. Found: C, 60.07; H, 6.36; N, 5.21; S, 11.64.

cis-3-Carboxamidocyclohexanol.—The lactone of 3-hydroxycyclohexanecarboxylic acid[27] (63 g, mp 117–119°) was treated with 220 ml of concentrated aqueous ammonia at room temperature for 2 hr. After cooling in ice, the precipitated solid was collected and an additional crop obtained by concentration of the filtrate under reduced pressure. The crude amide was crystallized from ethyl acetate: mp 176–178.5°; yield 75%.

Anal. Calcd for $C_7H_{13}NO_2$: C, 58.72; H, 9.15. Found: C, 58.51; H, 8.97.

cis-3-Carboxamidocyclohexyl acetate was prepared by treatment of the amide with acetic anhydride and pyridine at room temperature for 20 hr. The white crystalline solid obtained upon removal of the excess pyridine and acetic anhydride under vacuum was crystallized from 1:1 benzene–ligroin (bp 60–90°): mp 131.5–133°; yield 68%.

Anal. Calcd for $C_9H_{15}NO_3$: C, 58.43; H, 8.11. Found: C, 59.09; H, 7.97.

cis-3-Cyanocyclohexyl Acetate.—*cis*-3-Carboxamidocyclohexyl acetate (48.5 g) was added to 90 ml of redistilled thionyl chloride and heated under reflux for 2 hr. Excess thionyl chloride was removed under reduced pressure to give a residual oil which solidified on chilling. The crude *cis*-3-cyanocyclohexyl acetate was crystallized twice from ethanol–water, mp 39–41°.

Anal. Calcd for $C_9H_{13}NO_2$: C, 64.65; H, 7.84. Found: C, 64.48; H, 7.92.

cis-3-Cyanocyclohexyl Tosylate.—*cis*-3-Cyanocyclohexyl acetate was hydrolyzed to *cis*-3-cyanocyclohexanol with 0.2 *N* NaOH, and the progress of the reaction was monitored by infrared. After 22 hr, the ester band was absent. Crude *cis*-3-cyanocyclohexanol (**16**) was isolated by continuous extraction with ether, and concentration of the ether extracts. The crude alcohol was treated directly with *p*-toluenesulfonyl chloride in the usual manner to afford *cis*-3-cyanocyclohexyl tosylate, mp 67–68° (from CCl_4).

Anal. Calcd for $C_{14}H_{17}NO_3S$: C, 60.21; H, 6.13. Found: C, 60.03; H, 5.97.

trans-3-Carboxamidocyclohexyl Acetate.—*trans*-3-Hydroxycyclohexanecarboxylic acid[28] was converted into *trans*-3-acetoxycyclohexanecarboxylic acid by treatment with acetic anhydride and pyridine. The crude *trans*-3-acetoxycyclohexanecarboxylic acid was treated with thionyl chloride and the crude acid chloride poured into concentrated aqueous ammonium hydroxide, in a fashion similar to that described for the *trans*-4 isomer above. The precipitated solid was crystallized twice from benzene to give *trans*-3-carboxamidocyclohexyl acetate, mp 105–106°, whose infrared spectrum was consistent with the assigned structure.

trans-3-Cyanocyclohexyl Tosylate.—*trans*-3-Carboxamidocyclohexyl acetate (21 g) was refluxed with 41.5 ml of redistilled thionyl chloride for 2 hr. Excess thionyl chloride was removed, and 17 g (85%) of *trans*-3-cyanocyclohexyl acetate was collected by distillation at 123–125° (5 mm). This ester was hydrolyzed with 0.2 *N* NaOH, and the progress of the hydrolysis was monitored on aliquots by infrared. After 20 hr hydrolysis was complete. The crude *trans*-3-cyanocyclohexanol (**15**) was isolated by extraction with ether. The crude *trans*-3-cyanocyclohexanol was converted into the tosylate in the usual way. The crude tosylate crystallized very slowly, and was purified by crystallization from ether, mp 47–48° (11 g, 40% over-all yield from *trans*-3-carboxamidocyclohexyl acetate).

Anal. Calcd for $C_{14}H_{17}NO_3S$: C, 60.21; H, 6.13; N, 5.02; S, 11.46. Found: C, 60.12; H, 6.15; N, 4.93; S, 11.34.

Kinetic Method.—The usual sealed ampoule technique was used. As all the kinetic measurements were carried out in acetic acid, with solutions containing approximately twice the concentration of the initial sulfonate ester, the progress of the reactions was followed by titration with perchloric acid in acetic

(25) D. S. Noyce, G. L. Woo, and B. R. Thomas, *J. Org. Chem.*, **25**, 260 (1960).

(26) N. R. Campbell and J. H. Hunt, *J. Chem. Soc.*, 1379 (1950).

(27) D. S. Noyce and D. B. Denney, *J. Amer. Chem. Soc.*, **74**, 5912 (1952).

(28) D. S. Noyce and H. I. Weingarten, *ibid.*, **97**, 3098 (1957).

acid either to the bromphenol blue end point or potentiometrically.

Product Analysis.—The products formed under the conditions of the kinetic measurements were determined for each of the compounds studied. The products represented a normal product distribution (large excess of inversion over retention, predominant formation of olefin) for a typical solvolysis of cyclohexyl compounds. The detailed results are presented in Table V.

Registry No.—**2**, 19556-66-2; **3**, 19556-67-3; **4**, 19556-68-4; **4** (3,5-dinitrobenzoate derivative), 19556-69-5; **5**, 19556-70-8; **6**, 19556-71-9; **8**, 19556-72-0; **9**, 19556-73-1; **10**, 19556-74-2; **10** (3,5-dinitrobenzoate derivative), 19594-76-4; **11**, 19556-75-3; **12**, 19556-76-4; *trans*-4-chlorocyclohexyl acetate, 19556-77-5; *trans*-4-chlorocyclohexyl 3,5-dinitrobenzoate, 19556-78-6; *trans*-4-bromocyclohexyl 3,5-dinitrobenzoate, 19556-96-8; *cis*-4-carboxamidocyclohexanol, 19556-97-9; *cis*-4-carboxamidocyclohexyl acetate, 19556-98-0; *cis*-4-cyanocyclohexyl tosylate, 19556-99-1; *trans*-4-carboxamidocyclohexyl acetate, 19557-00-7; *trans*-4-cyanocyclohexyl tosylate, 19557-01-8; *cis*-3-carboxamidocyclohexanol, 19557-02-9; *cis*-3-carboxamidocyclohexyl acetate, 19557-03-0; *cis*-3-cyanocyclohexyl acetate, 19557-04-1; *cis*-3-cyanocyclohexyl tosylate, 19557-07-4; *trans*-3-carboxamidocyclohexyl acetate, 19557-05-2; *trans*-3-cyanocyclohexyl tosylate, 19557-06-3.

Polarity Effects on the Acetolysis of Substituted 1-Decalyl Methanesulfonates[1]

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All four stereoisomers of 4-cyano-1-decalol containing the *trans*-decalin moiety have been synthesized and characterized. The rates of acetolysis of the methanesulfonates of these compounds have been measured. *trans*-4α-Cyano-1β-decalyl methanesulfonate (equatorial cyano and equatorial methanesulfonate) solvolyzes 3.2 times faster than *trans*-4α-cyano-1β-decalyl methanesulfonate (axial cyano and equatorial methanesulfonate) in agreement with calculations based on a direct field effect model. In contrast, an inductive effect operating through the bonds would predict identical rates for these two compounds. The field effect model, based upon 70% charge separation at the transition state, predicts the reaction rates quite well for three of the four compounds in this study. The fourth compound, *trans*-4β-cyano-1α-decalyl methanesulfonate (axial cyano and axial methanesulfonate), reacts about twice as rapidly as predicted; this is probably the result of a complex mechanism for the axial methanesulfonate, as has been postulated in similar systems, involving participation of the adjacent ring juncture hydrogen (which is tertiary, axial, and in an antiperiplanar orientation to the leaving sulfonate group).

In the preceding paper, we have shown that the solvolysis of 4-halocyclohexyl methanesulfonates is most satisfactorily explained on the basis of a field effect.[2] However, the conformational mobility of simple cyclohexane systems adds an additional degree of uncertainty to this conclusion, and it seemed desirable to examine the effect of the polarity of substituents on reaction rate in conformationally rigid systems. For this purpose we have chosen to investigate the reactivity of a selected group of *trans*-decalin derivatives.

Condensation of 1-(1-acetoxyvinyl)cyclohexene with acrylonitrile produced a mixture of 4α-cyano- and 4β-cyano-1-acetoxy-$\Delta^{1,10}$-octalins. Mild hydrolysis afforded a mixture of four isomeric 4-cyano-1-decalones. The two major components of this mixture, *trans*-4α-cyano-1-decalone (**1**,[3] 65%), and *trans*-4β-cyano-1-decalone (**2**, 33%), were separated and purified. The two minor components (2% of the total mixture) were assigned the *cis*-4-cyano-1-decalone structures by virtue of their conversion into a mixture of **1** and **2**. The structure of **1** and **2** was established by hydrolysis to the known *trans*-4α-carboxy-1-decalone (**3**) and comparison with an authentic sample prepared by the method of Nazarov, Kucherov, and Segal.[4] This establishes that the cyano group is in the 4 position rather than the 3 position, which would have resulted from addition in the reverse direction in the Diels–Alder reaction. The assignment of configuration to **1** and **2**, respectively, comes from a consideration of their nmr spectra. *trans*-4β-Cyano-1-decalone has a peak for one proton at δ 2.93, in good agreement with the δ 2.91 chemical shift observed for the equatorial hydrogen atom adjacent to the cyano group in *cis*-4-*t*-butyl-1-cyanocyclohexane.[5] The peak for the hydrogen atom adjacent to the cyano group in **1** is not separated from the complex multiplet due to the ring protons. The corresponding peak for the axial hydrogen atom adjacent to the cyano group in *trans*-4-*t*-butyl-1-cyanocyclohexane is also obscured by the ring protons.[5]

Pure samples of *trans*-4α- and *trans*-4β-cyano-1-decalones were each reduced with aluminum isopropoxide; from **1** a 50:50 mixture of two alcohols was obtained, and from **2**, a 70:30 mixture of two different alcohols was formed. The mixtures of alcohols were separated by chromatography on alumina. The structures of these alcohols were established on the basis of their origins and their nmr spectra. The chemical shifts of the nmr peaks are listed in Table I with the chemical shifts of the peaks for known compounds in the cyclohexane series which are "conformationally pure." The methanesulfonates of these alcohols were then formed by standard methods. The structures of

(1) Supported in part by grants from the National Science Foundation, GP-1572 and GP-6133X.

(2) D. S. Noyce, B. N. Bastian, P. T. S. Lau, R. S. Monson, and B. Weinstein, *J. Org. Chem.*, **34**, 1247 (1969).

(3) Nomenclature in this paper will use the steroid conventions and numbering, with the hydrogen at C-10 in the β orientation. All the compounds in the present study are *dl* mixtures. Only one enantiomorph is shown in Scheme I for convenience.

(4) I. N. Nazarov, V. F. Kucherov, and G. M. Segal, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1241 (1956).

(5) N. L. Allinger and W. Szkrybalo, *J. Org. Chem.*, **27**, 4601 (1962).