Solvolysis of 3-Cyclohexenylcarbinyl Derivatives[1]

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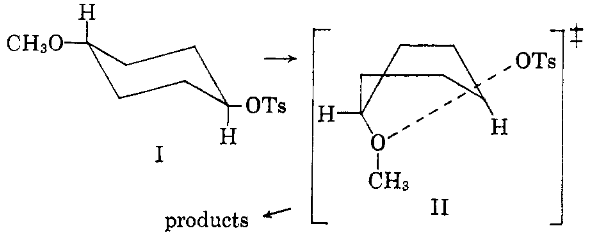
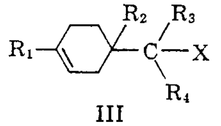
Several derivatives of 3-cyclohexene-1-methanol and cyclohexanemethanol containing two, one, or no α-methyl groups have been prepared and their solvolytic rates determined. No rate enhancement from participation of the double bond was observed for any of the unsaturated compounds. Product analyses for selected examples substantiated this result. These rate data are compared with the analogous cyclopentene systems, which show considerable rate enhancement, and an approximate energetic analysis of the two cases is made.

The report by Noyce and Thomas[2] in 1957 that *trans*-4-methoxycyclohexyl tosylate (I) solvolyzed with 1,4-participation by way of the highly energetic boat-like transition state (II) prompted us to examine the possibility of analogous double-bond participation in the 3-cyclohexenylcarbinyl systems (III). If this participation were sufficiently important in stabilizing the transition state, it seemed possible that bicyclic products might be isolated. Because of the known strain of these bicyclic molecules it seemed plausible, however, that any bridge intermediate initially formed might be subsequently opened by solvent attack. For this reason and the fact that many of these products were unknown, our approach was largely kinetic with only convenient spot checks to confirm the kinetic evidence.



I II



III

Since the initiation of our study several groups of workers[3,4] have reported on the solvolysis of particular examples of the class of compounds embraced by formula III. Their partial results as well as the more complete study to be reported here have failed to produce evidence for double-bond participation. This absence of participation takes on added significance in view of the recent reports[3,5–7] of the facile double-bond participation in five and seven membered cycloalkenyl systems to give large rate enhancements and isolable bicyclic products. Experimental evidence and empirical calculations will be presented to suggest that participation in cyclohexenyl systems is just below the energetic threshold of observation and that accessible systems with appropriate substituents can be expected to give participation.

Syntheses.—For the present study of neighboring double-bond participation to form bicyclic molecules, a series of 3-cyclohexenylcarbinyl, cyclohexylcarbinyl, 1-methyl-3-cyclohexenylcarbinyl, and 1-methylcyclohexylcarbinyl derivatives were prepared. The syntheses of the precursor alcohols were carried out by conventional procedures with little difficulty and require no comment beyond that made in the experimental section. These syntheses are outlined in Charts I and II.

The preparation of the *p*-nitrobenzoates of the tertiary alcohols offered little difficulty. The *p*-toluenesulfonates of the primary and secondary alcohols were straightforward also, except for their tendency to be liquid at room temperature, which required the use of low temperature recrystallization techniques. All of the chlorides of the tertiary alcohols except that of dihydro-α-terpineol (XX) were prepared by shaking an ether solution of the alcohol with concentrated hydrochloric acid. The resulting chlorides appeared to be pure as judged by their analyses and the excellent first order kinetics obtained with them. That no rearrangements occurred during their preparation is indicated by the observation that introducing a 1-methyl group on the cyclohexyl or cyclohexenyl ring has essentially the same effect on the rate of chloride solvolysis as it does on the rate of *p*-nitrobenzoate solvolysis. Rearrangements were unlikely in the *p*-nitrobenzoate formation because of their method of preparation through alkoxide ions (see experimental).

In the case of the dihydro-α-terpineol (XX) the chloride was prepared by the more conventional procedure of shaking the pure liquid alcohol with

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[1] Taken in part from the dissertation of S. S. Chibber submitted in September 1961 to the Graduate School of Cornell University in partial completion of the requirement for the Ph.D. degree.

[2] D. S. Noyce and B. R. Thomas, *J. Am. Chem. Soc.*, **79**, 3093 (1957).

[3] R. S. Bly, Jr., and H. L. Dryden, Jr., *Chem. Ind.* (London), 1287 (1959).

[4] Mme. G. LeNy, *Compt. rend.*, **251**, 1526 (1960).

[5] R. Lawton, *J. Am. Chem. Soc.*, **83**, 2399 (1961).

[6] P. D. Bartlett and S. Bank, *ibid.*, **83**, 2591 (1961).

[7] The six-membered β-cyclohexenylethyl system also cyclizes readily to the very slightly strained bicyclo[2.2.2]octyl derivative. S. Winstein and P. Carter, *ibid.*, **83**, 4485 (1961).

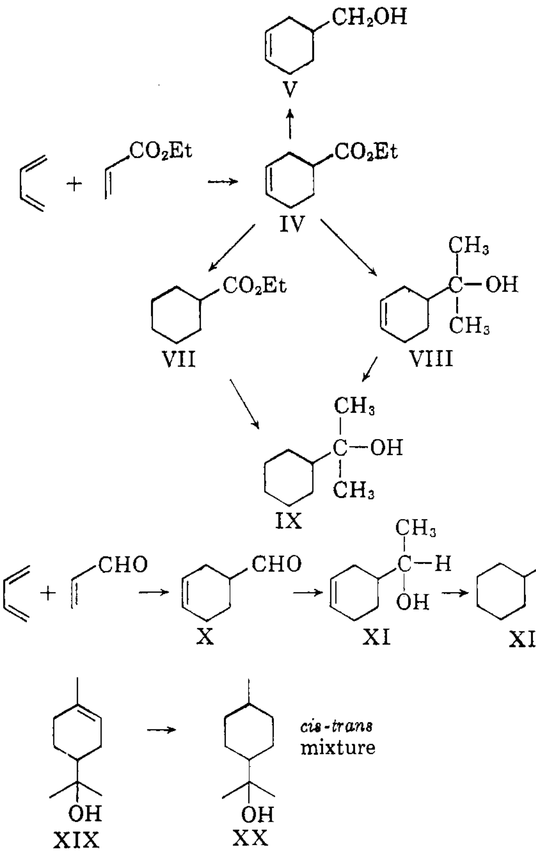


Chart I

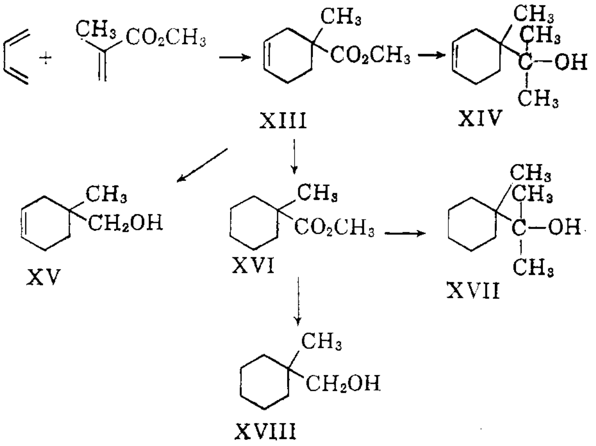


Chart II

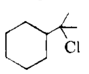
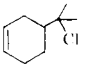
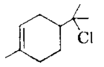
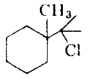
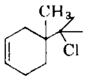
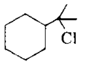
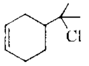
concentrated hydrochloric acid. The chloride resulting from this treatment apparently had undergone some ring enlargement since kinetic analyses indicated the presence of 50% of a very slowly solvolyzing impurity.

Kinetic Search for Double-Bond Participation.—Even if solvolysis of the 3-cyclohexenyl systems occurred without neighboring π-participation there would still occur a retardation in rate relative to the saturated analog because of the inductive effect of the double bond. The magnitude of this retardation can be estimated by a Taft $\rho^*\sigma^*$ treatment[8] for those esters and chlorides undergoing limiting solvolysis. With the value of 3.5 for ρ^{*9} and values of -0.26 for the cyclohexyl σ^{*10} and -0.12 for the 3-cyclohexenyl σ^* the ratio $k_{sat.}/k_{unsat.}$ is calculated to be 3.1.

Examination of Tables I, II, and III reveals nine saturated-unsaturated pairs of molecules which would be expected to undergo reasonably limiting solvolysis. These are the tertiary chlorides in Table I, the tertiary *p*-nitrobenzoates in Table II, and the neopentyl type primary tosylates of

TABLE I

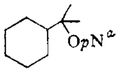
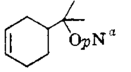
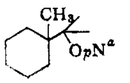
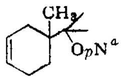
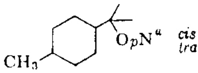
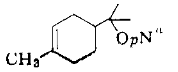
SOLVOLYSIS OF TERTIARY CHLORIDES AT 25.0°

Compound	Solvent	10^6k, sec.$^{-1}$	$k_{sat.}/k_{unsat.}$
	60% (v./v.) aqueous acetone	8.15	4.22
	60% (v./v.) aqueous acetone	1.93	
	60% (v./v.) aqueous acetone	2.19	3.7[a]
	60% (v./v.) aqueous acetone	26.3	4.07
	60% (v./v.) aqueous acetone	6.46	
	HCO_2H	633	4.8
	HCO_2H	131	

[a] Ratio based on assumed $k_{sat.}$ of 8.2×10^{-6} sec.$^{-1}$. The analogous data of Table II show that the effect of a 4-methyl is minor in the saturated series.

TABLE II

SOLVOLYSIS OF TERTIARY *p*-NITROBENZOATES IN 60% (v./v) AQUEOUS ACETONE AT 100.0°

Compound	10^5k, sec.$^{-1}$	$k_{sat.}/k_{unsat.}$
	5.89[b]	2.57
	2.29[b]	
	19.6	2.77
	7.07	
 *cis* or *trans*	5.35	2.22
	2.41	

[a] *para*-Nitrobenzoate. [b] Solvolysis at 99.84°.

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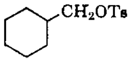
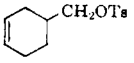
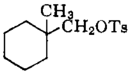
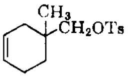
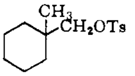
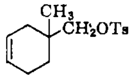
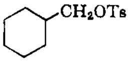
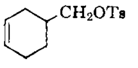
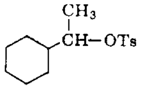
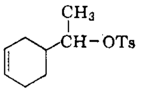
[8] R. W. Taft, Jr. in "Steric Effects in Organic Chemistry," M. S. Newman, ed., John Wiley and Sons, Inc., New York, 1956, Chapter 12.

[9] A. Streitweiser, Jr., *J. Am. Chem. Soc.*, **78**, 4935 (1956).

[10] C. F. Wilcox, Jr., and S. S. Chibber, *J. Org. Chem.*, in press. These values were obtained from ester hydrolyses using the fundamental definition[7] of σ^* rather than from secondary correlations.

Table III

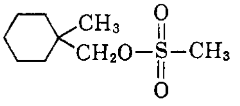
Solvolysis of Primary and Secondary *p*-Toluenesulfonates at 99.84°

Compound	Solvent	10^5k, sec.$^{-1}$	$k_{sat.}/k_{unsat.}$
	60% (v./v.) aqueous acetone	3.63	1.68
	60% (v./v.) aqueous acetone	2.16	
	60% (v./v.) aqueous acetone	1.55[a]	3.15
	60% (v./v.) aqueous acetone	0.492[a]	
	HOAc	0.45[a]	3.4
	HOAc	0.133[a]	
	90% (v./v.) aqueous acetone	0.251	1.35
	90% (v./v.) aqueous acetone	0.186	
	90% (v./v.) aqueous acetone	27.1	1.87
	90% (v./v.) aqueous acetone	14.5	

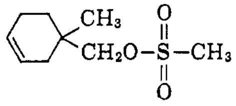
[a] Solvolysis at 100.0°.

Table III. For these compounds the average rate ratio of saturated to unsaturated is 3.4 ± 0.7 which is virtually identical with the value of 3.1 estimated for pure inductive effect of the double-bond with no π-participation. The idea that the rates of the unsaturated esters are determined by inductive factors alone is enforced if the variability of ρ^* with temperature, solvent, and structure is considered. Thus the tertiary chloride ratios in 60% (v./v.) aqueous acetone solutions are clustered around the single value 4.00 ± 0.20 and the tertiary *p*-nitrobenzoates are clustered around 2.50 ±0.30. Most of this spread in rate ratios can be accounted for by considering the different temperatures at which these rates were determined and expressing the retarding effect of the double-bond alternatively in terms of the extra energy it imposes for solvolysis. On this basis the retarding energy of the double bond for the nine molecules is 0.79 ± 0.08 kcal. whereas the energy estimated from the $\rho^*\sigma^*$ treatment is 0.77 kcal. The average energy deviation of 0.08 kcal. corresponds to a deviation in rate of only 12%. This remaining small difference might be elaborately accounted for in terms of variations in solvents or leaving group, but it seems better to conclude simply that double-bond participation, if it does occur at all in these nine systems, is minor.

Before concluding this section, it is worthwhile to comment on other comparisons that can be drawn from these kinetic data. First, the effect of introducing a β methyl group in the tertiary chlorides and *p*-nitrobenzoates (seven examples) is to increase the rate of solvolysis in 60% (v./v.) aqueous acetone by a nearly constant factor of three. This rate enhancement can be ascribed to a blend of inductive and steric factors alone. Little driving force from six-membered ring participation would be expected and indeed even in the exceedingly more favorable cases of the methane-sulfonates of 1-methylcyclohexanemethanol (XIX) and 1-methyl 3-cyclohexene-1-methanol (XX) only 50% of the solvolytic products are ring expanded.[3]



XIX



XX

In Table III the small $k_{sat.}/k_{unsat.}$ ratios for the unhindered primary and secondary tosylates are interpreted as arising from solvolyses with more nucleophilic character. From Streitwieser's value[9] for a ρ^* appropriate to the highly nucleophilic ethanolysis of primary tosylates the calculated ratio of $k_{sat.}/k_{unsat.}$ is 1.27. This implies that these two primary tosylates have little limiting character and that the secondary tosylate is intermediate between nucleophilic and limiting.[11] The effect of solvent change on solvolysis rates of the tosylates in Table III while subject to other interpretations is at least consistent with this picture. The small rate increase for the unhindered primary tosylate in changing from 90 to 60% (v./v.) aqueous acetone can be ascribed to the low m value suitable to solvolyses in the nucleophilic category.[11] On the other hand the small rate increase of the neopentyl type hindered tosylate in changing from acetic acid to 60% (v./v.) aqueous acetone is consistent with the unusually close Y values appropriate to tosylates undergoing limiting solvolysis.[12]

Product Search for Double-Bond Participation.—The lack of significant double-bond participation as indicated by the kinetics is further substantiated by product analyses of representative solvolyses. Solvolysis of α-terpinyl *p*-nitrobenzoate in 60% (v./v.) aqueous acetone at 100° with added calcium carbonate gave 23% α-terpineol, 69% limonene, and 8% terpineolene. The possible bicyclic products—camphene, bornylene, α-pinene, and β-pinene—which could have arisen had double-bond participation been important were specifically sought and shown to be absent within experimental error (*ca.* 1%). Without the added calcium carbonate to neutralize the developed *p*-nitrobenzoic

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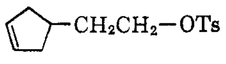
(11) S. Winstein, E. Grunwald, and H. W. Jones, *J. Am. Chem. Soc.*, **73**, 2700 (1951).

(12) S. G. Smith, A. H. Fainberg, and S. Winstein, *ibid.*, **83**, 618 (1961).

acid, the product mixture was much more complex with typical hydration products such as β-terpineol and *trans*-terpin being formed. This same difficulty occurred in the acetolysis of α-terpinyl chloride even in the presence of excess sodium acetate since both α- and β-terpinyl products were identified. Here again, however, none of the four bicyclic olefins were present. Similar negative evidence for double-bond participation has been reported by Mme. LeNy[4] for the acetolysis of 3-cyclohexenylcarbinyl tosylate and by Bly for the acetolysis[3] of 1-methyl-3-cyclohexenylcarbinyl tosylate.[13]

Discussion

The foregoing kinetic and product results indicate that double-bond participation plays a minor role in the solvolysis of the cyclohexenylcarbinyl systems. While all solvent and structure combinations have not been tried, it would appear that this lack of participation holds independent of high or low solvent nucleophilicity, high or low solvent ionizing power, and the degree of alkyl substitution on the carbinyl carbon atom. These results are in striking contrast to the work of Lawton[5] and Bartlett[6] with a 2-(Δ³-cyclopentenyl-ethyl tosylate (XXI) where double-bond participation was noticeable even in the highly nucleophilic solvent 50% aqueous ethanol and was dominating in the poorly nucleophilic solvents acetic acid and formic acid.



XXI

It is informative to estimate (roughly) the relative energetics for these two systems and attempt to single out the source of this different behavior. The required quantities are presented schematically in Fig. 1 where the left-hand side of the diagram refers to the cyclopentenyl system and the right-hand side to the cyclohexenyl system. Equation 1 relates, in the notation of Fig. 1, the ratio of solvent to double-bond participation in the cyclohexenyl case to the difference in free energies of the respective transition states

$$-2.303\ RT \log \frac{k_6^{\mathrm{S}}}{k_6^{\Delta}} = (F_6^{*,\mathrm{S}} - F_6^{\mathrm{G.M.}}) - (F_6^{*.\mathrm{S}} - F_6^{\mathrm{G.S.}}) \quad (1)$$
$$= F_6^{*.\mathrm{S}} - F_6^{*\Delta}$$

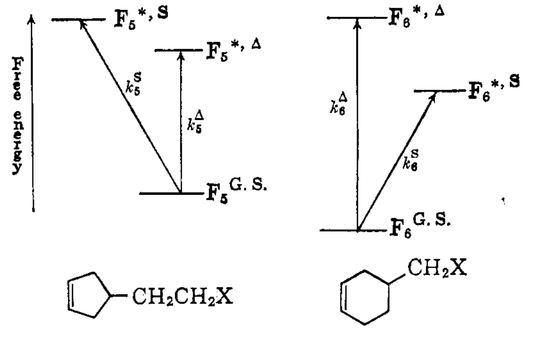


Fig. 1.—Free energy relationships in the solvolysis of cyclopentenylethyl and cyclohexenylcarbinyl derivatives.

Superscript S refers to solvent participation.
Superscript Δ refers to double-bond participation.

$$F_6^{*,\mathrm{S}} - F_6^{*,\Delta} = (F_6^{*,\mathrm{S}} - F_5^{*,\mathrm{S}} - F_6^{\mathrm{G.S.}} + F_5^{\mathrm{G.S.}}) \quad (2)$$
$$+ (F_5^{*,\mathrm{S}} - F_5^{*,\Delta})$$
$$+ (F_6^{\mathrm{G.S.}} - F_5^{\mathrm{G.S}})$$
$$+ (F_5^{*,\Delta} - F_6^{*,\Delta})$$

The right-hand side of equation 1 can be usefully expanded to include terms involving the cyclopentenyl free energy terms as in equation 2. In equation 2 the first bracketed term on the right-hand side is a measure of the relative rates of solvent attack in the two systems; for limiting solvolyses this term must be very close to zero. The second bracketed term represents the driving force for participation in the cyclopentenyl case. It can be calculated from the data of Bartlett[5] for the limiting formic acid solvolysis at 60° of XXI and its saturated analog to be *ca.* + 5.0 kcal. This value could be low by as much as 0.8 kcal. if the retarding effect of the double-bond on the limiting solvolysis had the factor of 3.4 it has with the present 1-methyl-3-cyclohexenylcarbinyl tosylate. The third bracketed term in equation 2 is the difference in ground state free energies of the two molecules in solution and can be estimated from available thermodynamic data. Since the difference in free energy of formation, $\Delta\Delta F_f^{60°}$, of cyclopentene and cyclohexene is close to the corresponding $\Delta\Delta F_f^{60°}$ for cyclopentane and cyclohexane,[16] it is reasonable to assume that the $\Delta\Delta F_f^{60°}$ for the 4-*n*-alkylcyclopentenes and the 4-(*n*-1)-alkylcyclohexenes will be approximated by the free energies of formation of the corresponding saturated compounds. Since this latter difference is nearly constant at 2.8 kcal. when *n* is greater than or equal to three it is not unreasonable to further suppose that 2.8 kcal. roughly approximates the difference in free energies in the two tosylates. Because of the similarity of the two tosylates the solvation energies should largely cancel so that $(F_6^{\mathrm{G.S.}} - F_5^{\mathrm{G.S.}})$ can be set equal to −2.8 kcal.[17] The last term in equation 2 is difficult to estimate because of the considerable

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[13] The recent report[14] that α-terpineol gives a 16% yield of camphene when treated with sulfuric acid has been shown to be in error and that no carbobicyclic olefins are formed in large amounts.[15]

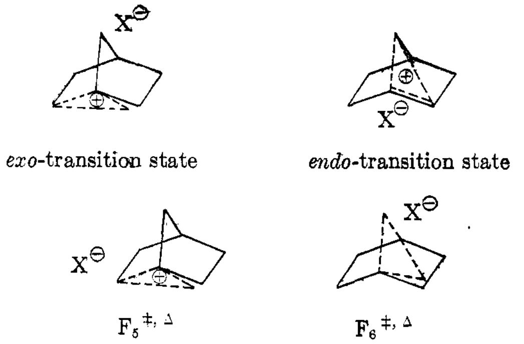
[14] E. Von Rudolph, *Can. J. Chem.*, **39**, 1 (1961).

[15] C. F. Wilcox, Jr., M. F. Wilcox, and S. S. Chibber, *J. Org. Chem.*, **27**, 2286 (1962).

[16] "American Petroleum Institute Research Project 44 at the National Bureau of Standards. Selected Values of Properties of Hydrocarbons," Tables 18x, 19x, 22x, and 23x.

[17] At 298°K. this becomes −3.3 kcal; at 398°K. it becomes −2.4 kcal.

[18] The *endo*-transition state depicted in Fig. 2 is not intended to imply extensive delocalization of charge but only the interaction of the full double bond with the developing carbonium ion. Although molecular orbital calculations have been carried out for this ion they are not presented because of the uncertainty of the detailed structure.



exo-transition state

endo-transition state

$F_5{}^{\ddagger,\Delta}$

$F_6{}^{\ddagger,\Delta}$

Fig. 2.—Structural relationships between the transition states for double-bond participation and for solvolysis of *exo*- and *endo*-norbornyl derivatives.[18]

uncertainty of even the structure of the two π-participation transition states. One plausible assumption is to suppose that this difference in free energies equals the free energy difference in the related transition states for the solvolysis of *exo*- and *endo*-norbornyl derivatives. The basis for this assumption is brought out most easily in pictorial form as in Fig. 2. With the observed *exo-endo* rate ratio for acetolysis of the tosylates at 25° of 350[19] along with a correction of 3.5 for internal return[20] and a rough estimate of 3 for the equilibrium constant between the *exo* and *endo* tosylates in the ground state,[21] $F_5{}^{*,\Delta} - F_6{}^{*,\Delta}$ is estimated to be about −4.8 kcal.[22]

Combination of these estimates for the four terms of equation 2 gives $F_6{}^{*,S} - F_6{}^{*,\Delta}$ a value of −2.6 kcal. at 60° which corresponds to a $k_6{}^S/k_6{}^\Delta$ ratio of 40 (very little double-bond participation). While this calculation is of course very crude, it does suggest that double-bond participation in the cyclohexene systems was just below the energetic threshold of observability and that proper choice and placement of substituents might bring about noticeable participation.[23] Used cautiously to avoid the steric complications implicit in Fig. 2, this type of calculation could be a useful guide for selecting favorable examples of double-bond participitation in cyclohexene molecules. Finally, it should be noted that this calculation further supports the view that the largest factor favoring participation in the cyclopentene case (compared to the nonparticipating cyclohexene examples) is the extensive charge delocalization in the Δ-5-transition state.[6,7] Of secondary importance is the relative instability of the ground state of the cyclopentene case relative to the cyclohexene molecules.

Experimental

3-Cyclohexene-1-methanol (V).—A solution of 7.7 g. (0.05 mole) of ethyl 3-cyclohexenecarboxylate (IV)[10] in 10 ml. of anhydrous ether was added dropwise to a stirred slurry of 1.9 g. (0.05 mole) of lithium aluminum hydride in 100 ml. of anhydrous ether and the stirring was continued for 2 hr. The resulting complex was destroyed by slow addition of 7.6 g. of water to the cooled reaction mixture. After the mixture had been stirred overnight, the ethereal solution was filtered and the precipitate thoroughly washed with dry ether. The solvent from the filtrate and washings was evaporated and the residue distilled to give 4.5 g. (83%) of V, b.p. 102° at 19 mm., $n^{25}\text{D}$ 1.4828; *p*-nitrobenzoate by Method A,[24] m.p. 59–61° (lit. b.p. 70.6–74.0. at 5 mm.,[25] 79–83 at 12 mm.,[26,27] 125–127° at 15 mm.,[28] $n^{20}\text{D}$ 1.4852[27]; *p*-nitrobenzoate,[26] m.p. 62°).

The ***p*-toluenesulfonate**[24] of the alcohol melted at 23–24°.

Anal. Calcd. for $C_{14}H_{18}O_2S$: C, 63.14; H, 6.81. Found: C, 62.85; H, 6.88.

Cyclohexanemethyl *p*-Toluenesulfonate.—Cyclohexylcarbinol (Eastman) was converted to its *p*-toluenesulfonate by the general method,[24] m.p. 32–33°.

Anal. Calcd. for $C_{14}H_{20}O_3S$: C, 62.75; H, 7.51. Found: C, 63.09; H, 7.60.

α,α-Dimethyl-3-cyclohexene-1-methanol (VIII).—To a stirred suspension of 7.7 g. (0.32 g.-atom) of magnesium chips in 100 ml. of anhydrous ether was added 42.6 g. (0.3 mole) of methyl iodide following the usual Grignard techniques. The mixture was refluxed for 0.5 hr. after the addition of the iodide. After the refluxing had been continued for an additional 0.5 hr., the Grignard complex was destroyed by dropwise addition of ice-cold dilute hydrochloric acid. The ether solution was washed with water and dried over magnesium sulfate. The solvent was evaporated and the residue distilled to give 9 g. (64%) of alcohol VIII, b.p. 110° at 23 mm., $n^{25}\text{D}$ 1.4800 (lit. b.p. 86–88 at 12 mm.,[29] 90 at 13 mm.,[30] 95–96 at 20 mm.; $n^{20}\text{D}$ 1.4826,[31,32] $n^{25}\text{D}$ 1.4787[29]).

The ***p*-nitrobenzoate** prepared by Method A,[24] m.p. 122.5–124°.

Anal. Calcd. for $C_{16}H_{19}O_4N$: C, 66.45; H, 6.57. Found: C 66.67; H, 6.69.

α,α-Dimethylcyclohexane Methanol (IX).—To a stirred ether solution of methylmagnesium iodide (0.3 mole) prepared as with compound VIII was added 15.6 g. (0.1 mole) of ester VII[10] and the mixture refluxed for an additional 45 min. The product was isolated as with VIII and gave on distillation 7 g. (74%) of IX, b.p. 104° at 30 mm., $n^{25}\text{D}$ 1.4656 (lit. b.p. 85–86 at 14 mm.,[33,34] 85.5 at 15 mm.,[35]

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[21] This value is estimated from alcohol and ester equilibrium for bicycloheptyl derivatives. Unpublished data of M. Sexton and M. F. Wilcox.

[22] It is to be expected that this ΔF is not too different at 100° because of the roughly similar structures.

[23] Indeed, kinetic and product results available to us in preliminary form support this conclusion. It was found that 1,4-dimethyl-3-cyclohexene-1-methyl tosylate acetolizes only 1.5 times slower than 1-methylcyclohexanemethyl tosylate instead of the factor of 3.4 expected for the case of no participation. Moreover, the solvolytic products include at least six olefins and four alcohols, a complexity of products to be expected for a solvolysis undergoing simultaneous solvent and double-bond participation.

[24] The description of *p*-nitrobenzoate, *p*-toluenesulfonate, and chloride derivative preparations is given later in the Experimental.

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94–95° at 20 mm.,[36] n^{12}_{D} 1.4720,[34] n^{20}_{D} 1.4638,[36] 1.4695,[33] n^{25}_{D} 1.4663). This same compound was also prepared by reduction of alcohol VIII.

The *p*-**nitrobenzoate** prepared by Method A,[24] m.p. 101–102° (lit.[37] m.p. 101–103°).

3-Cyclohexene-1-carboxaldehyde (X).—This aldehyde was prepared by the reaction of acrolein with butadiene using the procedure of Diels and Alder.[38] The crude product on distillation give 11 g. (40%) of aldehyde X, b.p. 70° at 12 mm., n_{D}^{25} 1.4677 (lit. b.p. 51–52° at 13 mm.,[38] 62° at 17 mm.,[39] 58–58.5° at 20 mm.,[31] n^{19}_{D} 1.4725,[40] n^{20}_{D} 1.4732[31]).

α-**Methyl-3-cyclohexene-1-methanol** (XI).—Following the procedure of Petrov and Sopov[31] an ether solution of methylmagnesium iodide reacted with aldehyde X. The product on distillation gave 6.6 g. (54%) of XI, b.p. 91° at 17 mm., n^{25}_{D} 1.4800 (lit.[31] b.p. 93–95 at 20 mm., n^{20}_{D} 1.4842).

The *p*-**nitrobenzoate** of alcohol XI was prepared by Method A,[24] m.p. 61–62°.

The *p*-**toluenesulfonate** was prepared by the general method,[24] m.p. 20.5–22°.

Anal. Calcd. for $C_{15}H_{20}O_3S$: C, 64.27; H, 7.19. Found: C, 64.17; H, 7.12.

α-**Methylcyclohexanemethanol** (XII).—A solution of 12.6 g. (0.1 mole) of alcohol XI in 50 ml. of ethanol was hydrogenated in a Parr apparatus using 10% palladium on charcoal as the catalyst. Distillation of the crude product gave 7.7 g. (60%) of XII, b.p. 95° at 17 mm., n^{25}_{D} 1.4620 (lit. b.p. 82–83° at 12 mm.,[33,41,42] 80° at 15 mm.,[43] 81–82° at 15 mm.,[44,45] 108–109 at 50 mm.,[46] n^{20}_{D} 1.4658, n^{25}_{D} 1.4635).

The *p*-**nitrobenzoate** was prepared by Method A,[24] m.p. 46–48°.

The *p*-**toluenesulfonate** was prepared by the general method,[24] m.p. 5–7°.

Anal. Calcd. for $C_{15}H_{22}O_3S$: C, 63.83; H, 7.85. Found: C, 64.02; H, 7.99.

α-**Terpineol** (XIX).—A commercial sample of α-terpineol was distilled and the fraction collected, b.p. 77° at 1 mm., n^{25}_{D} 1.4803 (lit.[47] b.p. 99–100 at 12 mm., n^{20}_{D} 1.4819).

The *p*-**nitrobenzoate** was prepared by Method A,[24] m.p. 140–142° (lit.,[48] m.p. 139°).

cis- **and** *trans*-**Dihydro**-α-**terpineol** (XX).—A solution of 30.8 g. (0.2 mole) of α-terpineol in 100 ml. of 95% ethanol was hydrogenated in a Parr apparatus with a pressure of 45 lbs./sq. inch and a slurry of 0.5 g. of 10% palladium-on-charcoal as a catalyst. The crude product on distillation gave 22 g. (71%) of alcohol mixture XX, b.p. 80° at 3.5 mm. n^{25}_{D} 1.4624 (lit.,[49] for *trans*-dihydro-α-terpineol, m.p. 34–35°, n^{20}_{D} 1.4630 and *cis*-dihydro-α-terpineol, m.p. 46.7–47°, n^{20}_{D} 1.4664).

The *p-nitrobenzoate* of mixture XX was prepared by Method A[24], m.p. 97–99° after three recrystallizations (lit.,[48] m.p. 96–97°). The solid from the mother liquors on repeated crystallizations gave mixed crystals, m.p. 78–95°. An attempted mechanical separation of the crystals failed to give significant purification.

Methyl 1-Methyl-3-cyclohexene-1-carboxylate (XIII).—In a steel bomb containing 20 g. (0.2 mole) of methyl methacrylate and 0.5 g. of hydroquinone was condensed 13 g. (0.24 mole) of butadiene. The bomb was sealed and then heated at 145° for 12 hr. The crude product on distillation gave 16 g. (52%) of XIII, b.p. 42° at 1.5 mm., n^{25}_{D} 1.4573 (lit. b.p. 64–65° at 10 mm.,[50] 79° at 20 mm.,[51] 116–117° at 100 mm.,[52] n^{20}_{D} 1.4600[50,51] and 1.4581[52]).

α,α-**1-Trimethyl-3-cyclohexene-1-methanol** (XIV).—To a stirred ether solution of methylmagnesium iodide (0.26 mole) prepared as with V, was added 15.4 g. (0.1 mole) of ester XIII and the reaction mixture refluxed for 1 hr. The Grignard complex was destroyed by addition of ice-cold dilute hydrochloric acid. The ethereal solution of alcohol XIV was washed with water, then dried over magnesium sulfate and finally the solvent removed. Because the infrared spectrum of the crude product indicated the presence of unchanged ester (absorption at 5.76 μ) the product was refluxed for 0.5 hr. with 25 ml. of a 4% potassium hydroxide solution in 75% aqueous methanol. The methanol was removed by distillation and the residue extracted with ether. This ethereal solution was washed with water, then dried over magnesium sulfate and finally distilled to give 6.4 g. (40%) of XIV, b.p. 78° at 3 mm., n^{26}_{D} 1.4866 (lit.[52] b.p. 126° at 20 mm., n^{20}_{D} 1.4922).

The *p-nitrobenzoate* was prepared by Method B,[24] m.p. 135–137°.

Anal. Calcd. for $C_{17}H_{21}O_4N$: C, 67.30; H, 6.98. Found: C, 67.10; H, 6.99.

1-Methyl-3-cyclohexene-1-methanol (XV).—A solution of 15.4 g. (0.1 mole) of ester XIII was added dropwise to a stirred slurry of 3.8 g. (0.1 mole) of lithium aluminum hydride in 200 ml. of anhydrous ether and the stirring continued for two additional hours. The reaction mixture was cooled and 15.2 g. of water added with stirring. The precipitate was removed by filtration and thoroughly washed with ether. The combined filtrate and washings were distilled to give 9.2 g. (73%) of XV, b.p. 76° at 6 mm., n^{25}_{D} 1.4812.

The *p-toluenesulfonate* was prepared by the general method, m.p. 24–26°.

Anal. Calcd. for $C_{15}H_{20}O_3S$: C, 64.22; H, 7.19. Found: C, 64.21; H, 7.24.

Methyl 1-Methylcyclohexanecarboxylate (XVI).—A solution of 15.4 g. (0.1 mole) of ester XIII was hydrogenated in the same manner as described for alcohol XII. The final distillation of the crude product gave 11.5 g. (74%) of XVI, b.p. 56° at 3 mm., n^{25}_{D} 1.4410 (lit. b.p. 35° at 3 mm.,[53] 70° at 35 mm.,[54] $n^{18.5}_{D}$ 1.4450,[54] n^{20}_{D} 1.4456[53]).

α,α-**1-Trimethylcyclohexanemethanol** (XVII).—To a stirred solution of methylmagnesium iodide (0.26 mole), prepared as with V, was added dropwise a solution of 15.6 g. (0.1 mole) of ester XVI in 20 ml. of ether and the reaction mixture was refluxed for one additional hour. The product was isolated by the same method used with XIV to give 12.5 g. (80%) of XVII, b.p. 88° at 6 mm., n^{25}_{D} 1.4718 (lit.[55] b.p. 120.4 at 40 mm., n^{20}_{D} 1.4776).

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The *p-nitrobenzoate* was prepared by Method B,[24] m.p. 120–121°.

Anal. Calcd. for $C_{17}H_{23}O_4N$: C, 66.85; H, 7.59. Found: C, 67.01; H, 7.85.

1-Methylcyclohexanemethanol (XVIII).—A solution of 15.6 g. (0.1 mole) of ester XVI in 20 ml. of ether was reduced with lithium aluminum hydride in the same manner as with XV. Distillation of the crude product gave 9 g. (70%) of XVIII, b.p. 55° at 2 mm., $n^{25}D$ 1.4665 (lit. b.p. 85° at 14 mm.,[56] 101° at 20 mm.,[54] $n^{20}D$ 1.4672,[57] 1.4674[54]).

The *3,5-dinitrobenzoate* was prepared in a manner analogous to Method B[24] for the *p*-nitrobenzoates, m.p. 77–79° (lit.,[54] m.p. 77–78°).

The *p-toluenesulfonate* was prepared by the general method,[24] m.p. 37–38°.

Anal. Calcd. for $C_{15}H_{22}O_3S$: C, 63.78; H, 7.84. Found: C, 63.78; H, 7.75.

Preparation of *p*-Nitrobenzoates. Method A.—The alcohol (0.01 mole) was added to a solution of *p*-nitrobenzoyl chloride (0.01 mole) in anhydrous pyridine. The solution was allowed to stand overnight and then poured into 200 ml. of water and the resulting precipitate then dissolved in ether. The ether solution was washed successively with ice-cold dilute hydrochloric acid and water and then dried over anhydrous magnesium sulfate. The ether was removed by distillation and the crude product recrystallized from methanol or absolute ethanol to give the *p*-nitrobenzoate in 50–60% yield.

Method B.—Phenyllithium was prepared by adding 63 g. (0.4 mole) of bromobenzene to a suspension of lithium ribbon clippings (1.05 g.-atoms) in 150 ml. of ether. Another 50 ml. of ether was added and the mixture heated under reflux for 3 hr. Unchanged lithium was removed by filtration through a pad of glass wool. The normality of the phenyllithium solution was determined by addition of an aliquot to water followed by titration of the aqueous solution against standard potassium acid phthalate solution.

The alcohol (0.01 mole) in 20 ml. of ether was converted into the lithium alkoxide by adding an equimolar amount of phenyllithium. To this was added a solution of 1.9 g. (0.01 mole) of *p*-nitrobenzoyl chloride in 20 ml. of ether. About 0.1 g. of *p*-nitrobenzoic acid precipitated and was removed by filtration. The filtrate was washed with sodium carbonate and then with water until the washings were colorless. The ether solution was then dried over magnesium sulfate. After the ether was removed, the crude product was recrystallized from absolute methanol or absolute ethanol to give the *p*-nitrobenzoate in 55–60% yield.

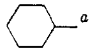
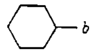
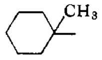
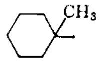
Preparation of *p*-Toluenesulfonates.—The same procedure was used as in the preparation of *p*-nitrobenzoates by Method A except that petroleum ether (30–60°) was used in place of the ether and the alcoholic recrystallization solvents. The crystallizations were carried out at low temperatures (down to *ca.* −80°) and 60–70% yields were obtained.

Preparation of Chlorides.—A solution of the tertiary alcohol (0.05 mole) in 5 ml. of ether was shaken with 45 ml. of concd. hydrochloric acid. The upper layer was separated and washed first with water and then with 5% sodium bicarbonate solution. To this layer was added 20 ml. of petroleum ether and the solution was then dried over magnesium sulfate. After the solvent had been removed by evaporation on a steam bath, the residue was distilled to give the chloride in *ca.* 75% yield. The physical constants and analytical data for the chlorides prepared in this manner are listed below in Table IV.

Solvents. Anhydrous Acetone.—One liter of C.P. acetone was refluxed for 24 hr. with 100 g. of Drierite and the acetone then distilled directly. The first 25% of the acetone was discarded and the next 50% collected and tested for dryness. Only acetone which did not give off more than a few stray bubbles on addition of calcium hydride was considered sufficiently dry for use in solvolysis.

TABLE IV

PHYSICAL CONSTANTS FOR TERTIARY CHLORIDES

R in $(CH_3)_2$ RCCl	B.p.	$n^{25}D$
 [a]	28° at 0.3 mm.	1.4680
 [b]	30–31.5° at 0.3 mm.	1.4808
 [c]	44–47° at 0.6 mm.	1.4789
 [d]	44° at 0.75 mm.	1.4919

[a] Lit.[58] b.p. 83° at 16 mm., $n^{25}D$ 1.4679. [b] *Anal.* Calcd for $C_9H_{15}Cl$: C, 68.03; H, 9.53; Cl, 22.34. Found: C 68.27; H, 9.41; Cl, 22.21. [c] *Anal.* Calcd. for $C_{10}H_{19}Cl$: C, 68.76; H, 10.96; Cl, 20.30. Found: C, 69.20; H, 10.79; Cl, 20.38. Lit.[59] b.p. 212–215°, $n^{20}D$ 1.4700. [d] *Anal.* Calcd. for $C_{16}H_{17}Cl$: C, 69.85; H, 9.85; Cl, 20.85. Found: C, 69.82; H, 9.92; Cl, 20.34.

Anhydrous Formic Acid.—Formic acid (Baker and Adamson C.P., 98–100%) was dried with boric anhydride in the manner described by Winstein and Marshall.[60] Karl Fischer titration indicated 0.07% (w./w.) water.

Anhydrous Acetic Acid.—Glacial acetic acid was distilled and then dried by the procedure of Fainberg and Winstein.[61]

Kinetic Measurements.—Solvolysis of the *p*-nitrobenzoate and *p*-toluenesulfonates was carried out using sealed ampule techniques. Where the esters were soluble in the cold solvent, 5-ml. aliquots of a 0.03 *N* stock solution were sealed in ampules. Where the esters were not completely soluble at room temperature in the selected solvent, a measured amount of a solution of the ester in dry acetone was transferred to the ampule and the solvent removed by evaporation in a 50° oven. Five-milliliter aliquots of the selected solvent were then added and the tubes sealed as above. It was determined in each case that the difficultly soluble esters were in solution at the elevated temperature of the rate bath. The acid liberated was titrated against methanolic sodium methoxide using Bromothymol Blue as an indicator with the *p*-nitrobenzoates and *m*-Cresyl Sulfone or Carvacrol Sulfone–phthalein with the tosylates. The infinity titer was taken as the average of the titer of four tubes which had been solvolyzed for at least ten half-lives.

The solvolysis of the tertiary chlorides at 25° was carried out in a 100-ml. volumetric flask from which 5-ml. aliquots were withdrawn at appropriate time intervals. The aliquot was quenched in 20 ml. of dry acetone and the liberated hydrochloric acid titrated against methanolic sodium methoxide using Bromophenol Blue as an indicator.

Formolysis of the tertiary chlorides was carried out in the manner described by Fainberg and Winstein.[61]

Acetolysis of the *p*-toluenesulfonates was carried out by the method of Winstein, Grunwald and Ingrahm.[62]

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