Experimental Section

Preparation and Purification of Materials. The preparation and purification of the α-disulfones and the method of purifying the dioxane used have already been described.[1a] Glyme (Ansul Co.) was purified by first distilling it from sodium and then distilling it from lithium aluminum hydride immediately before use. Triethylamine (Eastman Kodak) was distilled under nitrogen from barium oxide before being used.

Procedure for Kinetic Runs. The same general procedure previously used[3] for runs at 21.3° was also employed in the present work. The various Et_3N–Et_3NH^+ buffer solutions required were prepared by adding the calculated amount of standard perchloric acid to a standard solution of triethylamine in water. The ionic strength was maintained constant by addition of lithium perchlorate. The hydrolyses were followed spectrophotometrically in the manner previously described.[3]

Solvolyses of Tertiary α-Arylcycloalkyl and -polycycloalkyl Chlorides. Effects of Ring Size and Substituents in the Aryl Ring on the Solvolysis Rates

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Abstract: A series of α-arylcyclobutyl (**1-Z**), -cyclopentyl (**2-Z**), -cyclohexyl (**3-**, Z), -7-norbornyl (**4-Z**), and -2-adamantyl (**5-Z**) chlorides, in which the aryl rings are variously substituted for the study of substituent effects, was prepared and their solvolysis rates in 90% aqueous acetone were studied. The reactivities decrease in the sequence **2-Z** > **5-Z** > *t*-cumyl chlorides (**6-Z**) > **1-Z**–**3-Z** > **4-Z**; and for the parent α-phenyl (R = H) compounds, the relative rates at 25° are 369 for **2-H**, 23.4 for **5-H**, 6.68 for **6-H**, 1.40 for **1-H**, 1.00 for **3-H**, and 2.04×10^{-3} for **4-H**. The ρ–σ^+ treatments gave straight lines in all the systems and the ρ values obtained are −4.48 for **1-Z**, −4.10 for **2-Z**, −4.65 for **3-Z**, −5.64 for **4-Z**, −4.83 for **5-Z**, and −4.54 for **6-Z**. The rate-increasing effects arising from the transformation of the secondary cycloalkyl systems into the tertiary α-arylcycloalkyl system, k_ϕ/k_H, are 2.8×10^1 for the cyclobutyl, 4.6×10^3 for the cyclopentyl, 4.0×10^2 for the cyclohexyl, 1.7×10^3 for the isopropyl, 6.3×10^7 for the 7-norbornyl, and 1.4×10^5 for the adamantyl system. The relative importance of several factors governing the solvolysis reactivities is discussed.

Ring compounds exhibit a significant change in the facility of their solvolysis reactions with ring size, from small to large, and with cycle number, from monocyclic to polycyclic. In order to account for this change, a number of important factors and concepts of structure–reactivity relationships in organic chemistry have been introduced and demonstrated.[1] For example, the solvolysis reactivities of secondary cyclopropyl, cyclobutyl, cyclopentyl, and cyclohexyl *p*-toluenesulfonates in acetic acid have been found to be cyclopentyl–cyclobutyl > cyclohexyl ≫ cyclopropyl.[2–4] The solvolysis rates of tertiary α-methylcyclobutyl, -cyclopentyl, and -cyclohexyl chlorides in 80% ethanol have been found to be in the sequence cyclopentyl > cyclohexyl > cyclobutyl, and Brown has attempted with considerable success to rationalize these results in terms of "I strain."[5] The 7-norbornyl derivatives are extraordinarily unreactive in solvolysis; for example, 7-norbornyl brosylate solvolyzes (in acetic acid) 10^4 times more slowly than *n*-butyl brosylate,[6] 10^7 times more slowly than cyclohexyl brosylate, and 10^6 times more slowly than 2-adamantyl brosylate.[7] Substitution of a methyl group for the hydrogen at the reaction center of the 7-norbornyl derivative caused a rate enhancement of 5.1×10^7 (at 50°), the greatest yet reported.[8] Therefore, the effect of aryl substitution at the reaction center must be of considerable interest.

We have studied the rates and products in hydrolysis reactions of tertiary α-aryl-substituted cycloalkyl chlorides of the following fundamental ring systems in 90% aqueous acetone: α-arylcyclobutyl (**1-Z**), -cyclopentyl (**2-Z**), -cyclohexyl (**3-Z**), -7-norbornyl (**4-Z**), and -2-adamantyl (**5-Z**) chlorides. Combination of the present results with the reported data provides both the effect of aryl substitution and the relative effect of methyl and aryl substitutions. In addition, since sufficient varieties of substituents have been introduced into the aryl rings, it is possible to investigate whether or not linear free energy relationships are obtained by treatments of the rates with the Hammett–Brown relationship, $\log (k/k_0) = \rho\sigma^+$, and where obtained, the reaction constants, ρ, will be discussed as a measurement of the electron demand of a cationic center in a ring system. Although the objective was different, a recent study based on substantially the same technique was made of the substituent effect on the solvolysis of **2-Z**,

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[1] As reviews, (a) A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, pp 94–102; (b) C. A. Bunton, "Nucleophilic Substitution at a Saturated Carbon Atom," Elsevier Publishing Co., New York, N. Y., 1964, pp 39–50. In addition, refer to (c) E. M. Kosower, "An Introduction to Physical Organic Chemistry," John Wiley & Sons, Inc., New York, N. Y., 1968, pp 84–143.

[2] J. D. Roberts and V. C. Chambers, *J. Amer. Chem. Soc.*, 73, 5034 (1951).

[3] S. Winstein, B. K. Morse, E. Grunwald, H. W. Jones, J. Corse, D. Trifan, and H. Marshall, *ibid.*, 74, 1127 (1952).

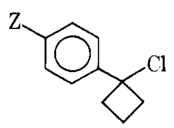
[4] H. C. Brown and G. Ham, *ibid.*, 78, 2735 (1956).

[5] H. C. Brown and M. Borkowski, *ibid.*, 74, 1894 (1952).

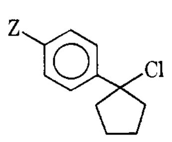
[6] Refer to H. Tanida, *Accounts Chem. Res.*, **1**, 239 (1968).

[7] P. von R. Schleyer and R. D. Nicholas, *J. Amer. Chem. Soc.*, **83**, 182 (1961).

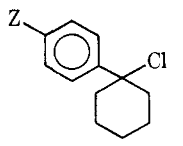
[8] H. Tanida, Y. Hata, S. Ikegami, and H. Ishitobi, *ibid.*, **89**, 2928 (1967).



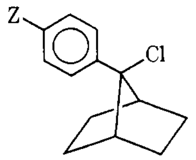
1-Z



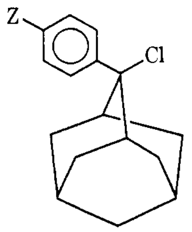
2-Z



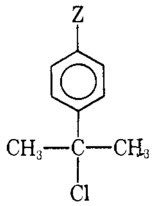
3-Z



4-Z



5-Z

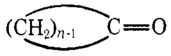


6-Z

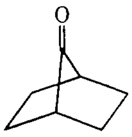
2-aryl-*exo*-2-norbornyl chlorides, and *t*-cumyl chlorides (**6**-Z) in ethanol by Brown and Takeuchi.[9] The hydrolysis solvent used in the present study is the same as that which Brown and his associates used for the solvolysis of **6**-Z, from which they obtained the σ^+ constants.[10] This may provide a convenience for comparison with the data on electrophilic side chain reactions[11] of benzenoid compounds.

Results

Preparations. The chlorides (**1**-Z–**5**-Z) were synthesized by Grignard reactions of the respective cycloalkanones (**7**–**11**) with arylmagnesium bromides followed by treatment of the resulting tertiary α-arylcycloalkanols (**12**-Z–**16**-Z) with hydrogen chloride using a previously reported method.[12] The commercially available *para*-substituted bromobenzenes (**17**-CH_3O, -CH_3, -H, -Cl) and ketones (**7**, **8**, **9**, **11**) were used in the Grignard reaction without further purifications. The bromide, **17**-CH_3S, was prepared by reduction of *p*-bromobenzenesulfonyl chloride with zinc in sulfuric acid followed by methylation with methyl iodide, and **17**-CF_3 was obtained by photobromination of *p*-bromotoluene (**17**-CH_3) followed by a fluorine exchange reaction of the *p*-bromobenzotribromide obtained with antimony trifluoride.[13] The preparation of 7-norbornanone (**10**) was by oxidation of 7-norbornanol with chromium trioxide in acetic acid[14a] or by the method reported by Gassman and Pape.[14b] All the Grignard reactions gave the corresponding tertiary alcohol in satisfactory yields and hydrochlorination of the alcohols did not give any rearranged products. The acetate of 2-(*p*-nitrophenyl)-2-adamantanol (**16**-NO_2) was obtained by nitration of the acetate of 2-phenyl-2-adamantanol with fuming nitric acid in acetic anhydride followed by separation of the *p*-nitro isomer from the reaction mixture using thin layer chromatography. The acetate of **16**-NO_2 was hydrolyzed in 60% aqueous acetone containing a few drops of hydrochloric acid; hydrochlorination then led to **5**-NO_2. The structures and purity of **1**-Z and **5**-NO_2 were confirmed by nmr spectra and vpc. All the chlorides, except the unstable **1**-CH_3S and **3**-CH_3S, were purified by recrystallization from *n*-pentane at a low temperature, prior to their uses for rate measurements. All of the α-arylnorbornyl and -adamantyl chlorides (**4**-Z and **5**-Z) were more stable than the α-arylcycloalkyl chlorides (**1**-Z, **2**-Z, and **3**-Z) and could be stored without decomposition at room temperature. The compounds thus prepared are listed in Table I, with the rate data and their physical and analytical data given in Table III in the Experimental Section.



7, $n = 4$
8, $n = 5$
9, $n = 6$



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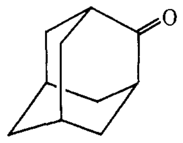
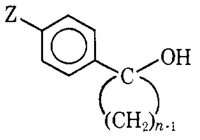
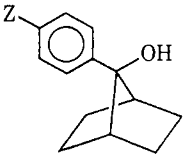


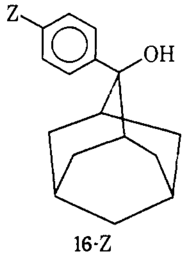
11



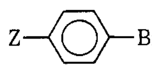
12-Z, $n = 4$
13-Z, $n = 5$
14-Z, $n = 6$



15-Z



16-Z



17-CH_3O, Z = CH_3O
17-CH_3S, Z = CH_3S
17-CH_3, Z = CH_3
17-H, Z = H
17-Cl, Z = Cl
17-CF_3, Z = CF_3

Rates. All rates were measured in a solvent prepared by mixing nine parts of acetone and one part of water at 25–26°. Rate measurements were carried out twice under identical conditions and averaged. In any given solvent, the rate constants were easily reproducible to 2%. However, since the rates were highly sensitive to minor changes in the water content, the same solvent batch was used for most of the rate measurements and new batches of solvent, when needed, were adjusted to give the original rate constant for *t*-cumyl chloride (our rate constant, 1.31×10^{-4} sec^{-1}, is slightly larger than that, 1.24×10^{-4} sec^{-1}, reported by Brown and his associates, presumably because of the low concentration of the chloride in our run).[15,16] Since the ρ values, presented below, could be seriously in error as a result of any uncertainty contained in the rate constants, the solvent was carefully checked several times at arbitrary intervals during the experiments. The theoretical infinity values were obtained in all runs except for **1**-CF_3, **3**-CF_3, and **5**-H, which gave 89, 90, and 93% of the theoretical values, respectively. The first-order rate constants obtained from the experimentally observed infinity titers were calculated

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(9) H. C. Brown and K. Takeuchi, *J. Amer. Chem. Soc.*, **88**, 5336 (1966).

(10) As a review, L. M. Stock and H. C. Brown, *Advan. Phys. Org. Chem.*, **1**, 35 (1963).

(11) For the definition of this term, see ref 10.

(12) (a) H. C. Brown and M.-H. Rei, *J. Org. Chem.*, **31**, 1090 (1966); (b) R. C. Hahn, T. F. Corbin, and H. Shechter, *J. Amer. Chem. Soc.*, **90**, 3404 (1968).

(13) R. J. Jones, *ibid.*, **69**, 2346 (1947).

(14) (a) H. M. Walborsky and D. F. Loncrini, *J. Org. Chem.*, **22**, 1117 (1957); (b) P. G. Gassman and P. G. Pape, *Tetrahedron Lett.*, 9 (1963).

(15) Essentially the same procedure was used in (a) H. C. Brown, Y. Okamoto, and G. Ham, *J. Amer. Chem. Soc.*, **79**, 1906 (1957); (b) H. C. Brown, J. D. Brady, M. Grayson, and W. H. Bonner, *ibid.*, **79**, 1897 (1957).

(16) We obtained a rate constant, 1.27×10^{-4} sec^{-1}, identical within experimental error with that obtained by Brown, *et al.*, when the concentration of the chloride was the same as they used.

Table I. Rate Constants and Activation Parameters from the Hydrolysis of the Tertiary Chlorides in 90% Aqueous Acetone

Compounds		Temp,		Calcd at 25°		
System	Subst	°C	10^4k_1, sec^{-1}	$\Delta H^{\ddagger}$, kcal	$\Delta S^{\ddagger}$, eu	Rel rate[a]
1	SCH_3	−20.0	1.07			
		−15.0	2.18			
		−5.0	6.33			
		25.0	128^b	15.2	−16.1	97.7 (467)
	CH_3	0.0	0.430			
		25.0	6.47	17.0	−16.2	4.96 (23.6)
	H	45.0	2.23			
		25.0	0.274	19.2	−15.1	0.209 (1.00)
	Cl	45.0	0.730			
		25.0	8.05×10^{-2}	20.2	−14.2	6.15×10^{-2} (0.294)
	CF_3	110.0	2.41			
		100.0	1.13			
		75.0	0.118			
		25.0	$4.56 \times 10^{-4\,b}$	22.4	−17.5	3.48×10^{-4} (1.66×10^{-3})
2	CH_3	−30.0	6.80			
		−20.0	25.0			
		−10.1	56.8			
		25.0	$1.30 \times 10^{3\,b,c}$	13.0	−19.0	992 (18.0)
	H	−20.0	0.443			
		−15.0	0.814			
		0.0	5.23			
		25.0	72.3^b	16.5	−13.1	55.2 (1.00)
	Cl	−10.0	0.394			
		0.0	1.55			
		10.0	4.68			
		25.0	26.3^b	18.0	−9.90	20.1 (0.364)
	CF_3	45.0	1.80			
		25.0	0.215	19.4	−14.7	0.168 (2.97×10^{-3})
3	SCH_3	−20.0	0.778			
		−10.0	2.78			
		−5.0	5.45			
		25.0	143^b	16.8	−10.6	109 (729)
	CH_3	0.0	0.271			
		10.0	1.03			
		25.0	5.82	19.2	−9.10	4.44 (29.7)
	H	45.0	1.91			
		25.0	0.196	20.9	−10.1	0.149 (1.00)
	Cl	45.0	0.566			
		25.0	5.34×10^{-2}	21.7	−10.0	4.08×10^{-2} (0.272)
	CF_3	110.0	3.69			
		100.0	1.47			
		75.0	0.135			
		25.0	3.15×10^{-4}	24.4	−11.1	2.40×10^{-4} (1.61×10^{-3})
4	CH_3O	0.0	0.702			
		10.0	2.30			
		20.0	6.59			
		25.0	11.1^b	17.2	−14.3	8.47 (2.79×10^4)
	CH_3S	45.0	5.20			
		35.0	1.67			
		25.0	0.643	19.1	−13.8	0.491 (1.62×10^3)
	CH_3	75.0	3.21			
		55.0	0.533			
		25.0	1.70×10^{-2}	21.0	−14.4	1.30×10^{-2} (42.7)
	H	110.0	3.13			
		100.0	1.24			
		75.0	0.131			
		25.0	$3.98 \times 10^{-4\,b}$	23.3	−14.4	3.04×10^{-4} (1.00)
5	CH_3	−20.0	0.481			
		−15.0	1.02			
		−5.0	4.13			
		25.0	159^b	18.7	−3.96	121 (34.6)
	H	0.0	0.200			
		10.0	0.749			
		25.0	4.59	19.7	−7.76	3.50 (1.00)
	Cl	0.0	5.63×10^{-2}			
		25.0	1.24	19.4	−11.4	0.947 (0.270)
	NO_2	100.0	2.91			
		75.0	0.273			
		25.0	$7.30 \times 10^{-4\,b}$	23.9	−11.2	5.57×10^{-4} (1.59×10^{-4})
6	H	25.0	1.31^d			

[a] Relative rates in parentheses were calculated taking as unity the rate of the unsubstituted compound in each the system. [b] Calculated by the Arrhenius plots using an IBM-360 computer. [c] The correlation coefficient of the Arrhenius plots for the compound was exceptionally low (0.995). [d] See ref 16.

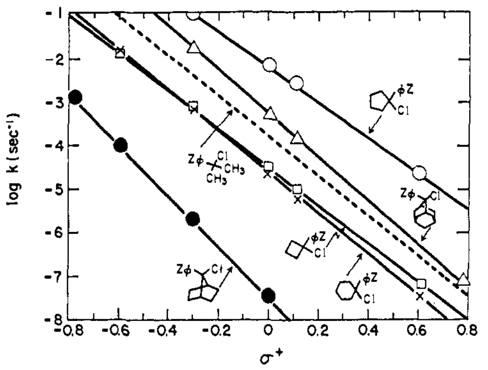


Figure 1. Hammett ρ–σ^+ plot. ρ: □, −4.48; ○, −4.10; ×, −4.65; ●, −5.64; △, −4.83; – – –, −4.54.

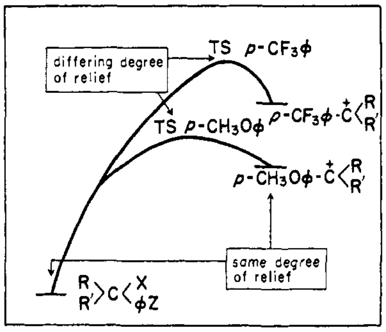


Figure 2. Diagram explaining the degree of strain relief in transition state.

by means of the least-squares method with an IBM computer, the correlation coefficients of all the plots being 0.999 ± 0.001. The rate constants and activation parameters thus obtained are listed in Table I. The relative rates at 25° were calculated taking both the rate for *t*-cumyl chloride and the rate for the parent compound as unity. Rates relative to the parent compound in each system are shown in parentheses.

Products. Hydrolysis of all the chlorides in 90% aqueous acetone proceeds without rearrangement to give the corresponding α-arylcycloalkanols (substitution) and arylcycloalkenes (elimination). Total yields of both the products, determined by vpc, were roughly quantitative. Exceptions were the hydrolyses of **1**-CF$_3$ and **3**-CF$_3$, which yielded the original alcohols in only 60 and 50%, respectively; the rest of their products were not fully investigated (Experimental Section).

The ρ–σ^+ Treatments. As shown in Figure 1, excellent straight lines were obtained by the ρ–σ^+ treatment of the rate data at 25° in each of the systems; the correlation coefficient are 0.999–0.998. It is likely that the experimental uncertainty in the rate constants introduces no serious difficulty in determining the ρ values to within an error of ±0.15 (for a ρ of 4.5, this error corresponds to ±3.3%). The ρ values obtained are −4.48 for **1**-Z, −4.10 for **2**-Z, −4.65 for **3**-Z, −5.64 for **4**-Z, −4.83 for **5**-Z, and −4.54 for **6**-Z.[10]

Discussion

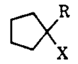
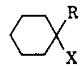
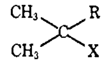
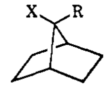
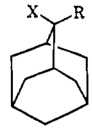
The substituent effects on rate in Table I arise from variation of the stabilization effect of the aryl rings on the cationic reaction center, while maintaining steric factors constant in the ground state of each system. The rate constants found range from a minimum factor of 6 × 10^3 (k_{CH_3}/k_{CF_3}) in **2**-Z to a maximum factor of 2.8 × 10^5 (k_{SCH_3}/k_{CF_3}) in **1**-Z. Over the whole range, when a molecule in one system is compared with its counterparts in the other systems (molecules bearing an identical substituent), the reactivities decrease in the sequence, **2**-Z > **5**-Z > **6**-Z[10] > **1**-Z–**3**-Z > **4**-Z, the reactivity differences between **2**-Z and **5**-Z and between **4**-Z and **3**-Z being significantly larger than the other differences, as shown in Figure 1. It is of considerable interest that **1**-Z is less reactive than **3**-Z when the substituent, Z, is strongly electron-supplying (CH$_3$S), while **1**-Z is more reactive than **3**-Z when Z is poorly electron-supplying or electron-withdrawing (CH$_3$, H, Cl, CF$_3$). The magnitude of the ρ values, which is a measure of the electron demand in the transition state, increases in the sequence, **2**-Z < **1**-Z < **6**-Z < **3**-Z < **5**-Z < **4**-Z. Here again, the ρ of **2**-Z and **4**-Z are apart from those of the other systems which are more or less constant within the range of −4.63 ± 0.2. These features may suggest either the existence of a unique factor(s) or an unusual contribution of known factor(s) in the two systems.

Rate constants in solvolyses of relevant secondary cycloalkyl derivatives (tosylates in acetic acid) and tertiary α-methyl-substituted cycloalkyl derivatives (chlorides in 80% ethanol) are summarized in Table II, together with the derived rate-accelerating effects due to the introductions of the aryl (k_{Ar}/k_H) and the methyl groups (k_{CH_3}/k_H) and, in addition, the ratio of the effects (k_{Ar}/k_{CH_3}). With the exception of the cyclobutyl systems, the same reactivity sequence was found in both the α-methyl and in the present α-aryl systems.

An important factor governing the reactivities of small ring compounds is doubtless an increase of angle strain in going from a ground state to a transition state, as greatly advocated by Brown.[4,5] One of the best known evidence for this is the fact that 1-methylcyclobutyl chloride solvolyzes five times more slowly than 1-methylcyclohexyl chloride. Although the present results do not disprove the importance of angle strain, the observed dependence of the relative reactivities of **1**-Z to **3**-Z upon substituents implies that the slow rate of 1-methylcyclobutyl chloride is very limited evidence.

The higher rate than any other counterpart, the lowest ρ value, and the rather large k_{Ar}/k_H and k_{CH_3}/k_H all support in the cyclopentyl system the major importance of the relief of torsional and/or steric strain accompanying the change in coordination number from four in the ground state to three in the transition state. The degree to which the ground state torsional and/or steric strain is relieved in the transition state will vary from compound to compound depending upon the location of the transition state along the reaction coordinate. Thus, a *para*-anisyl derivative would be expected to have its transition state early along the reaction coordinate; therefore relatively little strain would be relieved, and the rate would be relatively slower. On the other hand, a *p*-trifluoromethylphenyl substituent should give rise to a situation in which the transition state is much further along the reaction coordinate. In this situation, relief of ground state strain should have progressed to a very large extent by the time the transition state has been reached. This will tend to make the trifluoromethylphenyl rate faster, and the anisyl rate slower

Table II. Summary of Rate Constants of the Solvolyses of Secondary and Tertiary Cycloalkyl Derivatives at 25.0°

	R = ϕ, X = Cl		R = CH_3, X = Cl		R = H, X = OTs		Rate ratio		
	k_ϕ, sec^{-1}		k_{CH_3}, sec^{-1}		k_H, sec^{-1}				
Compounds	in 90% acetone	Rel rate	in 80% ethanol	Rel rate	Acetolysis	Rel rate	k_ϕ/k_H	k_{CH_3}/k_H	k_ϕ/k_{CH_3}
	2.74×10^{-5}	1.40	6.22×10^{-7} [a]	0.211	9.88×10^{-7} [b,c]	20.2	2.8×10^{1} [c]	0.63	44
	7.23×10^{-3}	369	3.67×10^{-4} [a]	124	1.58×10^{-6} [b]	32.4	4.6×10^{3}	2.3×10^{2}	20
	1.96×10^{-5}	1.00	2.95×10^{-6} [a]	1.00	4.88×10^{-8} [b]	1.00	4.0×10^{2}	6.0×10^{1}	6.6
	1.31×10^{-4}	6.68	9.24×10^{-6} [a]	3.13	7.74×10^{-8} [b]	1.59	1.7×10^{3}	1.2×10^{2}	14
	3.98×10^{-8}	2.04×10^{-3}		*d*	6.36×10^{-15} [e]	1.30×10^{-7}	6.3×10^{7}		
	4.59×10^{-4}	23.4	8.87×10^{-5} [f]	30.0	3.25×10^{-9} [e]	0.0665	1.4×10^{5}	2.7×10^{4}	5.2

[a] Calculated from the rate constants in ref 5. [b] Taken from ref 1b, 2–4. [c] When R = H, the solvolysis proceeds with rearrangement. [d] Very inert. [e] Reference 7. [f] The rate of the bromide are 3.46×10^{-3} sec^{-1}: J. L. Fry and P. von R. Schleyer, *J. Amer. Chem. Soc.*, in press. The rate for the chloride is calculated using the rate ratio of *t*-BuBr to *t*-BuCl, 39 (E. Grunwald and S. Winstein, *J. Amer. Chem. Soc.*, **70**, 846 (1948)).

than would be the case in the absence of such strain effects. For this reason, the magnitude of ρ in such a situation should be abnormally low. This is the case with **2**-Z. Figure 2 explains this discussion.[17] Following this argument, it is possible to account for the variation of relative reactivities of **1**-Z to **3**-Z due to substituents in the aryl rings. In cases where Z is electron-withdrawing, the transition state of **1**-Z will lie far along the reaction coordinate. This means that there will be considerable relief of strain in going to the transition state and the rate of **1**-Z will be enhanced relative to **3**-Z, where no such strain relief is possible. With the more electron releasing substituents, **1**-Z cannot benefit as much from relief of strain in the transition state; consequently, the rate is not so enhanced, and the derivatives react more slowly than the corresponding **3**-Z.[18] Similarly, the slower rate and greater magnitude of ρ in **3**-Z, relative to those in an acyclic counterpart, **6**-Z, can be explained by increase of strain in the transition state.

The enormous electron demand (the greatest in the present systems) at the reaction center of the 7-norbornyl system was evidenced, consistent with our previous claim,[8] by the largest value for $\rho(-5.64)$, the largest k_{Ar}/k_H, as well as the previously reported k_{CH_3}/k_H of 5.1×10^7 (50°, CH_3COOH).[8] These results are due to the extraordinary inertness of secondary 7-norbornyl derivatives.[6] As possible factors, Roberts, *et al.*,[19] have suggested the following: (1) steric hindrance to solvation of the 7-norbornyl cation by repulsions involving C_2 and C_3 (or C_5 and C_6) and their associated hydrogens, (2) an increase in steric strain during the change in hybridization from sp^3 to sp^2, and (3) Bredt's rule interdiction of a hyperconjugative stabilization due to the bridgehead hydrogens; the last (3) was postulated to be the most important. Schleyer[7] further clarified factor 2 by defining two process. (a) The C_1–C_7–C_4 angle is much smaller than normal.[20] Therefore, formation of the quasi-trigonal transition state with prefered 120° angles would be resisted. (b) The favorable skew relationship of the substituents upon C_1, C_7, and C_4 in the ground state would be converted to energetically unfavorable eclipsed conformations in the transition state. In contrast with the abnormal inertness of the 7-norbornyl derivative, secondary 2-adamantyl tosylate shows a normal reactivity (only 15 times slower than the cyclohexyl tosylate[7]), as listed in Table II. Whereas the rate of **4**-H is slower than that of **3**-H by a factor of 2.04×10^{-3}, the rate of **5**-H is faster by a factor of 23.4. The ρ from **5**-Z is normal and that from **4**-Z is abnormally large. These contrasts eliminate the importance of the factor 3 which is common to both the norbornyl and adamantyl systems; they also indicate that factor 2b is not important. An S_N2 nucleophilic displacement at C_7 of norbornyl derivatives is extremely difficult, as is, more generally speaking, that at a ring carbon of bridged cyclic compounds. It was recently pointed out that the rate-determining transition states of secondary 2-adamantyl derivatives possess limiting, open carbonium ion character (*viz.* no nucleophilic solvent participation) to greater extent than any other secondary substrate yet investigated.[21] Therefore, it is not under-

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(17) The discussion here owes much to a private communication from Professor P. von R. Schleyer. We thank him.

(18) A referee pointed out that, although the explanation of the different ρ's observed for **1**-Z and **3**-Z is plausible, the actual difference is so small that any explanation is gratuitous.

(19) W. G. Woods, R. A. Carboni, and J. D. Roberts, *J. Amer. Chem. Soc.*, **78**, 5653 (1956).

(20) For the angle in norbornane, the values of 93.2 and 96.0° were given by electron diffraction studies of two different groups, respectively: (a) Y. Morino, K. Kuchitsu, and A. Yokozeki, *Bull. Chem. Soc. Jap.*, **40**, 1552 (1967); (b) J. F. Chiang, C. F. Wilcox, Jr., and S. H. Bauer, *J. Amer. Chem. Soc.*, **90**, 3149 (1968). Also, refer to footnote 30 in ref 7.

(21) J. L. Fry, C. J. Lancelot, L. K. M. Lam, R. C. Bingham, and P. von R. Schleyer, *J. Amer. Chem. Soc.*, in press, and subsequent two papers.

Table III. Physical Properties of 1-Arylcycloalkanol Derivatives

Compounds	Mp or bp (mm), °C	n^{25}D	Calcd, % C	Calcd, % H	Found, % C	Found, % H
12-SCH$_3$	56.5–58		68.00	7.26	68.38	7.24
12-CH$_3$	91–92 (0.3)	1.5400	81.44	8.70	81.54	8.65
12-H	41–41.5		(lit. mp[a] 41–42°)			
12-Cl	103–104 (0.3)		65.76	6.07	65.32	6.01[b]
12-CF$_3$	54.5–55		61.11	5.12	60.80	5.44
13-CH$_3$	91–92 (0.3)	1.5400	(lit.[c] bp 79–84° (0.2), n^{18}D 1.5443)			
13-H	~10	1.5545	(lit.[d] bp 135–136° (12), n^{20}D 1.5473)			
13-Cl	57–58		(lit.[e] mp 60°)			
13-CF$_3$	40.5–41		62.60	5.69	62.82	5.98
14-SCH$_3$	63.0–64.5		70.22	8.16	70.44	8.18
14-CH$_3$	50–51		82.06	9.54	82.14	9.57
14-H	63–64		(lit.[f] mp 62°)			
14-Cl	84–85		68.40	7.18	68.45	7.23
14-CF$_3$	64–65		63.92	6.19	63.79	6.56
15-OCH$_3$	73.5–74.5		77.03	8.31	77.05	8.31
15-SCH$_3$	82–82.5		71.74	7.89	71.36	8.16
15-CH$_3$	85–86		83.21	8.97	83.40	8.99
15-H[g]	108–109 (0.7)	1.5553[h]	82.93	8.57	82.79	8.77
16-CH$_3$	75–77		84.25	9.15	83.88	9.50
16-H	78.5–79		84.16	8.83	83.48	8.87
16-Cl	105.5–107.5		73.13	7.29	72.95	7.29
16-NO$_2$[i]	139–141		68.55	6.71	68.30	6.64
1-CH$_3$	*j*		73.12	7.25	72.95	7.24
1-H	*j*		72.07	6.65	72.40	6.82[j]
1-Cl	*j*		59.72	5.01	59.44	4.97
1-CF$_3$	*j*		56.32	4.30	56.00	4.51
3-CF$_3$	*j*		59.43	5.37	59.72	5.48
4-SCH$_3$	88.5–90		66.51	6.78	66.76	6.82
4-CH$_3$	130–130.5		76.17	7.76	76.40	7.96
4-H	96–97		75.53	7.31	75.78	7.43
5-CH$_3$	101–102		78.29	8.12	78.34	8.05
5-H	66.0–68.0		77.87	7.76	77.57	7.84
5-Cl	89.0–91.0					
5-NO$_2$	102.5–103.5		65.86	6.22	65.74	6.21

[a] A. Burger and R. D. Bennett, *J. Med. Pharm. Chem.*, **11**, 687 (1960). [b] Calcd: Cl, 19.41. Found: Cl, 19.75. [c] J. P. Vila and R. Crespo, *Anales Real Soc. Espan. Fis. Quim.* (*Madrid*), *Ser. B*, **48**, 273 (1952). [d] C. D. Nenitzescu and I. Necsoiu, *J. Amer. Chem. Soc.*, **72**, 3483 (1950). [e] W. Winter, K. Stach, H. A. Friesewinkel, H. G. Kroneberg, and K. Stoepel, German Patent 1,110,155 (July 6, 1961); *Chem. Abstr.*, **56**, 12803 (1962). [f] M. Protiva and J. Urban, *Chem. Listy*, **42**, 175 (1948). [g] P. G. Gassmann and A. F. Fentiman, Jr., *J. Amer. Chem. Soc.*, **91**, 1545 (1969). [h] Measured at 25.5°. [i] The acetate of 2-(*p*-nitrophenyl)adamantan-2-ol. [j] No sharp melting point, gradually decompose.

standable that the factor 1 contributes very greatly to the inertness of 7-norbornyl derivatives. This all indicates that of primary importance is the factor 2a (angle strain), consistent with Schleyer's assertion.[7]

Whereas secondary 2-adamantyl tosylate acetolyzes more slowly than cyclohexyl and isopropyl tosylates, tertiary 2-aryl- and 2-methyl-2-adamantyl chlorides hydrolyze more quickly than the corresponding α-aryl- and α-methylcyclohexyl and *t*-cumyl and *t*-butyl chlorides. As a result, k_{Ar}/k_H and k_{CH_3}/k_H are great in the 2-adamantyl system. Although the cyclobutyl system exhibits an analogous but reverse position change in the sequence, it is omitted from the present discussion because of the rearrangement and ring cleavage accompanying the solvolysis of the secondary compounds. The solvolysis of not only the α-aryl compounds but also other tertiary compounds proceeds with "limiting" (S_N1) behavior,[22–24] so that solvents do not participate in the transition state. However, evidence was proposed that simple secondary substrates without neighboring groups, *e.g.*, isopropyl, solvolyze with considerable nucleophilic solvent assistance. It is understandable, in this connection, that isopropyl and cyclohexyl tosylates react rapidly due to solvent assistance, but secondary 2-adamantyl tosylate more slowly in the absence of such a benefit.

A number of other minor features are found in the present results, but a discussion of them should wait until further studies in other ring systems and in other solvents are carried out.

Experimental Section

Melting points were taken by capillary and are corrected. Boiling points are uncorrected. All the α-arylcycloalkanols prepared gave satisfactory analyses and their purities, except for that of **13-CH$_3$**, were checked by vpc. Almost all the chlorides gave the theoretical infinity titers in the solvolyses. Some exceptional chlorides, **1-CF$_3$**, **3-CF$_3$**, and **5-H**, which showed infinity titers somewhat less than theory, afforded satisfactory elemental analyses. Vpc analyses were performed on a Hitachi Perkin-Elmer Model F-6 or F-6-D using helium as a carrier gas. Nmr spectra were determined on a Varian A-60 spectrometer using tetramethylsilane as internal standard in carbon tetrachloride. Infrared spectra were measured on a JASCO Model IR-S. Properties and analyses of the new compounds prepared in this study are summarized in Table III.

***p*-Bromomethylthiobenzene (17-SCH$_3$).** *p*-Bromothiophenol was prepared by essentially the same method as that reported for thiophenol.[25] Methylation of *p*-bromothiophenol was carried out by

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[22] S. Winstein, E. Grunwald, and H. W. Jones, *J. Amer. Chem. Soc.*, 73, 2700 (1951).

[23] C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, Chapter VII.

[24] E. R. Thornton, "Solvolysis Mechanisms," Ronald Press, New York, N. Y., 1964.

[25] R. Adams and C. S. Marvel, "Organic Syntheses," Coll. Vol. I, John Wiley & Sons, Inc., New York, N. Y., 1941, p 504.

the method of Nodiff, *et al.*[26a] A sample of **17**-SCH$_3$ had mp 39.5–40.0° (lit.[26b] mp 39.0–40.0°).

General Comments on the Preparations of α**-Arylcycloalkanols.** The Grignard reagents of bromobenzene, *p*-bromotoluene, and *p*-bromochlorobenzene were prepared by the reactions of the respective bromides with magnesium metal in absolute ether. Since the reactions with *p*-methoxy- and *p*-bromomethylthiobenzenes were slow in ether, tetrahydrofuran was used to raise the reaction temperature. In the case of *p*-bromobenzotrifluoride, a few drops of methyl iodide were added as an initiator. Cycloalkanone in ether was added to a stirred solution of the Grignard reagent under nitrogen at 0–5°. After hydrolysis of the reaction mixture with aqueous ammonium chloride, the combined ether decantate and residue extract were dried and concentrated at reduced pressure, leaving the α-arylcycloalkanol.

2-*p*-Nitrophenyl-2-adamantyl Chloride (5-NO$_2$). 2-Phenyl-2-adamantyl chloride (700 mg) was solvolyzed in acetic acid containing sodium acetate to yield 640 mg of 2-phenyl-2-adamantyl acetate. Nitration of 640 mg of the acetate with 390 mg of fuming nitric acid in 6 ml of acetic anhydride gave 650 mg of a mixture of *ortho*, *meta*, and *para* isomers of 2-(nitrophenyl)-2-adamantyl acetate. The *p*-nitro isomer (135 mg) was separated from the mixture by thin layer chromatography on Kieselgel GF$_{254}$ nach Stahl (Merck) using a solvent mixture of 35:20 petroleum ether (bp 30–60°) and ether, and purified by recrystallization. The nmr spectrum of this acetate shows A$_2$B$_2$-type aromatic protons but no signals of aromatic protons arising from other isomers. The acetate (110 mg) was hydrolyzed in 60% aqueous acetone containing a few drops of hydrochloric acid to give the alcohol, which was subsequently hydrochlorinated to yield 105 mg of **5**-NO$_2$. The nmr spectrum (CCl$_4$) of the acetate showed δ 8.25–7.64 (quartet of triplets, 4, J = 9.0 Hz (*ortho* coupling), aromatic protons), 3.06 (m, 2, bridgehead adjacent to the acetoxyl), 1.84 (s, OAc), 2.40–1.60 (m, adamantane ring protons). The ir spectrum of the acetate showed characteristic bands at 860 (m) and 847 cm^{-1} (m).

Hydrochlorination of the Tertiary Alcohols. Since all of the tertiary alcohols were very reactive and readily converted into tertiary chlorides; an automatic hydrochlorinator, invented by Brown, *et al.*,[27] was employed. Any unstable chloride used in rate measurements was prepared separately for the each run, in order to avoid the presence of impurities arising from decomposition. Methylene dichloride was found most convenient as solvent in the preparation of the chlorides; it was removed on an ice bath at reduced pressure to prevent decomposition of the resulting unstable chlorides. All the chlorides were purified by recrystallization from *n*-pentane at low temperature (0 to −20°) avoiding the presence of moisture. The chlorides obtained were used immediately for the rate measurements.

Product Analysis. The hydrolysis products of **1**-CF$_3$, **1**-Cl, **2**-CF$_3$, **3**-CF$_3$, **4**-H, and **5**-Cl were analyzed by vpc (1 m, 8% diethylene glycol succinate polyester, at 150–170°) using 2-indanol as internal reference. The original alcohol was given by **1**-CF$_3$ in 60% yield; other products, whose vpc peaks appeared very early, were not fully investigated because of difficulty in their separation. Compound **1**-Cl gave the original alcohol quantitatively. Analysis of the products from **2**-CF$_3$ by vpc indicated only olefin, hydrochlorination of which gave the original **2**-CF$_3$ entirely. Fifty per cent of the original alcohol was found in the products from **3**-CF$_3$; the rest were not fully investigated. Compound **4**-H gave over 99% of original alcohol, plus a minor component. Although the products from **5**-Cl were not investigated by vpc, their hydrochlorination gave the original **5**-Cl, which was identified by comparison of infrared spectrum and melting point. No data indicating rearrangement were obtained in the product analyses.

Kinetic Measurements. The procedure utilized for the determination of the rate constants was similar to that previously reported by Brown, *et al.*[15] Temperatures were controlled to ±0.03°. The tertiary chloride (300 mg) was dissolved in the solvent (60 ml) and brought to reaction temperature. Aliquots (6 ml), removed at appropriate intervals of time, were run into 60 ml of cold (0°) dry acetone to stop the reaction and free hydrogen chloride was titrated with 0.02 *N* sodium hydroxide. Indicator was prepared by mixing 3 drops and 2 drops of ethanol solutions of bromocresol green and methyl red, respectively. Because of the rapidity of the solvolysis reactions of **1**-SCH$_3$, **1**-CH$_3$, **2**-H, **2**-Cl, **3**-SCH$_3$, **3**-CH$_3$, **4**-OCH$_3$, **5**-CH$_3$, and **5**-H, the hydrogen chloride formed in these reactions was determined by titration with a standard solution of sodium ethoxide in absolute ethanol (0.02 *M*) at −20 to −10°. Since **2**-CH$_3$ solvolyzed too fast to be measured by titration, a technique based on direct measurement of half-life time of the hydrolysis was used. A 0.02 *M* solution of the chloride in acetone and a 0.05 *M* aqueous NaOH solution were separately prepared. To 2 ml of the latter solution (accurately taken by weight) were added a few drops of indicator, 8 ml of anhydrous acetone, and then 10 ml of the chloride solution (also taken by weight), to adjust exactly the composition of the mixture to 9 parts of acetone and 1 part of water. At the infinity time of the reaction, the excess hydrogen chloride formed was titrated with about 4.5 ml of a 0.02 *M* aqueous NaOH solution. Then, the concentration of NaOH in the 0.05 *M* NaOH solution was slightly corrected to half the value of the infinity titer of the hydrochloric acid formed from hydrolysis. A mixture of 2 ml of this corrected NaOH solution, 8 ml of acetone, and few drops of the indicator was brought to the reaction temperature, and then added to 10 ml of the chloride solution which had also been maintained at the reaction temperature. The time required to change the initial blue color of the reaction mixture to yellow green was measured. This measurement of half-life time was repeated three times under identical conditions and averaged to obtain the rate constants of the chloride. However, the data obtained may be unreliable because of a side reaction of acetone in this basic solution.

Acknowledgment. We thank Mr. H. Ishitobi for his technical assistance in part of this work.

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(26) (a) E. A. Nodiff, S. Lipschutz, P. N. Craig, and M. Gordon, *J. Org. Chem.*, **25**, 60 (1960); (b) H. F. Wilson and D. S. Tarbell, *J. Amer. Chem. Soc.*, 72, 5200 (1950).

(27) H. C. Brown and M.-H. Rei, *J. Org. Chem.*, **31**, 1090 (1966).