(q, 2, J = 9 Hz, CF_3CH_2), 6.65 (s, 3, CH_3OCH), 6.68 (s, 3, CH_3OCH_2), and *ca.* 8.3 (m, 4, methylene); mass spectrum (70 eV) *m/e* 143 (base peak); ir (neat) 1280 cm^{-1} (CF_3).

Anal. Calcd for $C_8H_{15}F_3O_3$: C, 44.44; H, 6.99; F, 26.36. Found: C, 44.14; H, 7.04; F, 26.48.

A better estimate of the yield of **8** was obtained by gas chromatographic analysis using internal standards. In a typical experiment the accurately weighed ester (*ca.* 0.4 g) was solvolyzed as above, the reaction mixture was cooled, and cyclohexyl acetate and *n*-octyl alcohol were accurately weighed into the reaction mixture. The mixture was vigorously shaken and analyzed directly on a 20% FFAP on Chromosorb P column. The yield of **8**, determined from the relative peak areas suitably corrected for minor differences in detector response, was 70%.

Trifluoroethanolysis Products from 5,5-Dimethoxy-1-pentyl Tosylate (2, *n* = 3).—The tosylate (2.82 g) was diluted with 95 ml of 0.130 *M* sodium trifluoroethoxide–trifluoroethanol and heated at 70° for 14 hr. The mixture was cooled, filtered, and concentrated. Ether (*ca.* 35 ml) was added to precipitate the remaining salts. The mixture was filtered, concentrated, and distilled. A single high-boiling component was isolated (0.5 g), bp 95° (17 mm), $n^{27}D$ 1.3816. This material was further purified by preparative gas chromatography and identified as 1,5-dimethoxy-1-trifluoroethoxypentane (**9**): nmr (CCl_4) 5.50 [t, 1, J = *ca.* 5 Hz, $(CH_3O)_2CH$], 6.23 (q, 2, J = 9 Hz, CF_3CH_2); 6.70 (s, 3, CH_3OCH), 6.75 (s, 3, CH_3OCH_2–), and *ca.* 8.5 (m, 6, methylene); mass spectrum (70 eV) *m/e* 143 (base peak); ir (neat) 1280 cm^{-1} (CF_3).

Anal. Calcd for $C_9H_{17}F_3O_3$: C, 46.95; H, 7.44; F, 24.76. Found: C, 46.85; J, 7.51; F, 24.79.

The yield of **9**, determined by gas chromatography using an internal standard, was *ca.* 25%. Although no attempt was made to recover the major solvolysis product, it was identified as 2-methoxytetrahydropyran on the basis of its identical gas chromatography retention time with that of an authentic sample.

Registry No.—**1** (*n* = 2), 23068-87-3; **2** (*n* = 2), 23068-88-4; **2** (*n* = 3), 23068-89-5; **2** (*n* = 4), 23068-90-8; **4** (*n* = 3), 23068-91-9; **6** (*n* = 2), 17082-61-0; **7**, 23074-20-6; **8**, 23074-21-7; **9**, 23074-22-8; 1-octyl tosylate, 3386-35-4.

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Cyclopropylcarbinyl *p*-Toluenesulfonate Solvolysis. IV. Correlation with Cholesteryl Tosylate Solvolysis Rates

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The solvolysis rates of cholesteryl and cyclopropylcarbinyl (**3**-H) tosylate have been determined in a series of solvents of varying ionizing strength. The correlation of the cholesteryl tosylate solvolysis rates with those of **3**-H reflects a mechanistic similarity between the two substrates. The solvolysis rates of 1-*p*-nitrophenylcyclopropylcarbinyl tosylate (**3**-NPh) have been determined in acetic acid and ethyl alcohol. The solvolysis of **3**-NPh relative to **3**-H is retarded by a factor of 10^{-1}. Comparison of the substituent effect upon the solvolytic reactivity of **3**-H with related compounds supports a transition state with little charge localized at the methinyl carbon.

The rates of ionization of *p*-methoxyneophyl tosylate, log k_{ion}, in several solvents provide a useful scale of solvent polarity for measuring the response of an anchimerically assisted reaction to solvent variation.[2] Earlier work[3] revealed that solvolysis rates of cyclopropylcarbinyl arenesulfonates, although obeying a limiting SN1 mechanism, are poorly correlated by such a scale.

This finding, coupled with more recent observations,[4,5] suggests that a substrate subject to homoallylic rather than phenyl anchimeric assistance would be a more suitable model reaction for correlating cyclopropylcarbinyl arenesulfonate solvolysis rates.

That cholesteryl tosylate solvolyses are assisted by homoallylic interaction[6] has been well established.[6,7] Accordingly, reaction rates of cholesteryl tosylate have been measured in a solvent series of varying ionizing and nucleophilic strength.[8]

The kinetic data are given in Table I. The course of each reaction was followed by titrating the liberated *p*-toluenesulfonic acid. The solvolysis reactions of cyclopropylcarbinyl tosylate (**3**-H) in the aqueous binary solvents demonstrated the previously reported "internal return" rearrangement,[9,10] which accounted for 5–15% of the starting material. The purities of the starting materials were, therefore, checked by methanolysis, where a rearrangement to less reactive tosylates does not occur.[10] The solvolysis rates of cholesteryl tosylate in aqueous dioxane solvents obeyed first-order kinetics up to 85% conversion, with the exception that the first 5% of reaction was accelerated.

All other reactions were strictly first order in *p*-toluenesulfonate and furnished, within experimental error, 100% of the theoretical amount of acid present.

Discussion

The correlation of the cholesteryl tosylate solvolysis rates with those of cyclopropylcarbinyl tosylate results in a dispersion of points into two accurately straight lines (*cf.* Figure 1) in contrast to scatter diagrams

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(2) S. G. Smith, A. H. Fainberg, and S. Winstein, *J. Amer. Chem. Soc.*, **83**, 618 (1961).

(3) D. D. Roberts, *J. Org. Chem.*, **29**, 294 (1964).

(4) D. D. Roberts, *ibid.*, **33**, 2712 (1968).

(5) D. D. Roberts, *ibid.*, **34**, 285 (1969).

(6) S. Winstein and E. M. Kosower, *J. Amer. Chem. Soc.*, **78**, 4347 4354 (1956).

(7) R. A. Sneen, *ibid.*, **80**, 3977 (1958).

(8) A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, pp 63–65.

(9) M. C. Caserio, W. H. Graham, and J. D. Roberts, *Tetrahedron*, **11**, 171 (1960).

(10) D. D. Roberts, *J. Org. Chem.*, **30**, 23 (1965).

TABLE I

Tosylate	Solvent, vol. %[a]	Temp, °C	k_1, 10^5 sec^{-1}
b	MeOH	50	31[c]
b	MeOH	40	16
b	50% MeOH–EtOH	50	21[c]
b	50% MeOH–EtOH	40	11
b	75% MeOH–EtOH	50	12
b	EtOH	50	10[c]
b	EtOH	40	3.5
b	n-PrOH	50	6.6[c]
b	n-PrOH	40	2.2
b	80% aq EtOH	50	42
b	80% aq EtOH	40	19
b	85% aq EtOH	50	33
b	90% aq EtOH	50	21[c]
b	90% aq EtOH	40	9.0
b	AcOH[d]	50	13.2
b	80% aq dioxane	50	11[b]
b	80% aq dioxane	40	3.4[c]
b	85% aq dioxane	50	9.0[c]
b	90% aq dioxane	50	4.0[c]
b	90% aq dioxane	40	1.0[c]
b	85% aq Me_2CO	50	10
b	85% aq Me_2CO	40	3.5
b	90% aq Me_2CO	50	5.8[c]
b	90% aq Me_2CO	40	1.9
e	50% MeOH–EtOH	20	7.0
e	75% MeOH–EtOH	20	4.7
e	n-PrOH	20	2.2
e	85% aq EtOH	20	84
e	90% aq EtOH	20	32
e	80% aq dioxane	20	11
e	85% aq dioxane	20	7.0
e	90% aq dioxane	20	1.4
e	85% aq Me_2CO	2;	9.0
e	90% aq Me_2CO	20	3.15
f	50% MeOH–EtOH	20	7.1
f	75% MeOH–EtOH	20	5.0
f	n-PrOH	20	2.2
f	85% aq EtOH	20	33.0
f	90% aq EtOH	20	20.0
f	80% aq dioxane	20	5.5
f	90% aq dioxane	20	1.4
f	85% aq Me_2CO	20	4.3
f	90% aq Me_2CO	20	2.4

[a] x vol. % binary solvent YZ means x volumes of Z plus $100 - x$ volumes of Y. [b] Cholesteryl. [c] Duplicate runs. [d] Taken from data of S. Winstein and R. Adams, *J. Amer. Chem. Soc.*, **70**, 838 (1948). [e] Cyclopropylcarbinyl tosylate. [f] 1-Phenylcyclopropylcarbinyl tosylate.

obtained for both mY[11] and log k_{ion} correlations. The dispersion of the data into more than one correlation line is typical[12] for a study involving several solvent systems and is in accord with the significantly different solvolytic behavior of cyclopropylcarbinyl tosylate in the two solvent series. Thus, in the ionizing solvents (correlation line I, Figure 1) significantly less than the theoretical amount of acid liberated at infinity and $\Delta S^{\ddagger}$ values of *ca.* −20 eu are observed, while in nucleophilic solvents (correlation line N, Figure 1) liberation of nearly the theoretical amount of acid at infinity and $\Delta S^{\ddagger}$ values of *ca.* −7 eu are observed.

Correlation of the solvolysis rates of **3**-H with those of cholesteryl tosylate over such a wide spectrum of

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

(12) A. H. Fainberg and S. Winstein, *ibid.*, **79**, 1597, 1602, 1608 (1957).

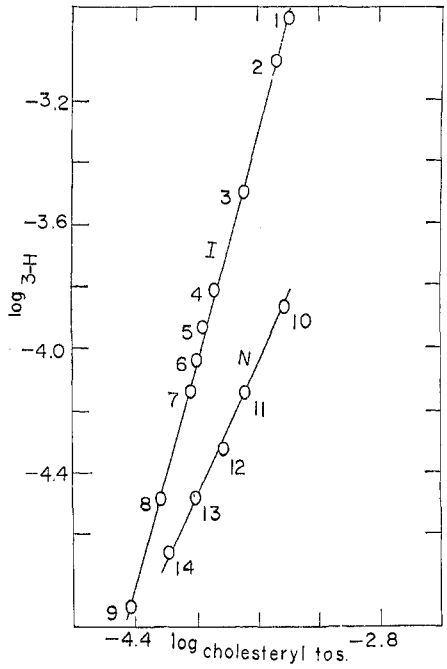
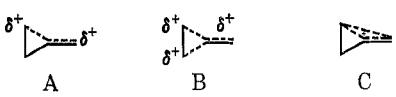


Figure 1.—The linear dependence of log (**3**-H) on log (cholesteryl tosylate): 1, 80% aqueous EtOH; 2, 85% aqueous EtOH; 3, 90% aqueous EtOH; 4, AcOH; 5, 80% aqueous dioxane; 6, 85% aqueous acetone; 7, 85% aqueous dioxane; 8, 90% aqueous acetone; 9, 90% aqueous dioxane; 10, methanol; 11, 50:50 methanol–ethanol; 12, 25:75 methanol–ethanol; 13, ethanol; 14, n-propyl alcohol.

solvents reflects a mechanistic similarity between the two substrates. This possibility is strengthened by the failure of a solvent polarity scale (log k_{ion}) based upon a compound known to undergo ionization assisted by neighboring-group participation to correlate with **3**-H solvolysis rates.

Many structures have been considered for the cyclopropylcarbinyl cation to accommodate various modes of electron delocalization. Among these are the homoallyl[13,14] (A), symmetrical homoallyl[14,15] or bisected form[16,17] (B), and bicyclobutonium[18,19] (C) ions.



A B C

Recently,[10,20] it was proposed, based upon solvolytic behavior, that the mode of electron delocalization in the cyclopropylcarbinyl cation varied with the nature of the solvent—structure A is favored in nucleophilic solvents while structure C (or possibly structure B) is favored in ionizing solvents. On the other hand, the mode of charge dispersal in the cholesteryl ion, stereoelectronically restricted to unsymmetrical homoallylic delocalization, is insensitive to medium effect. The partitioning of the solvents, therefore, into two correlation lines is in keeping with the solvent-variable

(13) M. Simonetta and S. Winstein, *ibid.*, **76**, 18 (1954).

(14) S. Winstein and E. M. Kosower, *ibid.*, **81**, 4399 (1959).

(15) C. G. Bergstrom and S. Siegal, *ibid.*, **74**, 145 (1952).

(16) C. V. Pittman, Jr., and G. A. Olah, *ibid.*, **87**, 2998, 5123 (1965).

(17) R. Hoffmann, *Tetrahedron Lett.*, No. 43, 3819 (1965).

(18) E. F. Cox, M. C. Caserio, M. S. Silver, and J. D. Roberts, *J. Amer. Chem. Soc.*, **83**, 2719 (1961).

(19) For a recent review, see C. D. Ritchie in "Carbonium Ions," G. A. Olah and Z. R. Schleyer, Ed., Interscience Publishers, Inc., New York, N. Y., 1969.

(20) D. D. Roberts, *J. Org. Chem.*, **31**, 2000 (1966).

TABLE II
SUMMARY OF SOLVOLYSIS RATES FOR *p*-SUBSTITUTED 1-PHENYLCYCLOPROPYLCARBINYL TOSYLATES

para substituent[a]	Solvent	Concn of salt, *M*	Temp, °C	k_1, 10^5 sec^{-1}	*b* value[b]	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu
H	AcOH		30	53.0		21.0	−4
H	AcOH	0.025[c]	30	84.0	23		
H	AcOH	0.051[d]	18	16.3[e]	1.4		
CH_3O	AcOH		25	62.0[f]		19.9	−6
CH_3O	AcOH	0.025[c]	25	90.0	18		
CH_3O	AcOH	0.024[d]	25	62.0	0.0		
NO_2	AcOH		25	1.5		21.9	−7
NO_2	AcOH	0.025[c]	30	5.1	34		
NO_2	AcOH	0.024[d]	30	3.0	4.4		
NO_2	AcOH		35	4.9			
NO_2	AcOH		45	16.2			
NO_2	AcOH		55	47.0			
NO_2	EtOH		45	7.1		19.0	−18
NO_2	EtOH		50	11.0			
NO_2	EtOH		60	30.0			
NO_2	EtOH		65	43.0			

[a] Initial concentration 0.020–0.030 *M*. [b] Calculated from the equation $k_t = k_t^0$ [1 + *b* (salt)]; A. H. Fainberg and S. Winstein, *J. Amer. Chem. Soc.*, **78**, 2763, 2767, 2777, 2780 (1956). [c] $LiOCl_4$. [d] NaOAc. [e] Taken from data of J. W. Wilt and . D. Roberts, *J. Org. Chem.*, **27**, 3430 (1962). [f] Taken from data of ref 4.

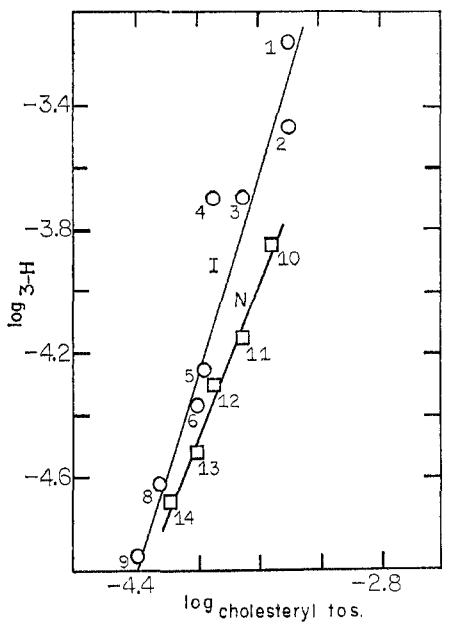


Figure 2.—The linear dependence of log (3-Ph) on log (cholesteryl tosylate): 1, 80% aqueous EtOH; 2, 85% aqueous EtOH; 3, 90% aqueous EtOH; 4, AcOH; 5, 80% aqueous dioxane; 6, 85% aqueous acetone; 8, 90% aqueous acetone; 9, 90% aqueous dioxane; 10, methanol; 11, 50:50 methanol–ethanol; 12, 25:75 methanol–ethanol; 13, ethanol; 14, *n*-propyl alcohol.

modes of charge dispersal in the cyclopropylcarbinyl cation.

Previously,[3] it was reported that the solvolysis rates of 1-phenylcyclopropylcarbinyl tosylate (3-Ph) were well correlated with log k_{ion} in four solvents. The incorporation of additional solvents in the study, however, yielded data which failed to fit this correlation. The correlation of the solvolysis rates of 3-Ph with those of cholesteryl tosylate follows the same general pattern (*cf*, Figure 2) as that observed for 3-H. The poorer fit for the 3-Ph data can be attributed to the introduction of additional solvation mechanisms by the phenyl group. Interestingly, in all the ionizing solvents, with the exception of acetic acid, the inclusion of the phenyl group has a slight rate-retarding effect.

The failure of 3-H to respond to 1-ring substitution in solvolysis reactions has been explained[4,5] by a transition-state geometry more closely resembling a homoallylic-like ion than a bicyclobutonium-like ion. Support for this explanation is based on the study of both substituent-[4] and leaving-group[5] effects. The kinetic data given in Table II reveal that *p*-nitrophenyl substitution at the 1-ring position has a rate-retarding effect of *ca.* 10^{-1} on the solvolytic reactivity of 3-H. The calculated salt orders also summarized in Table II are of the right magnitude[21] for an SN1-type reaction.

The products of acetolysis of 3-NPh and 3-Ar (1-*p*-anisylcyclopropylcarbinyl tosylate) are 1-*p*-nitrophenylcyclobutyl and 1-*p*-anisylcyclobutyl acetate, respectively. In order to establish that the initial products of acetolysis are rearranged cyclobutyl esters, the stabilities of 1-*p*-anisylcyclopropylcarbinyl and 1-*p*-nitrophenylcyclopropylcarbinyl acetate were determined in buffered acetic acid containing *p*-toluenesulfonic acid. Both cyclopropylcarbinyl esters were stable in the reaction medium for at least 10 half-lives.

The fact that both *p*-anisyl[4] and *p*-nitrophenyl substitution at the 1-ring position has only a small effect on the solvolytic reactivity of 3-H is inconsistent with a solvolysis transition state with significant charge development at the methinyl carbon. Furthermore, from theory[22] and experimental evidence, one would predict both significant rate enhancement by *p*-methoxy substitution and significant rate retardation by *p*-nitro substitution on a phenyl ring, assisting in the dispersal of positive charge in a solvolysis transition state. For example, the calculated value of k^{OMe}/k^{NO_2}, the ratio of acetolysis of the *p*-methoxy-substituted compound to that of the *p*-nitro-substituted compound, is 25,000 for neophyl brosylate[23] and 440,000 for *exo*-2-benznorbornenyl brosylate.[24,25] The fact that the value of k^{OMe}/k^{NO_2} for 1-phenylcyclopropylcarbinyl tosylate ace-

(21) A. H. Fainberg and S. Winstein, *J. Amer. Chem. Soc.*, **78**, 2763, 2767, 2777, 2780 (1956).
(22) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley & Sons, Inc., New York, N. Y., 1961, Chapter 12.
(23) R. Heck and S. Winstein, *J. Amer. Chem. Soc.*, **79**, 3432 (1957).
(24) H. C. Brown and G. L. Tritle, *ibid.*, **90**, 2689 (1968).
(25) D. V. Braddon, G. A. Wiley, J. Dirham, and S. Winstein, *ibid.*, **90**, 1901 (1968).

tolysis is 39, orders of magnitude less than that of the above, related compounds, is consistent with a homoallylic-like ion transition-state geometry where very little charge is localized at the methinyl carbon and where rearrangement[4] to a cyclobutyl cation is much faster than capture by solvent.

Experimental Section

Melting points were not corrected for stem exposure and were taken on a Mel-Temp apparatus. Infrared spectra were recorded on a Perkin-Elmer Model 21 spectrophotometer; ultraviolet spectra were obtained on a Beckman DK-2A spectrophotometer; and the nmr spectrum was obtained on a Varian HA-100 instrument with tetramethylsilane as internal reference standard. An F & M Model 700 gas chromatograph equipped with a hydrogen-flame detector and a 6 ft × 0.125 in. column of 10% Carbowax 20M on Chromosorb W was used for analytical gc work. All microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

Cyclopropylcarbinol was prepared in 84% yield by lithium aluminum hydride reduction of cyclopropanecarboxylic acid, bp 125° (760 mm) [lit.[15] bp 126° (760 mm)].

1-Phenylcyclopropylcarbinol was prepared in 87% yield by lithium aluminum hydride reduction of 1-phenylcyclopropanecarbonyl chloride, mp 32–33° (lit.[26] mp 32.5–33°).

Cyclopropylcarbinyl tosylate (3-H) was prepared according to published procedure.[15] The purity, calculated from "infinity" titers in methanolysis reactions, was 95%.

1-Phenylcyclopropylcarbinyl tosylate (3-Ph) was prepared according to established procedure,[26] mp 52° dec (lit.[26] mp 52° dec).

Cholesteryl tosylate was prepared in 85% yield by the usual method,[27] mp 131–132.5° (lit.[27] mp 131.5–132.5°).

Nitration of 1-Phenylcyclopropylcarboxylic Acid.—To a stirred solution of 48 g (0.3 mol) of 1-phenylcyclopropylcarboxylic acid[28] and 75 ml of acetic anhydride at 25° was added a cold solution of 62 g (0.92 mol) of 90% nitric acid and 140 ml (1.48 mol) of acetic anhydride at such a rate that the temperature did not rise above 25°. After stirring for an additional 1 hr at 25°, the mixture was poured into 1400 ml of ice–water and the product was extracted with benzene. The benzene extract was dried (Na_2SO_4) and concentrated, and the residue was allowed to solidify upon a watch glass to yield 50 g of crude, nitrated product. Gc analysis of a 1-g portion (converted into methyl ester by treatment with diazomethane) revealed the presence of two major and one minor bands, all with longer retention times than that for methyl 1-phenylcyclopropylcarboxylate.

Methyl 1-*p*-Nitrophenylcyclopropylcarboxylate (1).—The above mixture of nitrated acids (49 g) was converted into the corresponding methyl esters by treatment with diazomethane (*ca.* 0.8 mol) in ether. Distillation through a 20 × 1.5 cm glass helix packed column, monitored by gc, yielded 10 g of the pure *para* ester 1, mp 86–87°.

Anal. Calcd for $C_{11}H_{11}NO_4$: C, 59.72; H, 5.01; N, 6.33. Found: C, 59.64; H, 5.09; N, 6.31.

That the isomer with the longer gc retention time and higher melting point is the para compound is confirmed by the absorption maximum at 280 mμ characteristic of *p*-nitrophenylcyclopropane.[29] Additional definitive evidence for the assigned structure is provided by the nmr spectrum of 2.

1-*p*-Nitrophenylcyclopropylcarboxylic Acid (2).—Methyl 1-*p*-nitrophenylcyclopropylcarboxylate (5.5 g) dissolved in 100 ml of 85% (v/v) aqueous ethanol (0.3 *N* in NaOH) was maintained at 45° for 3 hr and then poured into 250 ml of ice water, filtered (no detectable quantity of precipitate was observed), and acidified with cold, dilute HCl. The precipitated acid was separated and air dried to yield 5.0 g (96%) of 2: mp 192–193.5°; λ_{max}^{EtOH} 280 mμ (ε 7900); nmr δ 1.16, 1.90 (complex multiplets, 4, cyclopropyl), 7.53 (d, 2, J = 8 Hz, aromatic), and 8.04 (d, 2, J = 8 Hz, aromatic).

Anal. Calcd for $C_{10}H_9NO_4$: C, 57.97; H, 4.38; N, 6.76. Found: C, 58.04; H, 4.45; N, 6.60.

1-*p*-Nitrophenylcyclopropylcarbinol (3).—A solution of borane in tetrahydrofuran (23 ml, 0.5 *M*) was added in 10 min to 4.8 g of 2. The addition was accompanied by the vigorous evolution of a gas. After 30 min at room temperature, the mixture was poured into 250 ml of ice and extracted with ether. The combined extracts were washed once with 1.0 *N* aqueous NaOH and twice with cold water and dried (Na_2SO_4), and after air evaporation of solvent yielded 3.9 g (87%) of crude alcohol, mp 52–54°. Two recrystallizations from petroleum ether (bp 30–60°)–benzene gave the analytical sample of alcohol 3: mp 55–56°; ir (Nujol) 3300 (OH) and 1023 cm^{-1} (primary alcohol CO).

Anal. Calcd for $C_{10}H_{11}NO_3$: C, 62.17; H, 5.74; N, 7.25. Found: C, 62.25; H, 5.82; N, 7.14.

1-*p*-Nitrophenylcyclopropylcarbinyl *p*-Toluenesulfonate (3-NPh).—The tosylate ester was prepared by reaction of 7.5 mol of the alcohol 3 in 7 ml of pyridine with 9 mmol of tosyl chloride at 0° over a period of 2 hr. After the usual work-up and recrystallization from petroleum ether–benzene, 2.0 g (77%) of the tosylate 3-NPh was obtained, mp 69° dec. The sample was stable at room temperature for longer than 2 weeks.

Anal. Calcd for $C_{17}H_{17}NO_5S$: C, 58.83; H, 4.93; N, 4.03; S, 9.23. Found: C, 59.10; H, 4.99; N, 3.85; S, 9.44.

Solvolysis of 1-*p*-Anisylcyclopropylcarbinyl Tosylate (3-An).—The tosylate 3-An (5 mmol) was solvolyzed in 25 ml of acetic acid (containing 6 mmol of sodium acetate) at 25° for 10 half-lives. The mixture was poured into 200 ml of ice–water and extracted with ether. The combined extracts were washed with saturated $NaHCO_3$ until neutral, dried over Na_2SO_4, and filtered, and the solvent was removed by rotovaporization. Analysis of the residue by gc revealed a single product peak with a retention time different from that of 1-*p*-anisylcyclopropylcarbinyl acetate (the sample was unstable and upon distillation or prolonged standing set to a tacky, polymeric substance). Analysis by infrared revealed a strong band at 1728 cm^{-1} (ester carbonyl) and a medium-intensity band at 945 cm^{-1}. The sample was transparent in the 990–960-cm^{-1} region.[30]

1-Phenylcyclobutyl acetate, as well as the acetolysis products of 3-NPh and 3-An, absorbs at 945 cm^{-1} and is transparent in the 990–960-cm^{-1} region.

Solvolysis of 1-*p*-Nitrophenylcyclopropylcarbinyl Tosylate (3-NPh).—The tosylate 3-NPh (5 mmol) was solvolyzed in 25 ml of acetic acid (containing 6 mmol of sodium acetate) at 35° for 10 half-lives. Work up as above and analysis by gc and infrared revealed that 1-*p*-nitrophenylcyclobutyl acetate was the exclusive product (99%).

Solvents.—The aqueous acetone solvents were prepared from conductivity water and acetone purified by distillation from potassium permanganate. Absolute methanol was prepared by distillation from magnesium turnings, and purified *n*-propyl alcohol was obtained by distillation from aluminum foil and mercuric chloride. Absolute ethanol and dioxane were prepared according to the methods of Fieser.[31]

Kinetic experiments were carried out as previously described.[3,10]

Registry No.—1, 23348-98-3; 2, 23348-99-4; 3, 23349-00-0; 3-H, 1015-45-8; 3-Ph, 1034-83-9; 3-NPh, 23349-01-1; 3-*p*-anisyl, 16728-04-4; cholesteryl tosylate, 1182-65-6.

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(26) J. W. Wilt and D. D. Roberts, *J. Org. Chem.*, **27**, 3430 (1962).

(27) E. S. Wallis, E. Fernholz, and F. T. Gephart, *J. Amer. Chem. Soc.*, **59**, 137 (1937).

(28) A. W. Weston, *ibid.*, **68**, 2345 (1946).

(29) R. Ketcham, R. Cavestri, and D. Jambotkar, *J. Org. Chem.*, **28**, 2139 (1963).

(30) 1-Phenyl-, 1-*p*-anisyl-, and 1-*p*-nitrophenylcyclopropylcarbinyl acetate absorb in the infrared at 975 cm^{-1} and are transparent in the 960–930-cm^{-1} region.

(31) L. F. Fieser, "Experiments in Organic Chemistry," 3rd ed, D. C. Heath and Co., Boston, Mass., 1957, p 285.