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Small-Ring Compounds. XLI. The Formolysis of Allylcarbinyl Tosylate[1]

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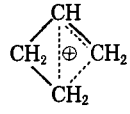
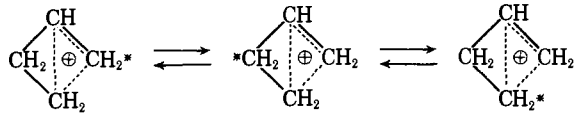
Allylcarbinyl tosylate was found to solvolyze in 98% formic acid 3.7 times faster than *n*-butyl tosylate. Changes in the rate ratio with nucleophilicity of the solvent suggests different mechanisms for these solvolyses. The formolysis products of allylcarbinyl tosylate were found to be virtually identical with those from cyclobutyl tosylate. Deuterium-labeling experiments indicated complete scrambling of the methylene groups in the ring-closed products. The results are interpreted in terms of formation of bicyclobutonium ion intermediates.

The products and rates of solvolytic reactions of cyclopropylcarbinyl and cyclobutyl compounds have been interpreted in terms of intermediate formation of bicyclobutonium ions, I.[2] Isotopic labeling experi-



I

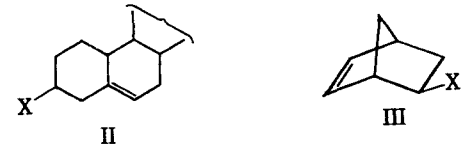
ments have shown that extensive shuffling of methylene carbons occurs in the deamination of cyclopropylcarbinyl-[2] and allylcarbinylamines,[3] reactions of thionyl chloride with cyclopropylcarbinol and cyclobutanol,[4] and in the reaction of cyclopropylcarbinol with Lucas reagent.[2] To account for these rearrangements, the three possible methylene-labeled bicyclobutonium ions (Ia–c) are considered to interconvert readily, thereby shuffling ^{14}C- or deuterium-labeled methylene groups between the 2-, 3-, and 4-positions. Each of these is believed to be able to react with nucleophilic reagents to



Ia Ib Ic

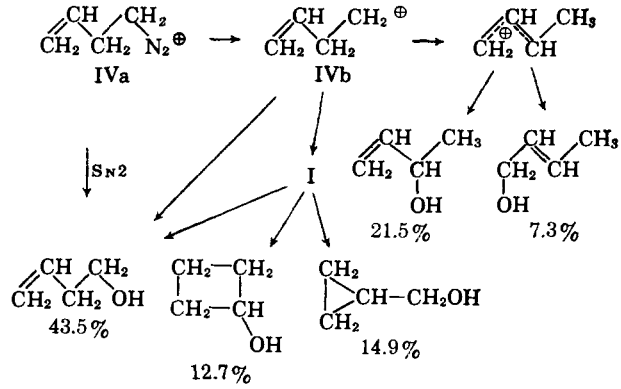
give the same proportions of cyclopropylcarbinyl, cyclobutyl, and allylcarbinyl derivatives with, of course, the possibility of the label winding up in different positions depending on whether or not the product arises from Ia, Ib, or Ic. To explain the observed C^{14} results it is necessary to assume that equilibration between Ia–c is rapid, but not instantaneous, compared to the rate of reaction with solvent.

Theoretically, cations of structure I could also arise from solvolytic reactions of allylcarbinyl compounds. Studies of the stereochemistry and the kinetics of the solvolyses of cholesteryl, II,[5] and dehydronorbornyl, III,[6] systems indicated an important interaction between a carbonium ion and a β-vinyl substituent. Nonetheless, previous investigations of the solvolyses of allylcarbinyl chloride,[2] benzenesulfonate,[7] and β-naphthalenesulfonate[8] afforded no evidence for bicyclobutonium ion intermediates even though such intermediates can very reasonably be invoked to account for the products from the nitrous acid deamination of allylcarbinylamine.[3] However, deamination of amines has the disadvantage that comparative kinetic data cannot be obtained and "hot" carbonium ions may be produced.[9] The products (Chart I) from the deamination of allylcarbinylamine are not those expected if all of the reaction is occurring through the bicyclobutonium species—the methylallyl alcohols presumably arising from hydride shifts occurring in competition with bicyclobutonium ion formation in the decay of the initial "hot" allylcarbinyl cation, IVb. Further complication is provided by the fact that at least part of the allylcarbinyl derivatives formed may arise from an SN2-like substitution on the diazonium ion, IVa.[10]



II III

CHART I



If previous formulations of the energetics of the reactions of allylcarbinyl derivatives are correct, SN1-type solvolysis of an allylcarbinyl compound would be expected to exhibit a small but measurable rate enhancement and give product ratios characteristic of bicyclobutonium ion intermediates. To check on these predictions, the products and the kinetics of the

(1) Supported in part by the National Science Foundation and the Office of Naval Research.

(2) R. H. Mazur, W. N. White, D. A. Semenow, C. C. Lee, M. S. Silver, and J. D. Roberts, *J. Am. Chem. Soc.*, **81**, 4390 (1959).

(3) E. Renk and J. D. Roberts, *ibid.*, **83**, 878 (1961).

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

(5) S. Winstein and R. Adams, *J. Am. Chem. Soc.*, **70**, 838 (1948).

(6) S. Winstein, H. M. Walborsky, and K. Schreiber, *ibid.*, **72**, 5795 (1950).

(7) C. G. Bergstrom and S. Siegel, *ibid.*, **74**, 145 (1952).

(8) M. Hanack and K. Görler, *Chem. Ber.*, **96**, 2121 (1963).

(9) See, for example, J. D. Roberts, C. C. Lee, and W. H. Saunders, Jr., *J. Am. Chem. Soc.*, **76**, 4501 (1954); A. Streitwieser, Jr., *J. Org. Chem.*, **22**, 861 (1957); D. J. Cram and J. E. McCarty, *J. Am. Chem. Soc.*, **79**, 2866 (1957); B. M. Benjamin, H. J. Schaeffer, and C. J. Collins, *ibid.*, **79**, 6160 (1957).

(10) J. A. Berson and A. Remanick, *ibid.*, **86**, 1749 (1964).

formolysis of allylcarbinyl tosylate have been investigated.

Results

Solvolysis Rates.—The rate of solvolysis of *n*-butyl tosylate (V) was determined using nuclear magnetic resonance (n.m.r.) spectroscopy to follow the rate of disappearance of the *p*-methyl resonance of the tosylate ester and the rate of appearance of the *p*-methyl resonance of the free toluenesulfonic acid. At time t the fraction solvolyzed C was calculated from $C = y/(x + y)$ where x = intensity of methyl resonance of the tosylate ester at time t and y = intensity of methyl resonance of toluenesulfonic acid at time t. The rate of solvolysis was then calculated from the plot of log $(1-C)$ *vs.* time.

The rate of solvolysis of allylcarbinyl tosylate (VI) was also determined using n.m.r. spectroscopy. Here the proton resonance of the *p*-methyl of the tosylate ester was found to overlap the resonance of the β-protons of the allylcarbinyl group. For this compound, the rate of disappearance of the resonance of the α-protons of the tosylate ester was measured using diglyme as an internal n.m.r. standard. The diglyme concentration was approximately 0.1 that of the tosylate ester. At time t the fraction solvolyzed C was calculated from $C = 1-(xs_0/x_0s)$ where x_0 = intensity of the central peak of the resonance of the α-protons of the tosylate at time t_0, s_0 = intensity of the methylene resonance of the internal standard at time t_0, x = intensity of the central peak of the resonance of the α-protons of the tosylate at time t, and s = intensity of the methylene resonance of the internal standard at time t. Again the rate of solvolysis was calculated from a plot of log $(1-C)$ *vs.* time.

The results are summarized in Table I. Each rate constant is the average of three separate determinations. At 50°, in 80% formic acid, the rate ratio k_1^{VI}/k^{V} is 1.3, while in 98% formic acid the ratio is 3.7.

TABLE I

RATES OF FORMOLYSIS OF ALLYLCARBINYL TOSYLATE AND *n*-BUTYL TOSYLATE

Compound, tosylate	Formic acid in solvent, %	Temp., °C.	$k_1 \times 10^6$, sec.$^{-1}$
n-Butyl	80	79.1	36
	80	51.6	2.1
	98	50.3	0.84
Allylcarbinyl	80	79.1	60
	80	51.6	2.8
	98	50.3	3.1

Product Studies.—A detailed analysis of the n.m.r. spectra of the samples used in the rate studies showed that, in 98% formic acid, the products after many half-lives were allylcarbinyl and cyclobutyl formates, while the product after several months was a single component assigned the structure of 1,3-diformoxybutane on the basis of its n.m.r. spectrum in formic acid (sextet at 4.8, triplet at 3.9, quartet at 1.7, and doublet at 1.0 p.p.m., with areas of 1:2:2:3, respectively). This compound undoubtedly arises from an acid-catalyzed addition of formic acid to allylcarbinyl formate.

The stabilities of cyclopropylcarbinol, cyclobutanol, and allylcarbinol were determined in 98% formic acid containing added *p*-toluenesulfonic acid. Cyclopropylcarbinyl formate was found to rearrange to cyclobutyl formate (with added *p*-toluenesulfonic acid, the rate of rearrangement is estimated to be about the same as the rate of solvolysis of VI). Cyclobutyl formate is stable in formic acid (with added *p*-toluenesulfonic acid, the rate of rearrangement is less than 0.1 the rate of solvolysis of VI). Allylcarbinyl formate is also stable in formic acid. In formic acid containing 10% sodium formate, cyclopropylcarbinyl formate rearranges to cyclobutyl formate at about 0.1 the rate of solvolysis of VI.

Allylcarbinyl tosylate was also solvolyzed in various mixtures of formic acid and sodium formate. The formate esters were hydrolyzed in dilute sodium hydroxide. The resultant alcohols were analyzed by vapor-phase chromatography on a 1,2,3-tris(2-cyanoethoxy)-propane (TCEP) column. The results are summarized in Table II.

TABLE II

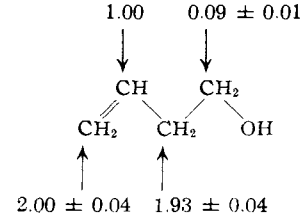
FORMOLYSIS PRODUCTS OF ALLYLCARBINYL TOSYLATE AND CYCLOBUTYL TOSYLATE[a]

Compound, tosylate	% $NaCHO_2$[b]	Time, days	Products[c] Cyclopropylcarbinol	Cyclobutanol	Allylcarbinol	Ratio, ▷-CH_2OH / □-OH
Allylcarbinyl	20	18	12.3	13.4	74.3	0.92
	15[d]	21	14.4	32.0	53.6	.45
	10	18	23.1	37.2	39.7	.62
	5[d]	21	3.3	70.2	26.5	.05
Cyclobutyl	20[d]	21	41.7	52.1	6.2	.80
	15[d]	21	29.8	60.8	9.4	.48
	10	10	42.5	52.5	5.2	.81
	5[d]	21	3.7	90.2	6.1	.04

[a] Analyzed by v.p.c. using a 20-ft. TCEP column. [b] Weight per cent in 98% formic acid. [c] All analyses ±1%. [d] These experiments were run concurrently under identical conditions.

To provide a comparison for the product ratio expected from the bicyclobutonium intermediate in formic acid, the products from the solvolysis of cyclobutyl tosylate in various formic acid–sodium formate mixtures were determined by the method described above. These results are included in Table II.

The labeled compounds, 1,1-dideuterio-3-butenyl tosylate (VII), was prepared from 1,1-dideuterio-3-butenol obtained by reduction of methyl 3-butenoate with lithium aluminum deuteride. Analysis of the tosylate by n.m.r. indicated greater than 99% isotopic purity. The labeled tosylate was solvolyzed (to ~95% completion) in formic acid containing 10% sodium formate. The formate esters were hydrolyzed with dilute sodium hydroxide. The alcohols were isolated by continuous ether extraction and separated by preparative v.p.c. The material recovery was estimated to be greater than 80%. The 60 M.c.p.s. n.m.r. spectrum of the resultant allylcarbinol is shown in Fig. 1. The integrated areas of the proton resonances were determined by averaging thirty separate integrations using a digital voltmeter for integral measurements. These gave, after normalization, the following proton distribution.



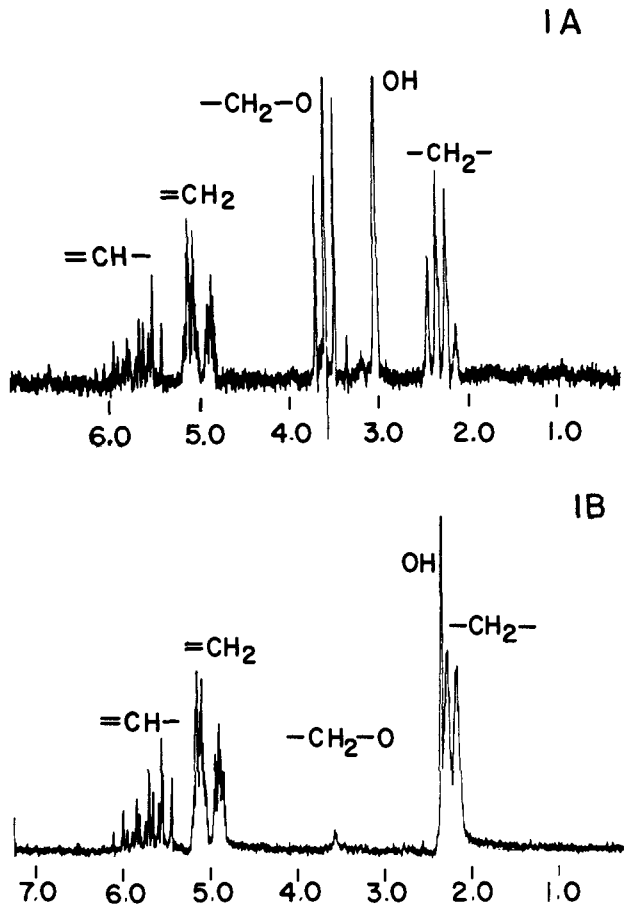


Fig. 1.—A, the 60-Mc.p.s. nuclear magnetic resonance spectrum of allylcarbinol; B, the 60-Mc.p.s. nuclear magnetic resonance spectrum of allylcarbinol-d_2 from the formolysis of 1,1-dideuterio-3-butenyl tosylate. All spectra were run in deuteriochloroform solvent.

The 60-Mc.p.s. n.m.r. spectrum of the recovered mixture of cyclopropylcarbinol and cyclobutanol from the formolysis of 1,1-dideuterio-3-butenyl tosylate is shown in Fig. 2. The integrated areas of the proton resonances were determined by averaging ten separate integrations using a digital voltmeter. For the cyclopropylcarbinol, the ratio of the α-methylene protons to the β-ring protons was found to be 1.00 to 2.00. For the cyclobutanol, one cannot clearly distinguish the resonances for the 2- and 3-positions of the ring, but the general appearance of the spectrum suggests that the deuterium label is statistically distributed between the methylene groups.

Discussion

If the double bond does not participate anchimerically in the ionization of allylcarbinyl tosylate, one would predict from a comparison of the acidities of the corresponding acids that the allylcarbinyl compound would solvolyze slower than the saturated analog by about a factor of 2. If both reactions actually correspond to bimolecular displacement of the tosylate group by a solvent molecule, the rates should show the same sensitivity to an increase in the nucleophilicity of the solvent. However, if the two compounds do not solvolyze by the same mechanism, their solvolysis rates should not respond identically to an increase in the nucleophilicity of the solvent. The argument here is

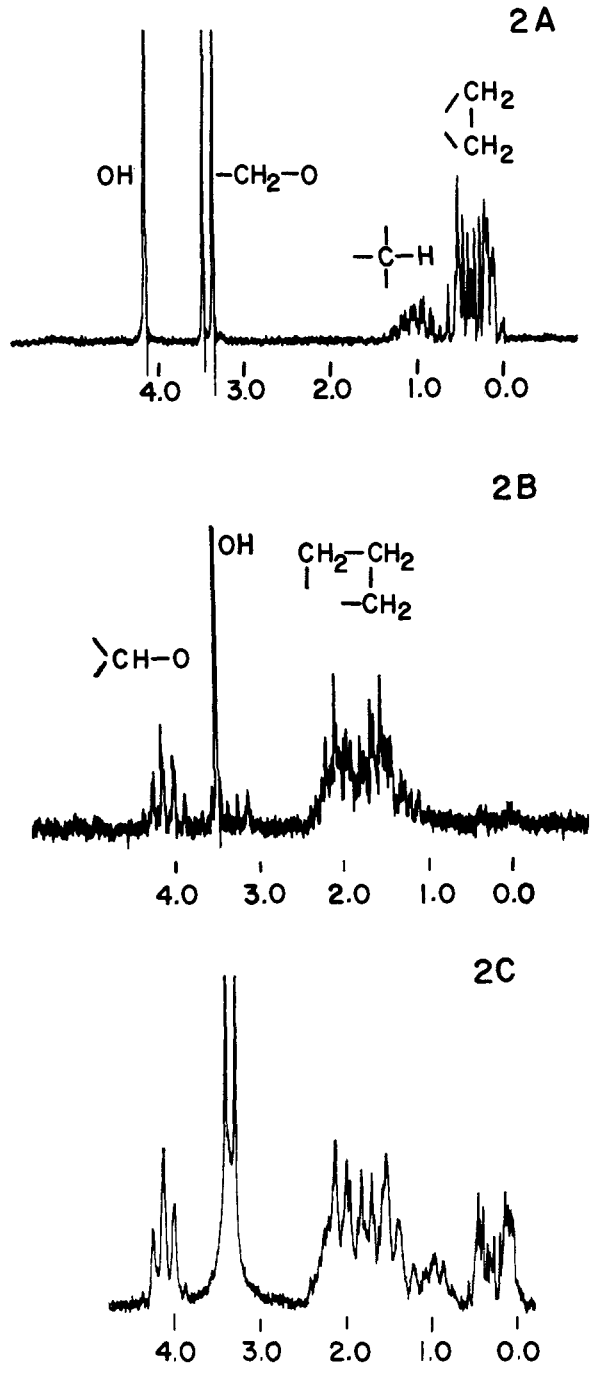


Fig. 2.—A, the 60-Mc.p.s. nuclear magnetic resonance spectrum of cyclopropylcarbinol; B, the 60-Mc.p.s. nuclear magnetic resonance spectrum of cyclobutanol; C, the 60-Mc.p.s. nuclear magnetic resonance spectrum of the mixture of cyclopropylcarbinol-d_2 and cyclobutanol-d_2 from the formolysis of 1,1-dideuterio-3-butenyl tosylate. All spectra were run in deuteriochloroform solvent.

the one used by Bartlett and Bank[11] with respect to anchimeric assistance in the formolysis of β-cyclopentenylethyl tosylate and its saturated analog.

In 98% formic acid, allylcarbinyl tosylate solvolyzes faster than *n*-butyl tosylate by a factor of 3.7; however, in 80% formic acid, the rate ratio decreases to 1.3. The relative insensitivity of the rate of solvolysis of allylcarbinyl tosylate to the change in the nucleophilicity of the solvent suggests that it is solvolyzing by an

(11) S. Bank and P. D. Bartlett, *J. Am. Chem. Soc.*, **83**, 2591 (1961).

SN1 mechanism. Both the corrected rate ratio $k^{VI}/k^{V} = 7.5$ and the difference in sensitivity of the rates to solvent changes suggests (but, of course, does not unequivocally prove) that allylcarbinyl tosylate is solvolyzing by a different mechanism from its saturated analog.

The products from the solvolysis of allylcarbinyl tosylate are not all stable in 98% formic acid. In the presence of sodium formate, the products are more stable but then a competitive SN2 reaction of the tosylate with formate occurs, as evidenced by the increasing percentage of allylcarbinyl products with increasing formate concentration. By extrapolation to zero concentration of sodium formate, it is predicted that approximately 10% of the products would have the allylcarbinyl structure under these conditions if the products were completely stable. The ratios of cyclopropylcarbinyl to cyclobutyl formate produced are essentially the same for the solvolysis of allylcarbinyl tosylate and cyclobutyl tosylate under comparable conditions. At high sodium formate concentration, the ratio of cyclopropylcarbinyl to cyclobutyl products is ~1.0. Since this ratio should be insensitive to sodium formate concentration, we can expect the initial product composition in 98% formic acid to be 45 ± 5% cyclopropylcarbinyl, 45 ± 5% cyclobutyl, and 10 ± 5% allylcarbinyl formates. This is in good agreement with the product mixtures usually obtained in carbonium-ion reactions of cyclopropylcarbinyl and cyclobutyl compounds. Thus, the reactions of cyclopropylcarbinylamine and cyclobutylamine with nitrous acid, the solvolysis of cyclopropylcarbinyl, cyclobutyl, and allylcarbinyl derivatives,[12,13] the reactions of cyclopropylcarbinol and cyclobutanol with thionyl chloride, and cyclopropylcarbinol with hydrogen bromide or phosphorus tribromide[14] all give mixtures having closely similar relative amounts of products with the cyclopropylcarbinyl, cyclobutyl, and allylcarbinyl structures.

In contrast to allylcarbinylamine deaminations[3] (Chart I), no methylallyl alcohols are obtained in the solvolysis of allylcarbinyl tosylate. The occurrence of these allyl alcohols in deamination implies that the initial carbonium ions from these two different reactions are not identical. The initial carbonium ion from the amine deamination is probably a highly energetic, lightly solvated, classical allylcarbinyl cation. This carbonium ion can be deactivated by collisions to yield the bicyclobutonium ion; or it can undergo a hydride shift to produce a methylallyl cation. In solvolysis, double-bond participation produces the bicyclobutonium ion without competing hydride shifts. The methylallyl alcohols from the amine deamination are thus abnormal products arising from a "cascade effect" for the hot carbonium ion produced in the decomposition of the diazonium ion.

The studies of the products from the solvolysis of labeled allylcarbinyl tosylate provide additional support for entrance into the equilibrating bicyclobutonium ion system from the allylcarbinyl side. As predicted from other results,[3] the isotopic label is essentially statistically distributed between the methylene groups for both the cyclopropylcarbinyl and cyclobutyl products. The large percentage of allylcarbinyl products in SN2 displacement under the conditions of the study makes determination of the label distribution in the allylcarbinyl products from the SN1 reaction difficult. The difference observed for the distribution of the label in the 2- and 4-positions of the allylcarbinyl product are within experimental error and do not warrant further discussion at this time.

Recently Brown[15] has stated his conviction that there is no evidence for nonclassical cations in the carbonium-ion type reactions of cyclopropylcarbinyl derivatives. Arguments for such intermediates based on solvolytic rate enhancements for cyclopropylcarbinyl halides and *p*-toluenesulfonates are dismissed by him on the grounds that solvolysis of some cyclopropylcarbinyl derivatives give no rearranged products but still show enhanced rates. Formation of rearranged products is not a *necessary* consequence of the intervention of nonclassical cations as intermediates. Indeed, a logical extension of Brown's argument would be to hold that there is no evidence for stabilization of a benzyl cation by the electrons of the aromatic system because only benzylic derivatives are observed as solvolysis products.

The problem of solvolysis rates of cyclopropylcarbinyl derivatives deserves at least a consistent treatment. On the one hand, the enhanced rates were ascribed[15] to relief of strain in the transition states for formation of intermediates with unspecified but "classical" structure, and on the other, to some vague steric or electronic effect of a cyclopropyl ring operating so as to retard borohydride reductions of ketones.

It is our view that there can be no relief of strain in any *classical sense* in the ionization of a cyclopropylcarbinyl derivative to give a classical cyclopropylcarbinyl cation. However, relief of strain could well be associated with the delocalization of the bonding electrons of the cyclopropane ring to the developing cationic center as $X^{\ominus}$ leaves from $(CH_2)_2CHCH_2X$. However, any intermediate which takes advantage of such delocalization has the structural features which are normally regarded as conferring nonclassical character. If the enhanced rates result from such electron delocalization, it would obviously be partly an electronic and partly a steric effect because the ring atoms move farther apart. Possible balances between these effects have been discussed in detail.[16] It would be quite wrong to maintain that because steric effects are involved at all the intermediates formed must be classical in nature. Furthermore, it is most unlikely that any reasonable steric effect could account for very much of the rate enhancement. Cyclopropylcarbinyl chloride is about 1/15 as reactive as *t*-butyl chloride in SN1 reactions and can therefore be estimated to be about $10^{10}/15 \approx 10^{9}$ times more reactive in forming a carbonium ion than a primary chloride.[17] Such a rate difference corresponds to a difference in activation energy on the order of 11 kcal.— an amount substantially more than the *maximum* of 7 kcal. of angle-strain relief which a cyclopropylcarbinyl derivative would experience in forming a transition state for carbonium ion formation even if *com-*

(12) J. D. Roberts and R. Mazur, *J. Am. Chem. Soc.*, **73**, 2509 (1951).
(13) J. D. Roberts and V. C. Chambers, *ibid.*, **73**, 5034 (1951).
(14) E. F. Cox, M. C. Caserio, M. S. Silver, and J. D. Roberts, *ibid.*, **83**, 2719 (1961).
(15) H. C. Brown, "The Transition State," Special Publication No. 16, The Chemical Society, London, 1962, p. 155.
(16) M. E. H. Howden and J. D. Roberts, *Tetrahedron*, **19**, Suppl. 2, 403 (1963).
(17) S. Winstein and J. H. Marshall, *J. Am. Chem. Soc.*, **74**, 1120 (1952).

plete relief of strain were to occur corresponding to production of an allylcarbinyl cation.[18]

The answer to the question of whether or not rate enhancements are present in the solvolysis of cyclobutyl chloride and aromatic sulfonates depends to a degree on the choice of model compounds. If one compares cyclobutyl derivatives with the corresponding cyclopentyl derivatives, the rates are the same to within a factor of 10 and one might conclude that there is nothing abnormal about the rates of solvolysis of cyclobutyl compounds. Such a conclusion ignores both the predicted increase in angle strain (*I*-strain) in the transition state for carbonium ion formation from the cyclobutyl compound and the relief of eclipsing strain in the solvolysis of cyclopentyl derivatives (also called *I*-strain) which has been evoked to account for their enhanced reactivity relative to cyclohexyl derivatives. If the solvolysis of cyclopentyl compounds is actually accelerated and the solvolysis of cyclobutyl compounds is expected to be decelerated by steric factors, then the fact that cyclobutyl derivatives are at least as reactive as cyclopentyl derivatives speaks for a considerable degree of rate enhancement in the four-ring series. We believe this enhancement occurs because the transition state has bicyclobutonium character.

It has been reported that different product distributions are found in the methanolysis of cyclopropylcarbinyl and cyclobutyl β-naphthalenesulfonates and therefore that different intermediates are involved.[19] However, the high proportion of cyclopropylcarbinyl products from the methanolysis of cyclopropylcarbinyl β-naphthalenesulfonate is also consistent with a competing SN2 displacement of the β-naphthalenesulfonate group by methanol.

Although equilibrating classical cations could conceivably account for the rearrangements encountered in carbonium-ion-type reactions of cyclopropylcarbinyl, cyclobutyl, and allylcarbinyl derivatives, such a formularion is hardly consistent with the product ratios observed in these reactions. The allylcarbinyl cation would be expected on the basis of strain to be ~7 kcal. more stable than classical cyclopropylcarbinyl cation and, since the product ratio should approximately reflect their relative stabilities, one would therefore expect to observe almost exclusively allylcarbinyl products. However, cyclopropylcarbinyl and cyclobutyl products are invariably found to predominate under conditions of kinetic control.

Experimental

Allylcarbinyl Tosylate.—3-Butenonitrile (47.3 g.) was hydrolyzed to 3-butenoic acid with concentrated hydrochloric acid.[20] There was obtained 39.2 g. of product, b.p. 68–70° (13 mm.). Lithium aluminum hydride reduction of 27.8 g. of 3-butenoic acid gave 11.9 g. of allylcarbinol, b.p. 110–113°.[2] The reaction of 2.0 g. of allylcarbinol with 7.0 g. of *p*-toluenesulfonyl chloride in collidine gave 5 g. of allylcarbinyl tosylate, b.p. 150° (~6 mm.).

***n*-Butyl Tosylate.**—*n*-Butyl tosylate, b.p. 135° (~2.5 mm.),[21] was prepared from *n*-butyl alcohol.[20]

Cyclobutyl Tosylate.—Cyclobutanol (10.0 g.) was esterified with *p*-toluenesulfonyl chloride to give 12.4 g. of cyclobutyl tosylate,[22] m.p. 23°.

1,1-Dideuterio-3-butenyl Tosylate.—To 10.0 g. of 3-butenoic acid in diethyl ether was added 4.8 g. of diazomethane in diethyl ether. The solvent was removed and the product distilled to give 9.6 g. of methyl 3-butenoate, b.p. 103–105° (745 mm.). To 2.0 g. of lithium aluminum deuteride in 70 ml. of ether was added a solution of 9.6 g. of methyl 3-butenoate in 20 ml. of ether over a 1-hr. period. The mixture was hydrolyzed with saturated ammonium chloride solution and extracted three times with ether. The combined ether extracts were dried over sodium sulfate. The ether was removed through a 20-cm. Vigreux column and the product distilled through a 30-cm. Holzman column to give 3.6 g. of α,α-dideuterioallylcarbinol, b.p. 110–113°. The n.m.r. spectrum of the product was as expected for 1,1-dideuterio-3-buten-1-ol. The reaction of 3.5 g. of 1,1-dideuterio-3-buten-1-ol with *p*-toluenesulfonyl chloride in collidine gave after distillation 2.6 g. of the tosylate. Integration of the area where the α-protons would fall in the n.m.r. spectrum of the tosylate indicated an isotopic purity of >99%.

Solvolysis Product Studies.—A sample of the tosylate (~0.2 g.) was placed in a Pyrex tube (18 × 150 mm.), and solvent was added; the tube was sealed and placed in a constant temperature bath at 50°. After the specified length of time, the tube was removed from the bath, cooled in Dry Ice, and opened; the contents were poured into a 100-ml. round-bottomed flask. A 20% sodium hydroxide solution was added with cooling until a pH of 8 to 9 was obtained. The mixture was stirred at room temperature for 3 hr. and then continuously extracted with ether for 24 hr. The ether extract was dried over sodium sulfate and the volume reduced to ~5 ml. by removal of the ether through a 20-cm. Vigreux column. The mixtures were analyzed by v.p.c. on a 20-ft. 1,2,3-tris(2-cyanoethoxy)propane column at 120°. The analyses were calibrated by comparison with known mixtures of similar concentrations.

Rate Studies.—Approximately 0.03 g. of the tosylate was placed in a 4.94-mm.-o.d. thin-walled Pyrex tube. Approximately 1 ml. of solvent was added and the tubes were sealed. The sealed tubes were placed in a constant-temperature bath. For each measurement, the tubes were removed from the oil bath and cooled to −10° in an ice–methanol bath. Immediately before measurement, the tubes were removed from the ice–methanol bath and placed in the probe of the Varian A-60 at 37°. Seven to ten spectra were taken of each sample for each measurement. After removal from the probe, the tubes were transferred back to the ice bath and then back to the constant-temperature bath. For each measurement, the tubes were out of the constant-temperature bath for 20 min. and were in the probe for 5 min.

(18) J. W. Linnett, *J. Chem. Phys.*, **6**, 692 (1938).

(19) H. C. Brown, unpublished results presented at a seminar at the California Institute of Technology, Nov., 1962, and at the Reaction Mechanisms Conference, Brookhaven, N. Y., Sept., 1962.

(20) "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p. 851.

(21) "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 145.

(22) V. C. Chambers, Ph.D. Thesis, Massachusetts Institute of Technology, 1950.