uv spectral determinations and Miss Walia Halim (The University of Alberta) for excellent technical assistance.

Registry No.—ii, 51022-59-4; iii, 51022-60-7; iii hydrochloride, 51096-70-9; **1**, 16667-61-1; **3**, 2627-64-7; **4**, 51014-72-3; **5**, 51014-73-4; **6**, 51014-74-5; **7**, 20535-16-4; **8**, 524-69-6; **9a**, 51014-75-6; **9b**, 51014-76-7; **10**, 40110-98-3.

References and Notes

(1) This work was generously supported by Grant No. A5890 from the National Research Council of Canada and The University of Alberta.
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(3) University of Alberta Postdoctoral Fellow, 1969–1971. Present address: Fachbereich Chemie der Universität Konstanz, D-7750 Konstanz, Postfach 733, West Germany.
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(20) In these papers, the compounds are named as 4-aminoimidazole-5-carboxamidines (or carboxamides).
(20a) Note Added in Proof. An X-ray crystallographic analysis of this product is in agreement with the assigned structure. The formic acid molecule is associated with the basic amidine function as would be expected. (Dr. M. N. G. James, Department of Biochemistry, private communication.)
(21) (a) Intermediate formation of the corresponding $N^3 \rightarrow 2'$-arabinocyclonucleoside from **3**, which would have been ring opened to give 5-amino-1-(2-deoxy-β-D-arabinofuranosyl)imidazole-4-carboxamide-$N^5 \rightarrow 2'$-cyclonucleoside instead of iii, was suggested by a referee on the basis of inspection of models. This possibility is precluded by the absence of coupling ($J_{1'-2'} < 0.7$ Hz) of the anomeric proton of iii (and ii), which demands a trans 1′,2′-proton geometry (see ref 31, pp 330–331), as well as by the double-irradiation experiments (*i.e.*, triplet and doublet patterns for the 3′ and 2′ protons upon irradiation of the 2′ and 3′ frequencies, respectively) outlined in the Experimental Section. (b) R. Mengel, *et al.*, in preparation.
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A Solvolytic Investigation of Cyclobutylcarbinyl and Related *p*-Bromobenzenesulfonates

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The solvolysis rates of cyclobutylcarbinyl (**4**-OBs), cyclopentylcarbinyl (**5**-OBs), cyclohexylcarbinyl (**6**-OBs), and 1-adamantylcarbinyl (AC-OBs) brosylates have been determined in a series of solvents. The extent of rearrangement of **5**-OBs is sensitive to reaction conditions, including buffer. The kinetic and product distribution data indicate that solvent capture of a carbon-bridged species accounts for 99% of the acetolysis product of **4**-OBs, 91% of **5**-OBs, and 0% of **6**-OBs.

The occurrence of Wagner–Meerwein type rearrangements in solvolysis reactions of cycloalkylcarbinyl derivatives has been well demonstrated.[2] To the extent that the current view of solvolysis reactions[3] is correct, the observation of Wagner–Meerwein type rearrangement products in the solvolysis of cycloalkylcarbinyl arenesulfonates is evidence for neighboring group participation in the ionization step *via* σ-bond delocalization of charge into the cycloalkane ring.

Although the study of the nature of σ-bond participation by the cyclopropane ring in solvolysis reactions has been the subject of considerable experimental and theo-

Table I
First-Order Solvolysis Rates

Brosylate	Registry no.	Solvent	Temp, °C	k_t, 10^5 sec^{-1}	ΔH^*, kcal/mol	ΔS^*, eu
4-OBs	51108-24-8	EtOH[a]	45	1.3		
		AcOH	45	3.4	24.9 ± 0.1[b]	−5.6 ± 0.3[b]
			55	11.7		
			65	35.9		
			75	111		
		CF_3CH_2OH	30	13.3	19.7 ± 0.1	−15.9 ± 0.3
			35	24.4		
			45	70.8		
			55	186.0		
		HCO_2H	35	210	20.3 ± 0.1	−9.6 ± 0.4
			45	630		
			55	1665		
5-OBs	38806-24-5	EtOH	45	0.21		
		AcOH	55	0.42	25.4 ± 0.1	−10.7 ± 0.4
			65	1.36		
			75	4.20		
		CF_3CH_2OH	35	0.64	23.6 ± 0.2	−10.4 ± 0.5
			45	2.22		
			55	7.30		
		HCO_2H	35	9.75	23.1 ± 0.1	−6.5 ± 0.4
			45	34.5		
			55	103.7		
6-OBs	51108-25-9	AcOH	55	0.053	27.8 ± 0.1	−7.2 ± 0.5
			65	0.200		
			75	0.675		
		CF_3CH_2OH	35	0.039	23.6 ± 0.2	−16 ± 0.8
			45	0.131		
			55	0.444		
		HCO_2H	35	0.51	25.3 ± 0.1	−5.3 ± 0.3
			45	1.96		
			55	6.78		
AC-OBs	51108-26-0	EtOH	45	0.0047		
		AcOH	55	0.033	29.6 ± 0.6	−3 ± 2
			65	0.111		
			75	0.488		
			100	7.44		
		CF_3CH_2OH	35	0.25	23.6 ± 0.2	−12.4 ± 0.6
			45	0.89		
			55	2.67		
		HCO_2H	55	24.1	24 ± 0.1	−6 ± 0.3
			75	219		
Neophyl	24517-38-2	CF_3CH_2OH	45[c]	40		

[a] Initial concentration 0.015–0.030 *M*. [b] One standard deviation unit from mean. [c] Average of two runs with standard deviation ±0.1.

retical work,[4] comparatively few such investigations have been carried out to elucidate the nature of σ-bond participation by the cyclobutane ring or the related cyclopentane and cyclohexane rings.

Neighboring group participation involving ring expansion has been postulated for the solvolysis of cyclobutylcarbinyl and cyclopentylcarbinyl derivatives,[5,6] and

$(CH_2)_n CHCH_2OBs$
$n + 1 = 4$, **4-OBs**
$n + 1 = 5$, **5-OBs**
$n + 1 = 6$, **6-OBs**

neighboring group participation by hydrogen has been postulated for the solvolysis of cyclohexylcarbinyl derivatives;[7] however, these studies were either carried out prior to development of current solvolysis reaction theory and/or with little attention given to the nature of the σ-bond participation, particularly in the case of the cyclobutane ring.

For these reasons, we undertook the present investigation of the solvolytic behavior of the following cycloalkylcarbinyl brosylates. This paper reports the analysis of both the reaction kinetics and product distribution data in an effort to gain further insight into the nature of the σ-bond participation by the cycloalkane rings in the ionization process. During the course of this investigation some related points of interest were developed and are included in this report.

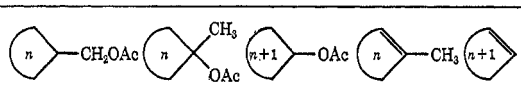
The data indicate that with *urea buffer* solvent capture of a carbon-bridged species accounts for 99% of the acetolysis product of **4-OBs**, 91% of the acetolysis product of **5-OBs**, and 0% of the acetolysis product of **6-OBs**.

The first-order rate constants for solvolysis of the cycloalkylcarbinyl brosylates and related substrates are summarized in Table I. The reaction progress was followed by titrating the liberated *p*-bromobenzenesulfonic acid and the reaction followed strictly first-order kinetic law up to at least 75% conversion furnishing, within experimental error,[8] 100% of the theoretical amount of acid present.

The product distribution data are collected in Table II. The vapor-phase chromatographic separations and characterizations of products were carried out on a Carbowax 20M silver nitrate column. Urea was used as a buffer to avoid an S_N2 displacement reaction by sodium acetate,[9] and the product studies were conducted at the same temperature (75°) as the kinetic investigations. Previously reported[5a,6,7,10a] stability studies have established that the reported products are indeed the initially formed products and not those of subsequent isomerization reactions.[10b]

On the basis[3] that primary solvolysis occurs by two discrete pathways—k_s, solvent assisted which leads to only

Table II
Summary of Product Runs, Acetolysis at 75° [a]



Brosylate	n[b]	A	B	C	D	E
4-OBs[c]	4	1		99[h]		
5-OBs	5	4.5	2.7	90.8[i]	0.8	1.2
6-OBs	6	47.5[f]	12.5[g]		40.0[i]	
c-C_5H_9OBs[e]	5[d]			80		20[k]

[a] Initial ester concentration 0.20 *M*; initial urea concentration 0.30 *M*. [b] The initial ring size of the cycloalkyl group. [c] The average of three runs. [d] Cyclopentyl brosylate. [e] Registry no.: 4596-40-1; [f] 937-55-3; [g] 16737-30-7; [h] 933-05-1; [i] 622-45-7; [j] 591-49-1; [k] 110-83-8.

Table III
Per Cent k_s Reaction for the Acetolysis of Selected Substrates at 75°

Substrate	% k_s This study	% k_s Lit. value	Ref
1-Adamantylcarbinyl OBs		0	3c
c-$C_4H_7CH_2OBs$	1[a]	1[b]	5c
c-$C_5H_9CH_2OBs$	4.5[a]	61[c]	7
c-$C_6H_{11}CH_2OBs$	47.5[a]	49[c]	7

[a] Buffered with urea. [b] At 100° without buffer. [c] At 120° with NaOAc.

Table IV
Variation in the *E*/*S* Ratio with Reaction Conditions for Acetolysis of Selected Substrates

Substrate	Temp, °C, buffer	% alkene	% acetate
c-$C_4H_7CH_2OBs$	100, none	nd	100[a]
	75, urea	nd	100[b]
c-C_5H_9OBs	50, KOAc	39	61[c]
	75, urea	20	80[b]
c-$C_5H_9CH_2OBs$	75, urea	2	98[b]
	80, NaOAc	78	23[d]
	80, NaOAc	74	25[e]
	120, NaOAc	11	89[f]
c-$C_6H_{11}OSO_2Ar$[h]	50, KOAc	85	15[c]
	100, NaOAc	81	19
	100, urea	80	20
c-$C_6H_{11}CH_2OBs$	75, urea	40	60[b]
	120, NaOAc	46	54[b]
	115, NaOAc	23	77[g]

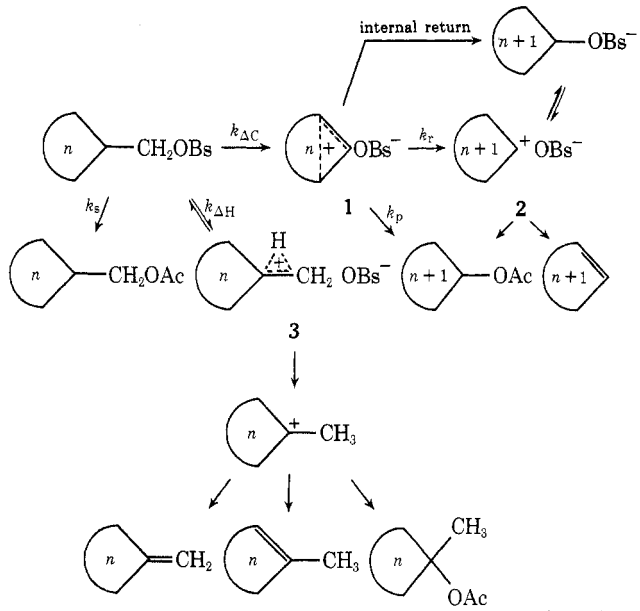
[a] Reference 5c. [b] This work. [b] Tosylate: J. D. Roberts and V. C. Chambers, *J. Amer. Chem. Soc.*, **73**, 5034 (1951). [d] Nasylate, ref 6. [e] Reference 12. [f] Tosylate, ref 7. [g] Tosylate: R. Kotani and S. Satoh, *J. Org. Chem.*, **30**, 3245 (1965). [h] Registry no. 953-91-3.

unrearranged products; and k_Δ, neighboring group assisted which leads to only rearranged products[11]—the data in Table III are readily obtained.

Not unexpectedly, the fraction of **5**-OBs solvolyzing *via* the k_s pathway (approximated by the fraction of cyclopentylcarbinyl acetate in the product mixture) is significantly lower than the literature value. Both Bartlett[6] and LeNy[12] reported yields of cyclopentylcarbinyl acetate (5.1 and 9.0%, respectively) substantially in agreement with that found in the present study. This result emphasizes that the extent of rearrangement (and the subsequent dissection of k_t into k_Δ and k_s) is sensitive to reaction conditions and, therefore, care should be taken that the kinetic and product data are obtained under the same reaction conditions.[13]

The data presented in Table IV provide further evidence for product sensitivity to reaction conditions. For

Scheme I



example, in the acetolysis of **5**-OBs the replacement of sodium acetate by urea as a buffer results in a dramatic increase in the yield of substitution product or the elevation of the reaction temperature for 80–120° produces a similar dramatic increase in the substitution product.

Since Bartlett, *et al.*,[9] have shown that urea is as effective as sodium acetate in stabilizing cyclohexene against conversion to cyclohexyl acetate under the reaction conditions, it is unlikely that the increased substitution produce observed with urea is due to an enhanced acid-catalyzed addition of acetic acid to cyclohexene. On the other hand, the increased substitution product observed at higher temperature may be attributed, at least in part, to an enhanced displacement reaction by acetate ion; that is, in the acetolysis of **5**-OBs the rate constant temperature profiles could be favorable for $k_2(AcO^-)$ at elevated temperatures.

Insight concerning this somewhat complicated product distribution picture is provided by Scheme I. A minimum of four product pathways are necessary to accommodate the product data: (1) k_s, a solvent-assisted pathway leading to unrearranged acetate;[14] (2) $k_{\Delta H}$, a neighboring hydrogen assisted pathway leading to non-ring-expanded olefins and tertiary acetates; (3) $k_{\Delta C}{}^1$, a σ-bond participation pathway, leading to bridged intermediate **1** which is attacked by solvent yielding ring-expanded acetates;[17] and (4) $k_{\Delta C}{}^2$, a σ-bond participation pathway leading to classical ion **2** which is attacked by solvent leading to both ring-expanded acetates and olefins. A fifth pathway, $k_{\Delta C}{}^3$, internal return isomerization to a secondary brosylate, has been proposed[6] for the acetolysis of **5**-OBs in the presence of sodium acetate buffer. Although this pathway cannot be ruled out in the present study, it is unfavored for two reasons: (1) the products of acetolysis of cyclohexyl arenesulfonates (see Table IV) are very rich in cyclohexene, just the opposite of that observed for the acetolysis of **5**-OBs, and (2) the acetolysis products of cyclopentyl brosylate (see Table IV) include at least 20% cyclopentene while none was detected in the acetolysis products of **4**-OBs.

Additional insight into the mechanistic details of the $k_{\Delta C}$ pathway proposed for the ring-expanded products observed in the acetolysis of **4**-OBs and **5**-OBs is provided by the relative rate data collected in Table V. The most striking feature of these data is the small effect of the methyl and phenyl substituents upon the acetolysis rates

Table V
Relative Rates of Acetolysis of 1-X-Cycloalkylcarbinyl Brosylates and the Relative Rates of Solvolysis of the Corresponding 1-X-Cycloalkyl Derivatives

Compound	X	Rel rate, 75°	Compound	X	Rel rate
c-$C_4H_6XCH_2OBs$	H	1.0	c-C_5H_8XCl[a]	H	1.0
	CH_3[b]	10		CH_3	1.75×10^5
	Ph[c]	1.9		Ph	6.6×10^8
c-$C_5H_8XCH_2OBs$	H	1	c-$C_6H_{10}XCl$[a]	H	1.0
	CH_3[b]	1		CH_3	3.33×10^4
	Ph[d]	34		Ph[d]	6.3×10^7

[a] H. C. Brown and M.-H. Rei, *J. Amer. Chem. Soc.*, **86**, 5008 (1964), at 25° in EtOH. [b] Reference 16. [c] Registry no.: 50978-05-7; [d] 51108-27-1.

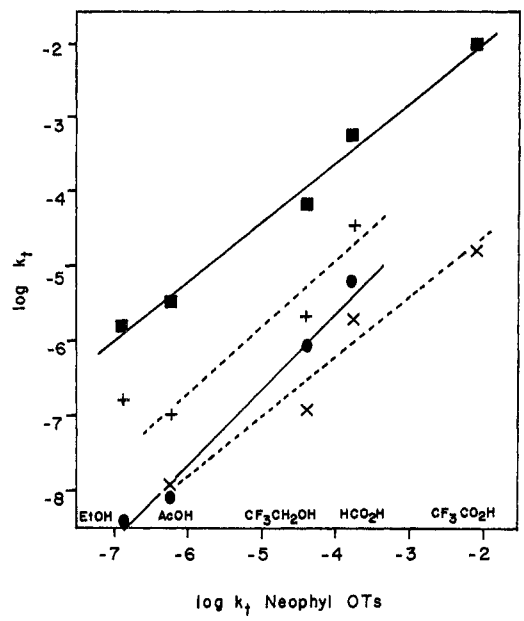


Figure 1. Plot of log k_t for 4-OBs (■), 5-OBs (+), 6-OBs (×), and AC-OBs (●) *vs.* log k_t for neophyl tosylate at 45°.

of 4-OBs and 5-OBs. This result clearly establishes that, in the conversion of 4-OBs or 5-OBs to ring-expanded products, the charge distribution in the transition state has little similarity to **2**, the localized charge species, but instead argues in favor of a delocalized structure similar to **1**.[18] Furthermore, the high yields of ring-expanded substitution products observed in the acetolysis of 4-OBs and 5-OBs (about 99% in each case) suggest[17] that **1**, instead of the rearranged, localized species **2**, is the intermediate attacked by solvent leading to the ring-expanded substitution products.

Such is not the case, of course, in the acetolysis of 6-OBs which does not produce any ring-expanded product. In this case the $k_{\Delta C}$ pathway is noncompetitive with both the k_s and $k_{\Delta H}$ pathways. It is of interest to note that, in the acetolysis of 6-OBs, $k_{\Delta H}$ makes a contribution to k_t approximately equal to that of k_s and therefore precludes the use of this substrate as a model for k_s solvolysis.

Winstein has provided a useful diagnostic test for the presence of a $k_{\Delta C}$ pathway by establishing the linearity of plots of log $k_{\Delta C}$ for *n*-propyl,[20] 2-phenylethyl,[3a] and 1-phenyl-2-propyl[21] tosylates *vs.* log k_t for neophyl tosylate as the solvent is varied.[22] Accordingly, the data for the solvolysis of 4-OBs, 5-OBs, 6-OBs, and AC-OBs were submitted to a similar analysis which produced the curves illustrated in Figure 1. The rate constant for the trifluoroacetolysis of 4-OBs at 45° (1×10^{-2} sec^{-1}) was derived from a log k_t *vs.* *Y* plot of carboxylic acid solvents where the *Y* value for trifluoroacetic acid (4.4), in turn, was derived from a plot of log k_t for neophyl tosylate *vs.* *Y* for carboxylic acids. The rate constant for the trifluoroacetolysis of 6-OBs was taken from the work of Krapcho and Johanson.[7]

Table VI
Some Slope Values for Correlation of Log k_Δ^R (RCH_2OTs) with Log k_t^N (Neophyl Tosylate) as Solvent is Varied

R	Temp, °C	Slope values	Ref
Et	75	0.85	20
$PhCH_2$	75	1.02	3a
t-Bu	75	0.83	20
c-C_4H_9	45	0.82[a]	This work
1-Adamantyl	45	1.02[a]	This work

[a] Brosylate k_Δ is equated with k_t.

The correlation coefficients for linearity of the various curves in Figure 1 are 0.99 (30° of freedom) for 4-OBs, 0.94 (20° of freedom) for 5-OBs, 0.94 (17° of freedom) for 6-OBs, and 0.99 (18° of freedom) for AC-OBs.

The good correlation between log k_t for 4-OBs and log k_t for neophyl tosylate is consistent with the nearly exclusive $k_{\Delta C}$ pathway proposed for the solvolysis of 4-OBs throughout the entire solvent series. It is interesting to note that the correlation coefficient for 4-OBs is identical with the value determined for AC-OBs, a compound that reportedly[3c] solvolyzes *via* an exclusively $k_{\Delta C}$ pathway involving a carbon-bridged intermediate due to steric inhibition of the k_s pathway.

The poor correlation between log k_t for 6-OBs and log k_t for neophyl tosylate is accountable by the significant contribution that k_s makes to k_t for the solvolysis of 6-OBs in solvents of low ionizing strength, while the poor correlation between log k_t for 5-OBs and log k_t for neophyl tosylate is attributed to the enhancement of k_t by k_s for the solvolysis of 5-OBs in the relatively nucleophilic solvent, ethanol.

The slope values for representative log k_Δ^R *vs.* log k_t^N (neophyl tosylate) correlations are listed in Table VI. Interestingly, the magnitude of these slopes varies only slightly from a mean value of 0.91 which reveals the change in log (k_Δ^R/k_t^N) with variable solvent is nearly insensitive to change in neighboring group (H, Me, cyclobutyl, or 1-adamantyl).

It is tempting to speculate that this slope insensitivity to neighboring group effect (δ_R) reflects a similar participation response, $\delta_m(k_\Delta/k_C)^R$, to medium effect (δ_m) by the various neighboring groups.[23] Because there is no suitable model for evaluating the unassisted ionization rates (k_C) of primary substrates, additional slope values will be determined in future studies to assess the validity of the assumption[23] $\delta_m(k_\Delta/k_C)_R/\delta_m(k_\Delta/k_C)^N \sim$ constant.

Another factor inherent in the estimate of extent of participation is the accompanying change in strain energy. For example, release of strain energy in going from starting material to transition state complex is expected[12,5c,24] to accompany σ-bond participation by the cyclobutane

ring. However, its magnitude is small compared to the change expected in going from starting material to the ring-expanded product,[25] and, more significantly, there appears to be a linear relationship[24b] between ring strain changes (either relief or increase) and extent of participation in solvolysis reactions which is nonfactorable.

Primary alkyl arenesulfonates which suffer acetolysis *via* the k_Δ pathway are characterized by values of ΔS^* that fall in the 0 to −10 eu range,[27a] while the acetolysis of simple, unbranched primary alkyl arenesulfonates is characterized by values of ΔS^* that fall in the range −19 ± 2 eu.[27b] The ΔS^* values reported in Table I for both the acetolysis and formolysis of **4**-OBs, **5**-OBs, and AC-OBs are consistent with the $k_{\Delta C}$ solvolysis pathway as outlined in Scheme I. A word of caution, however, is in order. The ΔS^* values for both the acetolysis and formolysis of **6**-OBs also fall in the range 0 to −10 eu, apparently due to a fortuitous blend of ΔS^* values for the competing k_Δ and k_s pathways.

It is of interest to note that the ΔS^* values for trifluoroethanolysis are *ca.* 10 eu more negative than the corresponding acetolysis values for **4**-OBs, **6**-OBs, and AC-OBs. This same phenomenon has been observed in the solvolysis of 1-arylcyclobutylcarbinyl brosylates[28] and can be attributed to greater hydrogen bonding solvation of the anion in the looser ion pair generated in trifluoroethanol.[29]

Experimental Section

Melting points were not corrected for stem exposure and were taken on a Mel-Temp apparatus. Infrared spectra were recorded on a Bausch and Lomb 1R 270 spectrophotometer and the nmr spectra were obtained on a Hitachi Perkin-Elmer R-24 instrument with tetramethylsilane as internal reference standard. A Beckman GC-4 chromatographic instrument equipped with a thermal conductivity detector and a 24 ft × 0.25 in. column of 20% Carbowax 20M, 2% $AgNO_3$ on Chromosorb W, AW-DMCS (45–60 mesh), was used for analytical gc work. All microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

Cyclobutylcarbinyl Brosylate (4-OBs). To a stirred solution of 2.6 g (30 mmol) of cyclobutylcarbinol [56% from cyclobutanecarboxylic acid (Aldrich Chemical Co.) and borane–tetrohydrofuran, bp 141° (750 mm) (lit.[30] bp 142–143° (750 mm)), ir spectrum consistent with assigned structure] in 40 ml of dry pyridine cooled to 0° was added 8.9 g (35 mmol) of *p*-bromobenzenesulfonyl chloride. After standing 17 hr at 5°, the mixture was carefully hydrolyzed by the slow addition of 20 ml of cold water (reaction temperature maintained between 0 and 5°) followed by the rapid addition of sufficient cold, dilute HCl to acidify the mixture. The precipitated ester was separated on a Büchner funnel (packed in cracked ice to prevent ester from melting) and washed several times with cold, dilute HCl, several times with cold water, and then with cold petroleum ether (bp 30–60°) and after air drying yielded 4.2 g (46%) of white needles (mp 20–25°). Recrystallization from petroleum ether (bp 30–60°)-ethyl acetate (50:5) gave 3.0 g (33%) of white crystals, mp 25° (lit.[5a] ~25°).

Cyclopentylcarbinyl brosylate (5-OBs) was prepared from *p*-bromobenzenesulfonyl chloride and cyclopentylcarbinol (Aldrich Chemical Co.) as described above in 65% yield: mp [after one recrystallization from petroleum ether (bp 30–60°)] 49.5–50° (lit.[31] mp 49.5–50°).

Cyclohexylcarbinyl brosylate (6-OBs) was prepared from cyclohexylcarbinol (Aldrich Chemical Co.) and *p*-bromobenzenesulfonyl chloride as described above in 70% yield: mp [after two recrystallizations from petroleum ether (bp 30–60°)] 41.5–42° (lit.[31] mp 42.5–43°).

1-Adamantylcarbinyl brosylate (AC-OBs) was prepared from 1-adamantylcarbinol [39% from 1-adamantylcarbonyl chloride (Aldrich Chemical Co.) and a 70% solution of sodium bis(2-methoxyethoxy)aluminum hydride in benzene (Aldrich Chemical Co.), mp 114.5–115.5° (lit.[16] mp 115–116°)] and *p*-bromobenzenesulfonyl chloride as described above in 72% yield: mp [after two recrystallizations from petroleum ether (bp 30–60°)] 103–104°. *Anal.* Calcd for $C_{17}H_{21}BrO_3S$: C, 53.00; H, 5.49; Br, 20.74. Found: C, 53.03; H, 5.45; Br, 20.98.

Preparation of Reference Olefins and Esters. Cyclopentene, cyclohexene, cycloheptene, and 1-methycyclohexene were purchased from Aldrich Chemical Co. and used as received. 1-Methylcyclopentene was prepared *via* acid-catalyzed dehydration of 1-methylcyclopentanol and the structure assignment confirmed by nmr. Cyclobutylcarbinyl acetate, cyclopentyl acetate, cyclopentylcarbinyl acetate, 1-methylcyclopentyl acetate, cyclohexyl acetate, cyclohexylcarbinyl acetate, 1-methylcyclohexyl acetate, and cycloheptyl acetate were prepared by published procedure[5,6] and their purity and structure assignment confirmed by comparison with recorded nmr data.[6]

Solvents. Absolute ethanol was prepared according to the method of Fieser.[32] Acetic acid solvent was prepared from 994.9 ml of glacial acetic acid (Matheson Scientific, 99.8%) and 5.1 ml of acetic anhydride. 2,2,2-Trifluoroethanol (Aldrich Chemical Co.) was redistilled prior to use.

Acetolysis Product Studies. Solutions (25 ml, 0.2 *M*) of the sulfonates **4**-OBs, **5**-OBs, and **6**-OBs in acetic acid (0.3 *M* in urea) were sealed in ampoules under N_2 and immersed in a constant temperature bath at 75 ± 0.1°. After 10 half-lives each solution was diluted with 150 ml of water and continuously extracted with ether for 48 hr. The ether extract was neutralized with $NaHCO_3$ and dried (Na_2SO_4), and most of the solvent was removed by controlled distillation with a Nester-Faust NFA-200 annular still. The composition (see Table II) of each residue was established by gc (using authentic reference olefins and esters) and confirmed by nmr analysis.

Rote measurements were accomplished by usual ampoule technique.[19] The titrating solutions were, for ethanolysis and 2,2,2-trifluoroethanolysis, 0.020 *N* sodium methoxide in anhydrous methanol[33] and, for acetolysis, 0.050 *N* sodium acetate in acetic acid. The indicators used were Bromthymol Blue (in water), Bromphenol Blue (in 20% aqueous EtOH), and Bromphenol Blue (in acetic acid), respectively.

Treatment of Kinetic Data. The thermodynamic activation parameters were obtained by IBM 1620 computer regression analysis. The linear correlations, slope values, and correlation coefficients were also obtained by IBM 1620 computer regression analysis.

References and Notes

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(13) See ref 3b for a similar finding for the acetolysis of 2-phenylethyl tosylate.
(14) The possibility that solvent attack on **1** could yield unrearranged acetate with retained configuration has not been excluded in this or previous studies[5c,6,7,15] but, based on recent solvolytic studies with neopentyl[16] and 1-adamantylcarbinyl[3c] tosylates, this pathway is poorly favored.
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(17) Bridged intermediate **1** is considered a geometrically unfavorable precursor for cyclohexene.[6]
(18) This substituent effect behavior is very similar to that of 1-*p*-X-phenylcyclopropylcarbinyl derivatives[19] where it is agreed[4] that ionization is anchimerically assisted by the cyclopropane ring.
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(22) Where it is generally agreed[3a] that neophyl tosylate ionizes with phenyl participation at a rate equal to k_t and dependent on solvent ionizing power but not nucleophilicity.
(23) This speculation is based on the following assumption: $\delta_m(k_\Delta/k_C)^R/\delta_m(k_\Delta/k_C)^N \sim$ constant where $\delta_m(k_\Delta/k_C)^R$ is defined in the text and $\delta_m(k_\Delta/k_C)^N$ is the participation response to medium effect by the phenyl group in neophyl tosylate.
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(25) The calculated strain release[26a] in going from starting material to the ring-expanded product is 19.5 kcal/mol which is equivalent to a log ($k_{4\text{-OBs}}/k_{5\text{-OBs}}$) value of 13; the measured value[26b] is −1.
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(33) Near the end of this series of experiments it was found that dilution of the 2-ml aliquots with 5 ml of acetic acid solvent followed by titration as with acetolysis samples gives much sharper end points.

Mechanism of the Catalyzed Thio-Claisen Reaction. Triggering of Concerted Rearrangement Processes

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Evidence is presented substantiating a thiophenolic intermediate in the thio-Claisen rearrangement of allylic phenyl sulfides under conditions (amine or carboxylic acid solvents at temperatures in the range 220–300°) only recently found to propitiate this reaction. This includes synthesis of the allyl thiophenol intermediate in relatively pure form, and converting it under normal reaction conditions to the same product distribution observed to form directly from the allyl phenyl sulfide substrate. The intermediate thiophenol is found to resist cyclization when present in its anionic form, and this is a basis for trapping it and preventing formation of the normal cyclization products. The intermediate anion is also shown to generate *o*-allyl side products as a result of nucleophilic displacement on the allylic carbon of the substrate. A number of anionic bases, but not their conjugate acids, are also found to catalyze the thio-Claisen, including phenoxide, acetate, and thiophenolate. Unlike the oxy-Claisen, where electrophilic agents are known to be exclusively catalytic, the thio-Claisen appears to be susceptible only to nucleophilic catalysis. This is confirmed by kinetic studies of the concentration rate dependencies (first order in substrate and catalyst) and reactivity as a function of structure among a series of amine catalysts. The relative catalytic efficiencies of the members of this series show no correlation with their base strengths, but do give evidence of a rough parallel with nucleophilicity. However, the scale of nucleophilic activities is very compressed compared to the range of rate variation in normal SN2 displacements, where a considerable degree of nucleophilic bonding is being created in the activation process. These and a number of other observations can be accounted by the proposal of a pericyclic transition state of thio-Claisen rearrangement which has been triggered by a nucleophilic attack at the allylic carbon of the substrate. The effect of the nucleophile is to bring about a small amount of displacement in the electron density of the C–S bond, and formation of a p orbital on the allylic carbon to accommodate the orbital requirements and the geometry of the [3,3] sigmatropic transition state.

The thermolysis of allylic phenyl sulfides[1] stands in contrast to that of their oxygen analogs in experiencing Claisen rearrangements. They exhibit extraordinary thermal stability and undergo propenylization and subsequent cleavage reactions[2,3] only at temperatures approaching 300°. In fact, the possibility of a thio-Claisen rearrangement to compete with degradative side reactions was established only recently (1962).[1,4-6] It was found that in solutions of carboxylic acid[5] or amine[1,4,6,7] solvents a facile rearrangement of Claisen character can be observed. This reaction has now been widely applied and is recognized to be of general preparative interest.[8-11]

The activation energy[12] for this "catalyzed" thio-Claisen is somewhat greater than for the oxy-Claisen and the products realized are thiocoumarans and thiochromanes which could have arisen from presumed *o*-allylthiophenyl intermediates. In an earlier communication[13] preliminary evidence for this presumption has been described. This is based on trapping some of the intermediate as the *o*-allylmethylthiophenyl ether and preventing cyclic product formation when the reacting mixture is quenched with KOH and CH_3I.

This report is intended to provide full documentation of the evidence bearing on the occurrence of an *o*-allylthiophenol intermediate corroborating the thio-Claisen nature of the catalyzed, thermal rearrangement of allylic phenyl sulfides. Additional lines of experimentation will also be discussed which were directed toward elucidating the role of catalytic agents which are often indispensable to obtaining a thio-Claisen reaction.

Results and Discussion

I. Evidence Substantiating a Thiophenolic Intermediate in the Thio-Claisen Rearrangement of Allyl Phenyl Sulfide (1). A. Cyclization of *o*-Allylthiophenol (2) under Typical Thio-Claisen Reaction Conditions. Independent synthesis of the intermediate **2** was achieved earlier[3] through a two-step reaction involving gas-phase pyrolysis of the *o*-allylthiocarbonate or *o*-allylthiocarbamate, **3**. Hydrolysis of the product, **3a**, in alkaline medium followed by acidification gave rise to **2**. The *o*-allylthiophenol had to be separated from propenylization (**5**) and cyclization (**6**) products, which could not be completely avoided even