and *trans*-bicyclohexanols with considerable success. The final alcohol fractions were of *ca.* 98% purity.

Spectral Measurements.—The quantitative infrared spectral measurements were made with two spectrophotometers, each operated as a double beam instrument. The following control settings were used with the Perkin–Elmer model 21 equipped with sodium chloride prisms: resolution, 960; gain, 5.5; response, 1; speed, 5; and suppression, O. The 2.5–16.0 μ range was scanned. The following control settings were used with the Beckman model IR-4 equipped with lithium fluoride prisms: gain, 2.0%; speed, 0.17 μ/ min.; period, 2.0 sec.; and slit, 2 × standard. The 3.0–5.0 μ range was scanned. The liquid alcohols were determined neat in a 0.018-mm. sodium chloride cell compensated against a sodium chloride block.

The complete infrared spectra of the various *cis*- and *trans*-3-bicyclohexanols are given in Table IV for neat liquid films. The data for the 3.0–5.0 μ region are from the Beckman IR-4 instrument with lithium fluoride optics, and for the 5.0–16. μ region from the Perkin–Elmer model 21 instrument with sodium chloride optics. The frequency ranges in parentheses indicate uncertain positions of maxima because of broadness of absorption bands.

TABLE V

OBSERVED PEAK HEIGHTS OF CHARACTERISTIC ABSORPTION BANDS OF THE *cis*-3-BICYCLO[3.1.0]HEXANOLS

|	(In absorbance units)[a]			
Alcohol	Carbinyl D 2151	Cyclopropyl D 2266	D 670	Carbinyl H 745
A-OH	0.0	0.0	0.0	0.710
B-OH	.246	.0	.0	.0
C-OH	.081	.098	.335	.445
D-OH	.0	.097	.331	.680
E-OH	.050	.064	.222	.574
H-OH[b]	.163		.016	.026
	(.245)		(.024)	(.039)

[a] Measured on Perkin–Elmer model 21 spectrophotometer equipped with sodium chloride optics; frequencies in cm.$^{-1}$.
[b] The available material at hand was insufficient to fill the infrared cell. Therefore, the values need to be increased. A factor of 1.5 has been chosen so that the intensity at the 2151 cm.$^{-1}$ band represents about 100% deuterium. These increased values are given in the parentheses and are used in the calculations.

In Table V are summarized some of the quantitative measurements on the various alcohol specimens for the analysis of deuterium scrambling made in Table I.

Proton magnetic resonance spectra of the *cis*-3-bicyclo-[3.1.0]hexanols were measured by R. Gillespie using a Varian V-4300-B high resolution spectrometer equipped with a 12-inch magnet and super-stabilizer. The frequency was fixed at 40 Mc./sec., and a magnetic field of about 9400 gauss was used. Determinations were made on the pure neat liquids. Sample tubes of 5-mm. outside diameter were used, and a sealed capillary tube of about 1-mm. diameter filled with distilled water was placed inside the sample tube. Samples were spun during the measurements. The line of the water peak was used as reference to measure shifts. The shifts of the peaks were determined by the use of the 60 c.p.s. audio-frequency side band method. The sign of the shift is chosen to be positive when the resonance falls at a higher applied field than the reference. In Table VI are summarized the observations on undeuterated *cis*-3-bicyclo-[3.1.0]hexanol.

TABLE VI

PROTON MAGNETIC RESONANCE SPECTRUM OF *cis*-3-BICYCLO[3.1.0]-HEXANOL
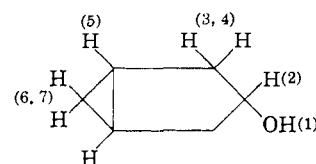
Cycles per second[a]	Relative area		Hydrogen
	Obsd.	Theory	assignment
8	1.84	2	1,2
91	0.24	4	3,4
112[b]	3.44		
140	2.48	2	5
161	2.16	2	6,7

[a] Relative to water, uncorrected for a bulk diamagnetic effect at 40 Mc. [b] Sharp peak; little, if any, splitting.

Kinetic Measurements.—First-order rate constants for acetolysis of 0.01 *M* toluenesulfonates A-OTs and B-OTs at 50.0° were determined simultaneously by the procedure employed previously.[3] For the undeuterated A-OTs the observed 10^5 *k* was 2.46 ± 0.04, while for the deuterated B-OTs it was 2.35 ± 0.04. In the latter case, there was some indication of a slight upward trend in the rate constant during the run.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF CALIFORNIA AT LOS ANGELES, LOS ANGELES 24, CALIF.]

Allylic Rearrangements. L. Reactions of α- and γ-Trifluoromethylallyl Alcohols with Thionyl Chloride and Thermal Decomposition of the Chlorosulfinate Intermediates[1]

BY J. A. PEGOLOTTI AND W. G. YOUNG

The reaction of α- and γ-trifluoromethylallyl alcohols with thionyl chloride in the solvents diethyl ether and thionyl chloride has been investigated. The effect of added tri-*n*-butylamine and its hydrochloride in these reactions was also studied. γ-Trifluoromethylallyl chloride was the only allylic chloride formed in these reactions. Kinetic and product studies from the thermal decomposition of α- and γ-trifluoromethylallyl chlorosulfinates were carried out with results indicating that the secondary chlorosulfinate decomposes by an S_Ni' process of concerted nature.

In previous studies of the mechanism and products from the reaction of allylic alcohols with thionyl chloride, attention has been directed primarily toward allyl alcohol itself,[2] α- and γ-methylallyl alcohols[3] and similar compounds where

the basic allylic skeleton has alkyl substituents.[4] The present investigation was initiated to study the effect which a non-reactive, highly electronegative substituent would evince in this reaction. The trifluoromethyl group appeared most suitable for a substituent with the aforementioned properties and was chosen for this purpose. The alcohols prepared for the investigation were α-trifluoromethylallyl alcohol (Ia) and γ-trifluoromethylallyl alcohol (IIa), alcohols analogous to the butenyl

(1) This work was supported in part by a grant to W. G. Young from the National Science Foundation.

(2) S. H. Sharman, F. F. Caserio, R. E. Nystrom, J. C. Leak and W. G. Young, *J. Am. Chem. Soc.*, **80**, 5965 (1958).

(3) (a) F. Caserio, G. E. Dennis, R. H. De Wolfe and W. G. Young, *ibid.*, **77**, 4182 (1955); (b) W. G. Young, F. Caserio and D. Brandon, *Science*, **117**, 473 (1953); (c) W. G. Young, F. F. Caserio, Jr., D. D. Brandon, *J. Am. Chem. Soc.*, **82**, 6163 (1960).
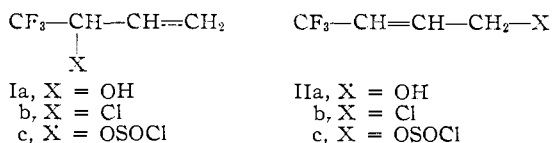
(4) R. H. De Wolfe and W. G. Young, *Chem. Revs.*, **56**, 753 (1956).

TABLE I

THE REACTION OF THIONYL CHLORIDE WITH α-TRIFLUOROMETHYLALLYL ALCOHOL, Ia, AND γ-TRIFLUOROMETHYLALLYL ALCOHOL, IIa

Run	Reactants Add (mol.)	To (mol.)	Solvent (ml.)	Reaction time	Unreacted alcohol	% IIb	% Chlorosulfinate[a]
1	SOCl₂ (0.008)	Ia (0.008)	Ether (30)	60 min.	100	0	0
2	Bu₃N (0.0003)	Run 1	Ether (30)	30 min.	50	0	50
3	Ia (0.008)	SOCl₂ (0.024)	SOCl₂	60 min.	54	0	46
4	Ia (0.008)	SOCl₂ (0.040)	SOCl₂	60 min.	34	0	66
5	SOCl₂ (0.016)	Ia (0.016) Bu₃N (0.016)	Ether (50)	60 min.	25	24	51
6	Ia (0.008)	SOCl₂ (0.040) Bu₃NHCl (0.008)	SOCl₂	60 min.	0	5	95
7	Ia (0.004)	SOCl₂ (0.020) Bu₄NCl (0.004)	SOCl₂	60 min.	20–25	0.5	70–75
8	SOCl₂ (0.008)	Ia (0.008) Bu₃NHCl (0.008)	Ether (25)	180 min.	14–24	5	71–81
9	SOCl₂ (0.008)	Ia (0.008) Bu₃NHCl (0.008)	Ether (25)	180 min.	32	5	63
10	SOCl₂ (0.008)	IIa (0.008)	Ether (25)	60 min.	43	0	57
11	SOCl₂ (0.015)	IIa (0.015)	Ether (50)	60 min.	25	3	72
12	SOCl₂ (0.016)	IIa (0.016)	Ether (50)	19 days	10	34	56
13	IIa (0.045)	SOCl₂ (0.045) Bu₃N (0.045)	Ether (250)	60 min.	0	100	0
14	IIa (0.008)	SOCl₂ (0.040) Bu₃NHCl (0.008)	SOCl₂	12 hr.	0	100	0

[a] In the reactions with Ia, the chlorosulfinate formed is Ic, while in reactions with IIa, the chlorosulfinate formed is IIc.

alcohols studied previously.[3] It was thought that the stabilizing effect of the trifluoromethyl group on the allylic system would be sufficient to afford isolation of the chlorosulfinate esters of these alcohols, α-trifluoromethylallyl chlorosulfinate (Ic) and γ-trifluoromethylallyl chlorosulfinate (IIc). A kinetic study of the decomposition of these chlorosulfinates could then be carried out, such a study complementing that of allyl chlorosulfinate, the only known stable allylic chlorosulfinate.[2] It should be noted that the butenyl chloroformates, carbon analogs of the chlorosulfinates, have been isolated and kinetic studies of their decomposition in various solvents published.[5]

$$CF_3—CH—CH=CH_2 \qquad CF_3—CH=CH—CH_2—X$$
$$\quad\quad |$$
$$\quad\quad X$$

Ia, X = OH   IIa, X = OH
b, X = Cl   b, X = Cl
c, X = OSOCl   c, X = OSOCl

Results of the Thionyl Chloride Reactions.— The reaction of the allylic alcohols Ia and IIa with thionyl chloride was investigated in two solvents, diethyl ether and thionyl chloride. In addition, the effect of added tri-n-butylamine, tri-n-butylamine hydrochloride and tetra-n-butylammonium chloride on this reaction was examined. A summary of the reactants, solvents, reaction time and products from these reactions is given in Table I. Product analyses were performed by vapor phase chromatography. The only allylic chloride produced in these reactions was the primary chloride, γ-trifluoromethylallyl chloride (IIb). The structure of this compound was established by ozonolysis which yielded trifluoroacetaldehyde and chloroacetaldehyde, characterized by their 2,4-dinitrophenylhydrazone derivatives. In addition, the

infrared spectrum of IIb showed absorption bands at 1680 and 965 cm.⁻¹ attributable to an internal double bond.[6] No evidence could be found for the presence of the secondary chloride, α-trifluoromethylallyl chloride (Ib) in any of these reactions. Moreover, attempts to prepare the secondary chloride Ib by several methods including the isomerization of γ-trifluoromethylallyl chloride with zinc chloride, the reaction of phosphorus trichloride with α-trifluoromethylallyl alcohol and the reaction of tri-n-butylamine hydrochloride upon di-α-trifluoromethylallyl sulfite were unsuccessful.

The possibility of the secondary chlorosulfinate Ic being a stable compound first presented itself during run 5, Table I, where the peak of an unknown compound was evident in the vapor phase chromatogram of the ether reaction mixture. Addition of water to the ether solution decomposed the compound, since the peak in question disappeared with immediate increase in the peak area of the parent secondary alcohol Ia. This decomposition is typical of chlorosulfinates. The secondary chlorosulfinate Ic was isolated by distillation of the reaction mixture from a run similar to run 6. A Volhard titration for chloride on a weighed amount of the compound accounted for 98% of theoretical chloride which would be present in Ic. The sulfites prepared by addition of n-amylchlorosulfinate to Ia and by addition of n-amyl alcohol to Ic were identical as shown by comparing the infrared spectra of the compounds. The proof of structure of the primary chlorosulfinate IIc was similar to that for Ic. Under conditions used by the vapor phase chromatography, IIc could not be observed on the chromatogram. However, by use of an internal standard in these reactions, n-butyl ethyl ether, the amount of IIc formed could

(5) K. L. Oliver and W. G. Young, J. Am. Chem. Soc., 81, 5811 (1959).

(6) L. G. Bellamy. "The Infrared Spectra of Complex Molecules," Second Edition. John Wiley and Sons, Inc., New York, N. Y., 1958.

be measured by adding water to the reaction mixture containing IIc and measuring the increase in the peak area of the parent alcohol IIa.

Discussion of the Thionyl Chloride Reactions.— The results of the reactions summarized in Table I indicate some unique features in the chemistry of the reaction of thionyl chloride with these allylic alcohols. In no other case known has an allylic chlorosulfinate actually been shown to be a stable product under such varying conditions as has the secondary chlorosulfinate Ic. Allyl chlorosulfinate, the only isolable allylic chlorosulfinate previously known, decomposes readily under conditions similar to those in runs 2–9.[3b] The stability of the chlorosulfinates Ic and IIc can be attributed to the stabilizing effect which a trifluoromethyl group is known to transmit to adjacent functional groups. For example, alcohols such as trifluoromethylethylcarbinol can be dehydrated only under the severe conditions of phosphorus pentoxide at 200°.[7] Also, 2,2,2-trifluoroethyl iodide reacts 17,400 times slower than ethyl iodide toward thiophenoxide ion in methanol at 20°, an effect due to the inductive effect of the trifluoromethyl group.[8] That the trifluoromethyl group affects the hydroxyl group of IIa far less than the hydroxyl group of Ia is suggested by consideration of runs 1, 2, 10 and 11. In order for the secondary chlorosulfinate Ic to form in ether, some amine (or amine hydrochloride) must be present, whereas the primary chlorosulfinate IIc forms readily in ether without amine present. Apparently the difference of reactivity of the alcohols toward thionyl chloride in dilute ether solution is attributable to a more highly nucleophilic oxygen in IIa than in Ia. In the case of IIa, the nucleophilicity of the hydroxyl group toward the sulfur atom of thionyl chloride is not greatly diminished, since it is "insulated" from the -I effect of the fluorines by a vinyl group. However, as indicated by the increased acidity of trifluoroethanol over ethanol,[9] there is a strong electron drain away from the hydroxyl group of Ia by the adjacent trifluoromethyl group. Thus, the function of the amine base in run 2 is to aid the removal of the acidic hydrogen from Ia, rendering the oxygen more nucleophilic.

It is noted that tri-n-butylamine hydrochloride does not facilitate the formation of Ic in ether (runs 8 and 9), as well as tri-n-butylamine (run 5). Since amine is necessary for the formation of the chlorosulfinate Ic in ether solution, it is possible that free amine is in equilibrium with amine hydrochloride, eq. A, and is the agent which causes

$$(n\text{-Bu})_3\overset{\oplus}{\text{N}}\text{H} \ \overset{\ominus}{\text{Cl}} \longrightarrow (n\text{-Bu})_3\text{N} + \text{HCl} \qquad \text{(A)}$$
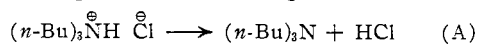
formation of Ic. A control reaction indicated that this is most likely correct. In an experiment similar to run 1, except that the ether was saturated with anhydrous hydrogen chloride gas, no products formed after ten hours. Upon resaturation of the ether, and addition of tri-n-butylamine, equimolar to Ia present, no products had

formed after three hours. The molar ratio of hydrogen chloride to amine was about 30 to 1, under which conditions the added amine was transformed into its hydrochloride, and the equilibrium in eq. A shifted completely to the right, so that there was no free amine present to catalyze formation of Ic. Although free amine is required to catalyze the formation of chlorosulfinate in ether, this is not the case in thionyl chloride as a solvent (runs 3 and 4). The formation of Ic necessitates amine catalysis only in dilute solution.

Runs 1–4 and 10–12 were designed to determine whether the trifluoromethyl group increases or decreases the ability of allylic chlorosulfinates to decompose by an $S_N i'$ products exclusively upon reaction with thionyl chloride in ether solution over a one-hour period.[3a] With Ia and IIa, the chlorosulfinate intermediate is completely stable during the same length of time, as shown by runs 2 and 10.[10]

Runs 5–8, 13 and 14 were designed to facilitate the displacement reaction by chloride ion upon the chlorosulfinates. The use of tri-n-butylamine as a base in thionyl chloride reactions in ether produces a soluble amine hydrochloride during the course of the reaction, thereby making available chloride ions for such displacements. The hydrogen chloride generated in the formation of the chlorosulfinates is not available for displacements reactions since it forms a tight complex with diethyl ether molecules.[11]

In order to determine how the primary chloride IIb arises from the secondary alcohol Ia in runs 5, 6, 8 and 9, the various pathways available to the formation should be examined. An $S_N i'$ mechanism does not appear to be operative, since in runs 3 and 4 large amounts of the chlorosulfinate are formed but there is no decomposition to IIb. Consequently, in runs 8 and 9, where a high yield of the chlorosulfinate is found, the small amount of primary chloride IIb must come from a different mechanism. One mechanism available for the formation of IIb in these runs is that of abnormal nucleophilic attack by a chloride ion from the amine hydrochloride, the $S_N 2'$ mechanism. In runs 6, 8 and 9, an equimolar amount of the hydrochloride was present at the beginning of the reaction, but in these runs less primary chloride was formed than in run 5 when both amine hydrochloride and free amine were present. Consequently, it would appear that amine hydrochloride is not the main source of chloride for production of IIb. However the chloride might come from amine complexes III or IV. Similar complexes to III have been isolated by Gerrard[12] and there is no apparent reason why a similar complex IV between the amine and thionyl chloride should not also form.

An interesting question arises as to why the chloride ions of the ammoniums salts III and IV should be more "available" for displacement than that of tri-n-butylamine hydrochloride. The an-

(7) K. N. Campbell, J. O. Knobloch and B. K. Campbell, J. Am. Chem. Soc., **75**, 5978 (1953).

(8) J. Hine and R. G. Ghirardelli, J. Org. Chem., **23**, 1550 (1958).

(9) A. L. Henne and R. L. Pelley, ibid., **74**, 1426 (1952).

(10) Whether IIb formed in runs 11 and 12 arose from an $S_N i$ process or by an $S_N 2$ reaction involving hydrogen chloride is not known.

(11) A. M. Buswell, W. H. Rodebush and M. F. Roy, J. Am. Chem. Soc., **60**, 2528 (1938).

(12) W. Gerrard, J. Chem. Soc., 688 (1936).

swer is most likely found in the degree of dissociation of these salts in solution. It has been shown that the dissociation constant of tetraalkylammonium picrates is much larger than that

$$\underset{\text{III}}{\underset{\text{CF}_3\text{—CH—CH=CH}_2}{\overset{\overset{\displaystyle O}{\overset{\|}{\underset{|}{O\text{—S—}\overset{\oplus}{N}Bu_3\ \overset{\ominus}{Cl}}}}}{}}} \qquad \underset{\text{IV}}{\overset{\overset{\displaystyle O}{\|}}{Cl\text{—S—}\overset{\oplus}{N}Bu_3\ \overset{\ominus}{Cl}}}$$

of the trialkylammonium picrates in various solvents.[13] This is postulated to be due to a tighter ion-pair existing in the trialkylammonium picrates, where hydrogen bonding is possible between the hydrogen on the nitrogen and the chloride ion, than in the tetraalkylammonium picrates, where such bonding is not possible. Since the ammonium complexes III and IV do not have the capacity for hydrogen bonding, it is quite likely that these complexes would be much more dissociated in solution than tri-*n*-butylamine hydrochloride, where such bonding can occur.

Tetra-*n*-butylammonium chloride was used in run 7 as a source of chloride ion similar to complexes III and IV. The results of run 7 show that tetra-*n*-butylammonium chloride produced only one-tenth the amount of primary chloride IIb as did tri-*n*-butylamine hydrochloride under identical conditions in run 6. Tetra-*n*-butylammonium chloride is quite similar to IV in that it supplies a chloride ion from an external source for attack upon the chlorosulfinate. Since run 7 produced such a small amount of primary chloride, this suggests that complex III is the intermediate by which this compound is predominantly formed. The stereochemistry inherent in III is quite favorable to an internal SN2' mechanism, since the chloride ion must be near the positive nitrogen and therefore in a *cis* relationship to the departing group, a stereochemistry apparently necessary for SN2' attack.[14] Inspection of a Fisher–Taylor–Hirschfelder model of complex III indicates that several conformations are available to this complex where steric hindrance is minimized and where the chloride ion is very close to the terminal carbon atom, facilitating attack upon the double bond.

$$\underset{\text{H}}{\underset{\text{H}}{\overset{\overset{\displaystyle O}{\|}}{\underset{CF_3}{\overset{}{\underset{}{}}}}}}$$

In summary, the rate of primary chloride formation from Ic appears to be dependent on the amount of III present, and this in turn is dependent upon the amount of free amine. Consequently, in the runs with amine hydrochloride, only a small amount of free amine is ever present through equi-

librium with the hydrochloride. In these cases, smaller amounts of IIb are produced than in run 5 where free amine is present.

When tri-*n*-butylamine is present in the thionyl chloride reaction, in ether with the primary alcohol IIa, a quantitative yield of IIb results (run 13), a similar result as that found by Caserio with γ-methylallyl alcohol where 100% of γ-methylallyl chloride was formed.[3c] Similarly, as noted in run 14, use of the amine hydrochloride yields solely IIb, whereas with γ-methylallyl alcohol, Caserio found that 26% of the product chloride was the SNi'-type product, α-methylallyl chloride. Possible reaction schemes are shown in eq. B and C for this reaction (with *p*-OH representing γ-trifluoromethylallyl alcohol). In eq. B, the primary chloride arises by attack of amine hydrochloride upon IIc. In eq. C, a complex between amine and IIc is postulated similar to III, with the product chloride arising by attack from the chloride ion of the complex or of the amine hydrochloride. If eq. C is the pathway, apparently an intramolecular SN2' reaction (such as III undergoes) cannot compete here with the rapid SN2 displacement by chloride ion.

$$p\text{-OH} + SOCl_2 + Bu_3N \longrightarrow p\text{-OSOCl} +$$

$$Bu_3\overset{\oplus}{N}H\ \overset{\ominus}{Cl} \longrightarrow p\text{-Cl} + So_2 + Bu_3\overset{\oplus}{N}H\ \overset{\ominus}{Cl} \quad (B)$$

$$p\text{-OH} + SOCl_2 + 2Bu_3N \longrightarrow p\text{-OSO}\overset{\oplus}{N}Bu_3\ \overset{\ominus}{Cl} + Bu_3\overset{\oplus}{N}H\overset{\ominus}{Cl}$$

$$\downarrow \qquad\qquad (C)$$

$$p\text{-Cl} + SO_2 + Bu_3N$$

Results of the Thermal Decomposition of the Chlorosulfinates.—The previous section describing the reactions of the trifluoromethylallyl alcohols with thionyl chloride indicated that the chlorosulfinates which formed did not readily decompose in ether solution without added amine. Both the chlorosulfinates Ic and IIc were isolable and stable for months in their pure form if kept at −20° and out of contact with moisture. In view of this stability, it was of interest to determine their rate of decomposition at elevated temperatures. The allylic chlorides formed as products would indicate the mechanism preferred for decomposition, SNi or SNi', and the sensitivity of the rate of decomposition to change in solvent would aid in determining whether a concerted or ion-pair process was involved.[15]

Table II summarizes the conditions used for the decomposition of Ic and IIc and the rate of decomposition observed in each run. as measured by the rate of evolution of sulfur dioxide gas in a nitrometer. The rates of decomposition measured followed first-order kinetics during the initial part of the decomposition, but a downward drift in the rate was observed after from 30 to 40% reaction. Apparently, the drifting rate was due to entrainment of the chlorosulfinate by the sulfur dioxide evolved. Only run 6 did not show this downward drift as the decomposition progressed. The chlorosulfinates used were known to be at least 97% pure in all kinetic runs, except run 6,

(13) C. Kraus, *J. Phys. Chem.*, **60**, 129 (1956).

(14) (a) W. G. Young, I. D. Webb and H. L. Goering, *J. Am. Chem. Soc.*, **73** 1076 (1951); (b) F. G. Bordwell. F. Ross and J. Weinstock, *ibid.*, **82**, 2878 (1960).

(15) See ref. 2 for a discussion of concerted and ion-pair processes in the decomposition of allylic chlorosulfinates.

TABLE II

THE DECOMPOSITION OF α-TRIFLUOROMETHYLALLYL CHLOROSULFINATE (Ic) AND γ-TRIFLUOROMETHYLALLYL CHLORO-SULFINATE (IIc)

Run	Chloro-sulfinate	Solvent	Reaction, %	Decomp. temp., °C.	10^5 k, sec.$^{-1}$	10^5 k, sec.$^{-1,a}$ $100°$
1	Ic	None	46	108–110	9.4 ± 1.4	6.5
2	Ic	None	25	103	7.1 ± 0.2	6.2
3	Ic	None	33	105–106	9.2 ± 1.4	7.3
4	Ic	Nitrobenzene	37	106–108	13.4 ± 0.8	10.0
5	Ic	n-Decane	39	124	9.2 ± 0.8	1.5
6	IIc	None	93	105	157 ± 12	126
7	IIc	None	40	139–142	4.1 ± 0.3	0.27
8	IIc	Nitrobenzene	48	115–116	15.3 ± 1.1	5.1
9	IIc	Nitrobenzene	55	118–120	33.3 ± 0.5	8.8

^{a} These rate constants have been extrapolated to 100° by making the assumption that a ten degree decrease in temperature decreases the rate constant by a factor of two.

where IIc was 88% pure, the purity being established by either refractive index or Volhard titration.

The products of the decompositions were analyzed by vapor phase chromatography. Both Ic and IIc formed the primary chloride IIb exclusively in all runs except run 7, where an unknown compound was formed in approximately an equal amount to that of IIb.

Discussion of the Thermal Decomposition of the Chlorosulfinates.—The results of the thermal decomposition of Ic and IIc as given in Table II do not encompass sufficient data so that definite conclusions as to the reaction mechanism of the decomposition can be formulated. However, there is an obvious difference in the behavior exhibited by these isomeric chlorosulfinates. In the neat decomposition of these compounds, the primary chlorosulfinate IIc gave two widely differing rate constants in runs 6 and 7, while the secondary chlorosulfinate Ic showed good reproducibility in the three runs 1, 2 and 3. In regard to runs 6 and 7, it should be recalled that chlorosulfinates in general and primary chlorosulfinates in particular are very susceptible to displacement by chloride ion in catalytic amounts.[2,16] The fact that in run 6 the chlorosulfinate was only 88% pure and the decomposition was very fast would indicate that decomposition in this case was primarily due to chloride ion catalysis, with varying amounts of catalysis probable in the other runs with IIc, also.

The decomposition runs with the secondary chlorosulfinate Ic appear to be more reliable since the rate of neat decomposition was reproducible, as runs 1, 2 and 3 indicate. Only primary chloride, the SNi' product, was observed in all five runs with Ic. Several possibilities can be advanced as to the method of formation of this chloride in addition to an SNi' mechanism. If Ic rearranged to IIc, subsequent SN2 attack by catalytic amounts of chloride ion would produce the primary chloride IIb. If this rearrangement does occur, addition of water to the decomposition mixture after partial reaction should liberate the parent alcohol IIa. This was checked in run 5 and vapor phase chromatography indicated IIa had not been formed. In addition, if a facile thermal rearrange-

ment of Ic to IIc does occur, a similar rearrangement of the p-bromobenzenesulfonate derivative (brosylate) of Ia to the brosylate derivative of IIa should also occur at elevated temperatures. However, during the course of this investigation, α-trifluoromethylallyl brosylate was shown to be stable for 35 days at 50° in 70% acetone–30% water. The possibility that an SN2' attack by chloride ion on Ic produces IIb is also unlikely, since, as is reported in another paper, an SN2' attack by chloride ion upon the brosylate of Ia should be about 10^5 times slower than an SN2 attack upon the brosylate of IIa. This difference does not exist between the rates of decomposition of Ic and IIc.[17]

It appears, in view of the previous arguments, that an SNi' mechanism can be postulated for the decomposition of Ic. This mechanism can be described as occurring by a concerted process, V, or intimate ion pair formation, VI, with subsequent collapse to product. Yet, as Winstein has pointed out,[18] the anion and cation of an intimate ion pair are close enough to interact with resulting covalent character. No sharp distinction would then be expected between the two types V and VI since they form extremes in a graded series. However, the extent to which the SNi' decomposition mechanism is more closely allied to an ionic or covalent intermediate in specific reactions can be gauged by studying the sensitivity of the rate of reaction to solvent ionizing power and the effect of change in substrate. Through the use of these criteria, the decomposition of allyl chlorosulfinate[2] and the decomposition of the butenyl chloroformates[5] appear to involve ion pairs such as VI. With α-methylallyl chloroformate, the rate of decomposition in nitrobenzene, a solvent of good ionizing properties, is 10,000 times faster than in n-decane, a solvent of poor ionizing properties. The increase in rate for the decomposition of Ic in nitrobenzene over n-decane is only a factor of seven. This would suggest that the decomposition of this secondary chlorosulfinate proceeds through a mechanism similar to V, a concerted mechanism.

It is also extremely interesting to compare the rates of decomposition of allylic chlorosulfinates when the substrate has been changed from allyl to α-trifluoromethylallyl. From the data of Shar-

(16) A. Streitwieser, Jr., and W. D. Schaeffer, J. Am. Chem. Soc., 79, 379 (1957).

(17) J. Pegolotti and W. G. Young, ibid., 83, 3258 (1961).
(18) S. Winstein and G. C. Robinson, ibid., 80, 169 (1958).

man[2] it can be calculated that in *n*-decane at 100°, α-trifluoromethylallyl chlorosulfinate decomposes at a rate about 10^3 times *faster* than allyl chlorosulfinate, the latter compound decomposing by initial ionization to the formation of an ion pair. If
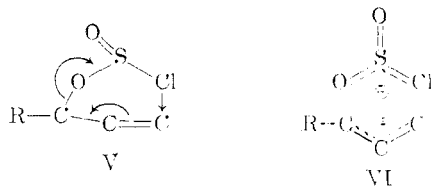
one considers that even a neighboring chloride or bromide *decreases* the rate of reaction by an SN1 mechanism[18a] by a factor of 10^4, it would appear highly unlikely that ion-pair formation occurs in the decomposition of Ic.[18b] From considerations of the effect of solvent change and substrate change upon the decomposition of Ic in runs 1–5. it would appear that this chlorosulfinate decomposes by a mechanism similar to V, where predominant covalent character is maintained in the intermediate through the rearrangement sequence.

Experimental

Preparation and Purification of Reactants. Thionyl Chloride.—Eastman Kodak Co. white label thionyl chloride was purified by the procedure of Cottle.[19]

Diethyl Ether.—Mallinckrodt anhydrous ether, analytical reagent, was used directly without further purification. The determination of water content by Karl Fischer titration upon ether from a freshly opened container showed it to have less than 0.01% by weight of water.

Ethyl *n*-Butyl Ether.—Eastman Kodak Co. white label ethyl *n*-butyl ether was run through a column of activated alumina for peroxide removal, then refluxed over fresh sodium three times for a period of 1 hour each time. The ether upon distillation had b.p. 91.5–92.0°, n^{25}D 1.3800.

Tri-*n*-butylamine.—Eastman Kodak Co. white label tri-*n*-butylamine was heated on a steam-bath overnight with an equal volume of acetic anhydride. The amine layer was then treated with water to hydrolyze any remaining acetic anhydride by heating for 2 hours on the steam-bath. After cooling, solid potassium carbonate was added to neutralize any acetic acid formed. The amine was separated and dried over potassium carbonate, then distilled with b.p. 120° (44 mm.) and n^{25}D 1.4280.

Tri-*n*-butylamine Hydrochloride.—The tri-*n*-butylamine hydrochloride used was prepared by Dr. K. O. Olivier from the reaction of tri-*n*-butylamine in diethyl ether with gaseous hydrogen chloride and recrystallization from diethyl ether. It was protected from moisture by storing in a vacuum desiccator.

Tetra-*n*-butylammonium chloride was prepared by Drs. I. Stevens and S. Smith[20] and protected from moisture by storing in a desiccator. Prior to use it was dried in an Abderhalden pistol at 2 mm. over refluxing acetone.

Nitrobenzene.—Eastman Kodak Co. white label nitrobenzene was distilled from phosphorus pentoxide and had n^{20}D 1.5522.

n-Decane.—Humphrey-Wilkinson *n*-decane was shaken in a separatory funnel with concentrated sulfuric acid twice, then washed with water, sodium bicarbonate solution, then water again, dried over magnesium sulfate, and distilled. It had b.p. 75° (25 mm.) and n^{20}D 1.4095.

γ-Trifluoromethylallyl alcohol was prepared by the procedure of McBee.[21]

α-Trifluoromethylallyl alcohol was prepared by means of a Grignard synthesis between vinylmagnesium bromide and trifluoroacetaldehyde. Trifluoroacetaldehyde was prepared by the method of Baird[22] or Pierce,[23] and vinylmagnesium bromide by the method of Normant.[24] A 5-liter, 3-necked flask equipped with mechanical stirrer, 1000-ml. dropping funnel with pressure-equalizing arm, and condenser, was flame dried under nitrogen. The system was maintained under nitrogen during the entire reaction. To the flask was added 73 g. (3.0 mol.) of magnesium turnings. The Grignard reagent was initiated by addition of 5 ml. of vinyl bromide (Matheson vinyl bromide purified by two distillations) in 50 ml. of tetrahydrofuran (purified by refluxing over potassium hydroxide pellets and distilling from lithium aluminum hydride) to the magnesium turnings with several drops of methyl iodide. The addition of 321 g. (3.0 mol.) of vinyl bromide in 1400 ml. of tetrahydrofuran (stabilized with 0.5 g. of quinone to reduce vinyl bromide polymerization) was at a rate sufficient to maintain a temperature of 40–50° in the reaction flask. Addition was complete in 5 hours, and the solution was then refluxed for 1 additional hour. The Grignard mixture was allowed to set overnight under nitrogen. The addition funnel was removed and 132 g. (1.67 mol.) of trifluoroacetaldehyde added as a gas to the vigorously stirred Grignard reagent by means of a glass apparatus leading from the flask containing the aldehyde directly into the reaction vessel. The rate of addition of aldehyde (b.p. −19°) was controlled by keeping the flask containing the aldehyde in a bath at −15°. Addition was complete in 2 hours. and the reaction mixture stirred 3 hours longer. The hydrolysis of the Grignard reaction mixture was by addition of 600 ml. of a saturated ammonium chloride solution, over a 2-hour period. The yellow solution was decanted, and the solid remaining was extracted with several 100-ml. portions of tetrahydrofuran. The combined tetrahydrofuran portions were successively dried over potassium carbonate, magnesium sulfate and calcium sulfate. Distillation of the tetrahydrofuran solution produced an azeotropic mixture of tetrahydrofuran and α-trifluoromethylallyl alcohol. The azeotropic mixture had a boiling point of 102–103°. Separation of the components of this azeotrope was achieved by elution chromatography in the following manner. A 2.5-foot column, 3.5 cm. in diameter, was packed with 550 g. of activated alumina, prepared as described by Fieser,[25] in J. T. Baker analyzed petroleum ether. To the column was added 150 g. of the azeotropic mixture. Elution by 2000 ml. of petroleum ether was followed by elution with 2000 ml. of ether. The pentane fractions contained some alcohol and were set aside for further chromatography. The ether fractions were distilled to yield α-trifluoromethylallyl alcohol (approximate yield of 45–50%), b.p. 91.5°, n^{25}D 1.3450.

Anal. Calcd. for $C_4H_5F_3O$: C, 38.10; H, 3.99. Found: C, 37.93; H, 4.21.

The α-naphthyl urethan derivative of the alcohol had m.p. 121–123°.

γ-Trifluoromethylallyl Chloride.—To a well-stirred mixture of 9.4 g. (0.075 mol.) of γ-trifluoromethylallyl alcohol and 13.9 g. (0.075 mol.) of tri-*n*-butylamine cooled in an ice–water-bath was added 8.9 g. (0.075 mol.) of thionyl chloride over 30 minutes, after which stirring was continued for 1 hour at room temperature. The mixture was flash distilled to remove the amine salt. Distillation of the flashed products gave 7.4 g. (70% yield) of γ-trifluoromethylallyl chloride, b.p. 82.5–83°, n^{25}D 1.3610.

Anal. Calcd. for $C_4H_4F_3Cl$: C, 33.24; H, 2.79; Cl, 24.53. Found: C, 33.45; H, 3.02; Cl, 24.27.

(18) (a) S. Winstein and E. Grunwald, *J. Am. Chem. Soc.*, **70**, 828 (1948). (b) Solvolysis of γ-trifluoromethylallyl chloride in aqueous silver nitrate, investigated during this study, also indicated a resistance to ionization in this system. *cis*- or *trans*-γ-methylallyl chloride is completely solvolyzed in 0.090 *N* aqueous silver nitrate in 12–15 minutes with equal amounts of α- and γ-methylallyl alcohols formed [W. G. Young, S. H. Sharman and S. Winstein, *J. Am. Chem. Soc.*, **82**, 1376 (1960)] a result indicative of an intermediate allylic carbonium ion. In comparison, γ-trifluoromethylallyl chloride in 1.0 *N* aqueous silver nitrate was only 91% solvolyzed in 10 days, with only γ-trifluoromethylallyl alcohol as a product alcohol, which suggests an SN2 mechanism for solvolysis in this case.

(19) D. L. Cottle, *ibid.*, **68**, 1380 (1946).

(20) S. Smith. Ph.D. Thesis, U.C.L.A., 1959.

(21) E. T. McBee, O. R. Pierce and D. D. Smith, *J. Am. Chem. Soc.*, **76**, 3725 (1954).

(22) M. Baird, H. Iserson and F. E. Lawlor, *ibid.*, **76**, 4027 (1954).

(23) O. R. Pierce and T. G. Kane, *ibid.*, **76**, 300 (1954).

(24) H. Normant, *Bull. soc. chim. France*, **728** (1957).

(25) L. F. Fieser, "Experiments in Organic Chemistry," Third Edition, D. C. Heath and Co., Boston, Mass., 1955.

n-Amyl Chlorosulfinate.—Twenty grams (0.22 mol.) of J, T. Baker analyzed *n*-amyl alcohol was added dropwise to a cooled ($-20°$) solution of 35.4 g. (0.29 mol.) of thionyl chloride in 50 ml. of redistilled pentane. Hydrogen chloride was removed from the cold solution using the water aspirator and the solution let stand overnight. The pentane was then removed by the water aspirator and the residual liquid distilled resulting in 22.6 g. (60% yield) of *n*-amyl chlorosulfinate, b.p. 55–58° (4 mm.) and n^{25}D 1.4570.

γ-Trifluoromethylallyl-*n*-amyl Sulfite.—A mixture of 3.0 g. (0.024 mol.) of γ-trifluoromethyl alcohol and 1.9 g. (0.024 mol.) of anhydrous pyridine was added dropwise over 30 minutes to a stirred, cooled (-20 to $-30°$) solution of 5.12 g. (0.03 mol.) of *n*-amyl chlorosulfinate. After the reaction mixture had stirred 45 minutes longer at room temperature, sufficient water was added to dissolve the precipitated pyridine hydrochloride. The layers were separated and the ether layer washed with two 5-ml. portions of dilute hydrochloric acid, dilute sodium bicarbonate solution and water. The ether solution was dried overnight over potassium carbonate. Distillation through a micro-column resulted in 2.05 g. (30% yield) of the γ-trifluoromethylallyl-*n*-amyl sulfite, b.p. 100–102° (4 mm.) and n^{25}D 1.4099.

Anal. Calcd. for $C_9H_{15}O_3F_3S$: C, 41.53; H, 5.81. Found: C, 41.90; H, 5.73.

α-Trifluoromethylallyl-*n*-amyl sulfite was prepared in exactly the same manner as γ-trifluoromethylallyl-*n*-amyl sulfite. It had b.p. 80–82° (5 mm.), n^{25}D 1.4030.

Anal. Calcd. for $C_9H_{15}O_3F_3S$: C, 41.53; H, 5.81. Found: C, 41.80; H, 5.95.

γ-Trifluoromethylallyl Chlorosulfinate.—A solution of 4.86 g. (0.041 mol.) of thionyl chloride in anhydrous ether was added through a dropping funnel to a stirred solution of 3.57 g. (0.027 mol.) of γ-trifluoromethylallyl alcohol in 60 ml. of anhydrous ether. The flask was maintained at 0° by means of an ice–water-bath, and the addition was over 1–1.5 hours. The reaction mixture was then stirred 1.5 hours longer. Ether was removed by distillation until about 8 ml. of solution remained. Final rectification was by distillation upon the micro-column resulting in 1.23 g. (22% yield) of γ-trifluoromethylallyl chlorosulfinate, b.p. 55° (6 mm.), n^{25}D 1.4220. The refractive index did not change over 5 minutes. An accurately weighed amount of the chlorosulfinate was treated with excess ice-cold dilute potassium hydroxide solution and this resulting solution was analyzed for chloride by the method of Volhard.

Anal. Calcd. for $C_4H_4F_3O_2Cl$: Cl, 17.0. Found: Cl, 16.6.

A solution of 0.135 g. (0.00153 mol.) of *n*-amyl alcohol and 0.12 g. (0.00153 mol.) of pyridine was added to 0.32 g. (0.00153 mol.) of the chlorosulfinate in 5 ml. of ether, cooled to $-30°$, over a 30-minute period. The reaction mixture was worked up in the same manner as described previously for γ-trifluoromethylallyl-*n*-amyl sulfite. All the low boiling components were removed on the aspirator, leaving a residue of 0.12 g., n^{25}D 1.4089. The infrared spectrum of this compound was identical with that of γ-trifluoromethylallyl-*n*-amyl sulfite except for a small carbonyl absorption in the above sulfite, probably due to *n*-valeraldehyde.

α-Trifluoromethylallyl Chlorosulfinate.—To a magnetically stirred solution of 14.3 g. (0.12 mol.) of thionyl chloride and 5.3 g. (0.024 mol.) of tri-*n*-butylamine hydrochloride, cooled in an ice-bath, was added 3.1 g. (0.024 mol.) of α-trifluoromethylallyl alcohol over a 45-minute period. Stirring was continued for 1 hour longer. The mixture was then flash distilled at 5 mm. to remove the amine salt. Distillation by means of a micro-column gave 2.78 g. (56% yield) of α-trifluoromethylallyl chlorosulfinate, b.p. 52° (39 mm.), n^{25}D 1.4088. The refractive index did not change over 5 minutes in the refractometer. An accurately weighed sample of this chlorosulfinate was treated with an excess of ice-cold dilute potassium hydroxide solution and the resulting solution was analyzed for chloride by the method of Volhard.

Anal. Calcd. for $C_4H_4F_3O_2SCl$: Cl, 17.0. Found: Cl, 16.7.

A solution of 0.29 g. (0.003 mol.) of *n*-amyl alcohol and 0.24 g. (0.003 mol.) of pyridine was added to a stirred solution of 0.70 g. (0.003 mol.) of the chlorosulfinate in 5 ml. of

ether, maintained at $-30°$ by means of a Dry Ice–acetone-bath. The reaction mixture was worked up as previously described for γ-trifluoromethylallyl-*n*-amyl sulfite. Volatile components were removed at the aspirator. The residue was 0.28 g., n^{25}D 1.4000. The infrared spectrum of this liquid was identical to that of α-trifluoromethyl-*n*-amyl sulfite, except for an alcohol band due to residual *n*-amyl alcohol.

Product Analysis.—A Perkin–Elmer vapor fractometer, model 154-B, was used for product analysis by vapor phase chromatography. The column used was the Perkin–Elmer "A" column, 2 meters in length. Helium was used as carrier gas. The relative amount of each product formed in a reaction was determined by measuring the area of the peak corresponding to that product and dividing this area by the total area of all product peaks. The area of each peak was calculated as the product of the peak height and the halfband width. In reactions where a quantitative measure of the products formed was desired, the internal standard method was used. In this method, a suitable volatile substance is added in known amount to the product mixture to be analyzed, with peak areas of product compounds then referred to the peak area of the internal standard. Ethyl *n*-butyl ether was used as the internal standard in this study. Factors necessary to correct for the difference between area per cent. and mole per cent. for internal standard and product were determined and applied.

The Reactions of α- and γ-Trifluoromethylallyl Alcohols with Thionyl Chloride.—The procedure utilized in the runs described in Table I for the reactions of α- and γ-trifluoromethylallyl alcohols with thionyl chloride was similar in every run. Addition of the reactants took place in the manner stated in Table I with addition time from 15 to 30 minutes. The temperature of the reaction mixture was maintained at 0° in all runs except runs 1 and 13 (24°) and runs 12 and 14 (4°). In runs with amine or amine salt present a flash distillation of the products proceeded product analysis by vapor phase chromatography. In runs without amine, the reaction mixture was analyzed for products directly after the allotted reaction time. In runs 7, 8 and 9, it was found that decomposition of α-trifluoromethylallyl chlorosulfinate occurred during the vapor phase analysis as a result of wet helium carrier gas. Passing the helium through a Dry Ice trap did not remove sufficient water to stop the decomposition. It was therefore necessary to measure the amount of chlorosulfinate formed by measuring the relative increase in the α-trifluoromethylallyl alcohol peak when water was added to the mixture, using the γ-trifluoromethylallyl chloride peak as the standard. Since the initial amount of alcohol could be measured only roughly, due to its identification peak tailing considerably from decomposition products, the amount of chlorosulfinate formed could only be measured to within 5–10% of the correct relative amount.

Kinetic Method in Chlorosulfinate Decomposition.—The rates of decomposition of α- and γ-trifluoromethylallyl chlorosulfinates as summarized in Table II were measured by the rate of sulfur dioxide evolution into a nitrometer filled with di-*n*-butyl phthalate. The nitrometer was of the type described by Steyermark[26] and had a 100-ml. capacity. The amount of chlorosulfinate used in each kinetic run was from 0.2 to 0.5 g. The volume of solvent used in runs with *n*-decane or nitrobenzene was about 5 ml. The general procedure utilized for these decompositions is as follows. The chlorosulfinate was transferred into a dry, tared 10-ml. standard taper flask in a dry-box. The flask was stoppered and accurately weighed to determine the amount of chlorosulfinate added. The flask was returned to the dry-box and, if solvent was used, it was added at this point. Then the flask was attached to a small spiral condenser, removed from the dry-box and attached to the nitrometer. A magnetically stirred oil-bath was used as a heat source. The temperature could not be controlled to better than ±2° during most rate measurements. The chlorosulfinate was also stirred by a magnetic stirring bar during the course of the decomposition. Before every reading of the amount of gas evolved, the leveling bulb of the nitrometer was lowered to the level of the di-*n*-butyl phthalate in the nitrometer.

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(26) A. Steyermark, "Quantitative Organic Microanalysis," The Blakiston Co., New York, N. Y., 1951.

The infinity volume, V_∞, for each kinetic run was determined through the ideal gas law formula $V = nRT/p$, where n is the moles of chlorosulfinate, R is the gas constant, T is room temperature and p is the corrected atmospheric pressure. The first-order rate constant was determined through the integrated first-order rate equation, In

$(1/1 - x) = kt$, where x is equal to V_t/V_∞ and V_t is equal to the volume of gas evolved at time t.

Allylic Rearrangements. LI. Displacement Reactions in Trifluoromethylallyl Systems[1]

BY J. A. PEGOLOTTI AND W. G. YOUNG

Kinetic studies of the reactions of azide ion in 70% acetone–30% water and iodide ion in anhydrous acetone with α- and γ-trifluoromethylallyl p-bromobenzenesulfonates and γ-trifluoromethylallyl chloride indicate that a γ-trifluoromethyl group enhances the rate of nucleophilic displacement upon allylic compounds. An SN2' mechanism for nucleophilic attack upon α-trifluoromethylallyl p-bromobenzenesulfonate is discussed.

As part of an investigation to determine the effect of the strong inductive group trifluoromethyl upon reaction mechanisms in the allylic system,[2] a study of bimolecular reactions was initiated with α- and γ-trifluoromethylallyl compounds. The major amount of previous work investigating displacement reactions upon allylic compounds has concerned the rates of reaction of allylic chlorides with such nucleophiles as iodide ion and ethoxide ion.[3] Although γ-trifluoromethylallyl chloride was prepared, the preparation of α-trifluoromethylallyl chloride was unsuccessful.[2] For this reason, it was necessary to prepare other compounds for the study. The compounds chosen in this respect were the p-bromobenzenesulfonate derivatives (brosylates) of α- and γ-trifluoromethylallyl alcohols. Generally, brosylates or tosylates (the p-methylbenzenesulfonate derivatives) of allylic alcohols are not stable; however, these brosylates were nicely crystalline stable compounds.

Kinetic studies were undertaken to determine the rate of reaction of α-trifluoromethylallyl brosylate (I), γ-trifluoromethylallyl brosylate (II), 1,1,1-trifluorobutyl brosylate (III), 4,4,4-trifluorobutyl brosylate (IV) and γ-trifluoromethylallyl chloride with potassium iodide in acetone. In addition, the rates of reaction of the allylic brosylates I and II with sodium azide in 70% acetone–30% water were measured. The rates with potassium iodide were followed titrimetrically while those with sodium azide were followed by vapor phase chromatography using an internal standard to measure the amount of product formed at specific intervals. Details of these methods of analysis will be found in the Experimental section. The rate constants derived from these studies are presented in Table I. In Table II, the relative reactivities of allylic chlorides toward potassium iodide in acetone are presented in relation to the reactivity of γ-trifluoromethylallyl chloride, while Table III compares the relative reactivities of the

(1) This work was supported in part by a grant to W. G. Young from the National Science Foundation.

(2) J. A. Pegolotti and W. G. Young, accompanying paper

(3) R. H. DeWolfe and W. G. Young, *Chem. Revs.*, **56**, 753 (1956).

saturated and unsaturated brosylates toward potassium iodide in acetone.
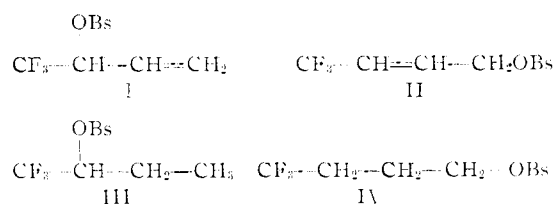
Discussion of the Results of Displacement Reactions upon γ-Trifluoromethylallyl Compounds.

The results of the kinetic studies of the reaction of potassium iodide in acetone upon the unsaturated and saturated primary brosylates II and IV and γ-trifluoromethylallyl chloride show that a γ-trifluoromethyl group increases the reactivity of the allylic system to SN2 displacement. This is illustrated in Table II, where it is noted that α trifluoromethylallyl chloride is 17 times more reactive toward potassium iodide than is allyl chloride itself, a larger increase in reactivity than that supplied by a γ-methyl group. It is also interesting to note that the rate of iodide displacement upon the allylic primary brosylate II is 113 times faster than upon the saturated primary analog IV. These observations are difficult to explain in the manner generally proposed for the increased reactivity of allylic compounds in SN2 reactions,[3] the stabilization of the transition state by the interaction of the π-electrons with the reaction center. If this stabilization did take place, there would necessarily arise a partial positive

$$CF_3 \cdot CH \cdots CH \cdots C\delta^+ \atop {\delta^+ \qquad \qquad Y\delta^- \atop \qquad X\delta^-}$$
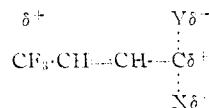
charge upon the carbon atom adjacent to the trifluoromethyl group and this partial positive charge cannot be stabilized by the trifluoromethyl group. It is much more desirable that a negative or partial negative charge be placed adjacent to a trifluoromethyl group to satisfy the electron-demanding