Tetrahedron. Vol. 30, pp. 2379 to 2384. Pergamon Press 1974. Printed in Great Britain

THE REARRANGEMENT OF BENZYLIC TRICHLOROMETHANESULFENATES TO SULFOXIDES AND CHLORIDES[1,a]

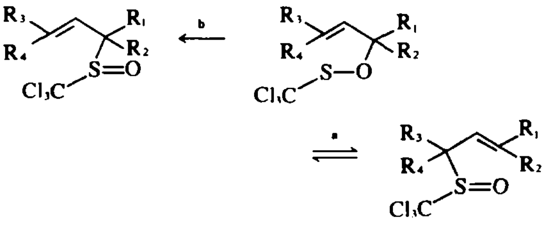
S. BRAVERMAN* and B. SREDNI
Department of Chemistry, Bar Ilan University, Ramat Gan, Israel

(*Received in the UK* 15 *November* 1973; *Accepted for publication* 5 *February* 1974)

Abstract—While benzyl trichloromethanesulfenate undergoes no rearrangement to sulfoxide even at high temperatures, the corresponding anisyl ester rearranges to *p*-anisyl trichloromethyl sulfoxide in hexane under mild conditions. Substitution of hexane by chloroform under similar conditions, lead to the formation of *p*-anisyl chloride and dichlorosulfine as main reaction products. This process is enhanced by the use of more polar solvents and higher temperatures. The conversion of trichloromethanesulfenate to chloride has also been observed with the benzyl and benzhydryl esters on heating in various solvents, though at very differing rates. Both rearrangements are suggested to take place by an ionization mechanism. Depending on the reaction conditions and nature of the substrate, the sulfenate anion can either recombine with the cation to give sulfoxide, or further dissociate to dichlorosulfine and chloride ion, which gives the benzyl chloride. The observation of an S_N1 type mechanism for rearrangement of sulfenates appears to be unique.

In recent years considerable interest has been focused on the thermal sulfenate-sulfoxide interconversion, not only because of its mechanistic and stereochemical interest,[2-5] but also because of its valuable application in the stereospecific and stereoselective synthesis of olefins.[6] Most of the mechanistic work performed has centred around the interconversion of allylic sulfoxides and sulfenates.[2,3] This interconversion represents a typical example of a generalized class of [2, 3] sigmatropic rearrangements[7] and has been studied independently by Mislow and coworkers[2] and by us.[3] The very large rate enhancement observed by Mislow and coworkers[2] for the racemization of optically active allylic sulfoxides as compared to dialkyl or diaryl sulfoxides, has prompted these authors to investigate the rearrangement of allylic sulfenates. On the other hand, our interest in the behaviour of these esters originated from previous studies on the [2, 3] sigmatropic rearrangement of allylic arenesulfinates to sulfones.[8,3f]

We have shown[3] that depending on the type of substitution, allylic trichloromethanesulfenates undergo rearrangement to allylic trichloromethyl sulfoxides by one of two different pathways.



The rearrangement by route **a**, which is accompanied by an 1,3-allylic shift and occurs spontaneously even at low temperatures is a reversible process believed to proceed by a concerted intramolecular mechanism. This type of process has been observed with allyl, crotyl and α,α-dimethylallyl trichloromethanesulfenates. On the other hand, the corresponding cinnamyl and γ,γ-dimethylallyl esters have been found to rearrange by route **b**, which proceeds only at higher temperatures, and could be explained in principle by some type of dissociation-recombination mechanism. The lack of an 1,3-allylic shift in this case is a result of the loss of conjugation energy and/or increase in steric crowding in the product, as well as the low driving force for the sufenate-sulfoxide rearrangement in general (ΔΔF ~ 3 kcal/mole).[2,4] As an extension of this work, and in order to study the mechanism of route **b** in further detail, we have investigated the behaviour of the chemically analogous benzylic system.

RESULTS AND DISCUSSION

(a) *Sulfenate-sulfoxide rearrangement.* This investigation was initiated by an examination of *p*-anisyl (*p*-methoxybenzyl) trichloromethanesulfenate **1**, which was prepared by the usual proce-

---

[a] Dedicated to the memory of the late Professor D. Darwish of the University of Alberta, Edmonton, Canada.

dure,[3,9] by reaction of the corresponding alcohol with Cl_3CSCl. This ester was found to undergo facile thermal rearrangement to the corresponding sulfoxide on heating in highly nonpolar solvents. The rate of rearrangement in hexane was conveniently measured by NMR by following the rate of decrease of the methylene NMR signal of **1** (singlet at τ 4·80, in $CDCl_3$). First-order rate constants and activation parameters for the rearrangement of **1** in hexane are shown in Table 1.

$R_1R_2CHOSCCl_3$

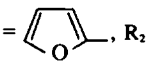
1: $R_1 = p\text{-}CH_3OC_6H_4\text{-}$, $R_2 = H$
2: $R_1 = C_6H_5$, $R_2 = H$
3: $R_1 = R_2 = C_6H_5$
4: $R_1 =$  , $R_2 = H$
5: $R_1 = C_6H_5$, $R_2 = CH_3$.

Table 1. Rate constants and activation parameters for the rearrangement of *p*-anisyl trichloromethanesulfenate 1[a] to *p*-anisyl trichloromethyl sulfoxide in hexane

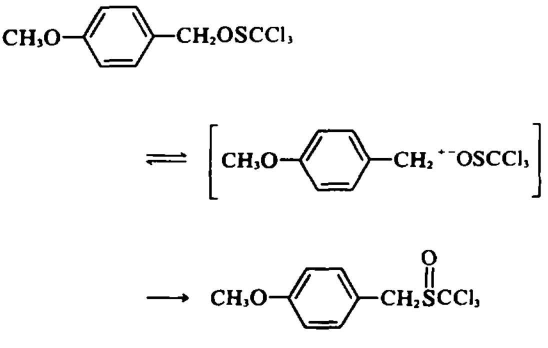
Temp °C	$k \times 10^5$, sec^{-1}	Activation parameters
44·0	0·48	$\Delta H^{\neq}$, 27·9 ± 0·5 kcal/mole
60·0	4·2 ± 0·09	$\Delta S^{\neq}$, 4·9 ± 1·6 eu
77·0	34·3 ± 0·3	

[a][Ester] = 0·042 M.

The positive entropy of activation tends to indicate that the observed 1,2 O→S shift does not take place by a concerted intramolecular mechanism, but rather by a homolytic or heterolytic mechanism. The homolytic mechanism could be excluded by a negative DPPH test, as well as by the lack of any free-radical type products, such as di-*p*-anisyl or thiosulfonate, as observed in the racemization of optically active benzyl *p*-tolyl sulfoxides,[4] which is believed to proceed by a free radical mechanism. In order to check the possible operation of an ionic mechanism, we have first attempted to measure the effect of solvent polarity on the rate of rearrangement. However, we have found that the rearrangement is very sensitive to the nature of the solvent. Thus, substitution of hexane by chloroform, under similar conditions, lead to the formation of *p*-anisyl chloride and dichlorosulfine as the main reaction products. This process is enhanced by the use of more polar solvents and higher temperatures (see Section b).

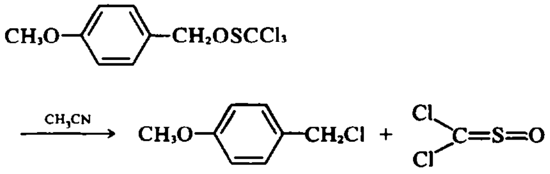
In sharp contrast to the facile rearrangement of **1**, we have found that benzyl trichloromethanesulfenate **2** does not undergo rearrangement to sulfoxide, and remains practically unchanged, even after five days of heating at 80° in hexane solution, or after heating for 24 h at 120° in benzene.[10] This result also contrasts to that reported[4] for the rearrangement of benzyl *p*-toluenesulfenate to benzyl *p*-tolyl sulfoxide which proceeds at a convenient rate ($k = 8{\cdot}75 \times 10^{-5}\ sec^{-1}$) at 120° in benzene solution. Although a radical pair mechanism has also been considered for this rearrangement,[4a] it was rejected in favor of a concerted intramolecular mechanism, on the basis of negative entropy of activation ($\Delta S^{\neq} = -2$ eu) and the predominant retention of configuration at carbon observed in the rearrangement of (−)-(R)-benzyl-α-d *p*-toluenesulfenate to (+)-benzyl-α-d *p*-tolyl sulfoxide.[4b] Obviously, such a mechanism cannot apply for the rearrangement of **1** to the corresponding sulfoxide, since it could not explain the enormous difference between **1** and **2**, with respect to this reaction. The same is true with regard to a free radical mechanism. On the other hand, the results are easily explained by an ionic mechanism in view of the well known rate enhancement of ionization of benzylic systems, of approximately four powers of ten, caused by a *p*-methoxy group.[11]

Further support for the suggested mechanism was obtained from the behaviour of other esters capable of developing stable carbonium ions. Thus, benzhydryl trichloromethanesulfenate **3** rearranged to the corresponding sulfoxide after 10 minutes of reflux of a hexane solution, while the rearrangement of the furfuryl ester **4** proceeded at a rate similar to that of **1**. These results are reminiscent to those reported for the rearrangement of benzyl and furfuryl thiocyanates to isothiocyanates,[12] as well as the rearrangement of benzylic sulfinates to sulfones and thionocarbamates to thiocarbamates.[11c,d] Information with regard to the type of ionization was obtained from an examination of the rearrangement of optically active (−)-α-phenylethyl trichloromethanesulfenate **5**, $[\alpha]_D^{20} = -20{\cdot}5°$ (ethanol), which rearranged on heating in hexane to (−)-α-phenylethyl trichloromethyl sulfoxide, $[\alpha]_D^{20} = -17{\cdot}8°$. This result tends to exclude ionization to dissociated ions as the major course of the rearrangement, since such a mechanism would yield a racemic product. On the basis of the evidence presented, we feel that the formation of trichloromethyl sulfoxides (including the cinnamyl) proceeds primarily by an ionization and ion pair recombination mechanism, e.g.:



While ion-pair mechanisms in nonpolar solvents are known in the literature,[13] the observation of such a mechanism for the rearrangement of sulfenates to sulfoxides[2–5] is apparently unprecedented.[14] Undoubtedly, this may be attributed to the relatively high acid strength of Cl_3CSOH, and the consequent high leaving group ability of its anion, as compared to sulfenate anions in general.[15] As mentioned above, the stability of the carbonium ion is also of crucial importance.

(b) *Sulfenate-chloride rearrangement.* As mentioned in the previous section the rearrangement of **1** was very sensitive to the polarity of the solvent. For example, substitution of the hexane by chloroform, under similar conditions, leads to the formation of a mixture composed of *p*-anisyl chloride, dichlorosulfine (70%, each) and the corresponding sulfoxide (30%), while the use of more polar solvents, such as methylene chloride or acetonitrile leads to the almost exclusive formation of the first products:



The possibility of the formation of *p*-anisyl chloride through the intermediacy of the sulfoxide was excluded by appropriate controls. For example, *p*-anisyl trichloromethyl sulfoxide remained completely unchanged after 5 h in refluxing chloroform. The conversion of trichloromethanesulfenate to chloride and dichlorosulfine has also been observed with the benzhydryl, furfuryl, and cinnamyl and even benzyl esters, on heating in various relatively polar solvents, though obviously at very differing rates. The second product, dichlorosulfine, ($Cl_2C{=}S{=}O$),[16] was isolated and identified with the aid of its infrared spectrum which shows three characteristic peaks[17] at 1150, 1050 and 950 cm^{-1}, and its mass spectrum (M^+, 130, 132, 134 in the ratio 1 : 0·6 : 0·1). This compound has recently been obtained also by the hydrolysis of trichloromethanesulfenyl chloride[18] and by the oxidation of thiophosgene.[19]

A kinetic study of the rearrangement of **1** and **2** to the corresponding chlorides under various conditions was performed by following the disappearance of the methylene signals in the NMR of the two esters, at τ 4·8 and τ 4·7, respectively. A summary of the first order rate constants, thus obtained, is presented in Table 2. Inspection of the data in this Table shows that the entropy of activation for the rearrangement of **1** in acetonitrile is positive ($\Delta S^{\ddagger}$, 10·5 ± 1·5 eu), which is indicative of a nonconcerted mechanism. Taking into account that the rearrangement to sulfoxide in nonpolar solvents proceeds by an ion-pair mechanism, it is conceivable that in the present case, dissociation to free ions is the major course of reaction. Evidence in support for this postulate is derived from an examination of the solvent and substituent effects on the rate of rearrangement as shown by the data in Table 2. Considering first the effect of the solvent, one finds that the rate of rearrangement of **1** is greatly enhanced by increasing the ionizing power of the solvent. A graph of log *k* for rearrangement of **1** to chloride in acetone, acetic anhydride, DMF, acetonitrile and nitromethane at 77° plotted against log *k* for ionization of *p*-methoxyneophyl tosylate[20] in the same solvents at 75° gives a straight line with a slope (*a* value[20]) of 0·9.

These data may be used as supporting evidence for an ionization mechanism for the reaction of *p*-anisyl trichloromethanesulfenate. A comparison between the rates of rearrangement of **1** and **2**, indicates that the former ester reacts by almost four hundred times faster. The size of this effect is also consistent with an ionic mechanism for the rearrangement. As observed in the rearrangement to

Table 2. Rate constants for the rearrangement of benzyl and *p*-anisyl trichloromethanesulfenates to the corresponding chlorides

Trichloromethane-sulfenate	Solvent	Temp., °C	[Ester], M	$k \times 10^5$, sec^{-1}
p-Anisyl	Acetone	77	0·042	6·9 ± 0·2
	Acetic Anhydride	77	0·041	28·2 ± 0·2
	DMF	77	0·043	38·3 ± 0·9
	Acetonitrile[a]	77	0·041	57·0 ± 1·2
	Nitromethane	77	0·040	91·2 ± 0·9
	Acetonitrile	42	0·042	0·5 ± 0·03
	DMSO	42	0·040	27·0 ± 0·3
	Acetonitrile	106		1345[b]
Benzyl	Acetonitrile	106	0·042	3·5 ± 0·09

[a] In this solvent, $\Delta H^{\ddagger}$ = 29·3 ± 0·49 Kcal/mole, $\Delta S^{\ddagger}$ = 10·5 ± 1·5 eu.
[b] Extrapolated from values at lower temperatures.

sulfoxide (Section *a*), the rate of rearrangement of the benzhydryl ester 3 to the corresponding chloride is higher than that of 1, and is completed within several minutes of heating at 80° in CH_3CN solution. Finally, we have found that the rearrangement of the optically active $(-)$-α-phenylethyl ester 5 gave a racemic chloride after heating for 6 h at 80° in acetonitrile. This result suggests that unlike the rearrangement to sulfoxide, the rearrangement to chloride proceeds by an ionization mechanism to the stage of dissociated ions. Subsequently the trichloromethanesulfenate anion undergoes fast decomposition to dichlorosulfine, and chloride anion which combines with the carbonium ion to give the observed product:

$$\mathrm{ROSCCl_3 \overset{slow}{\rightleftharpoons} R^+ + {}^-OSCCl_3}$$

$$\mathrm{Cl_3CSO^- \rightarrow Cl_2C{=}S{=}O + Cl^-}$$

$$\mathrm{R^+ + Cl^- \rightarrow RCl}$$

The instability of sulfenate anions is well known,[15] and evidence for the rapid decomposition of the trichloromethanesulfenate anion can be found in the spontaneous decomposition of Cl_3CSOH to dichlorosulfine and hydrogen chloride.[18] The main difference between the two rearrangements presented above lies in the ability of this anion to undergo recombination with carbonium ion to give sulfoxide or to undergo further decomposition. This in turn depends on the life time of the anion due to stabilization by the medium. The observed change in ths type of rearrangement with change in solvent polarity, becomes thus a natural consequence of the suggested mechanism. It is worthwhile noting that the rearrangement of trichloromethanesulfenates to chlorides is not completely new in the literature. Such a process has actually been observed during attempted thermal homolysis of the O–S bond in *t*-butyl trichloromethanesulfenate by Irwin and Kharasch.[21] Since the same volatile products were formed when this ester was decomposed as a liquid at 140° or as the vapor at 460°, a cyclic intramolecular mechanism has been prefered over an ion-pair mechanism.[21] However, no further mechanistic data were reported in support of this suggestion. Again, as outlined in Section (a) with regard to the sulfenate-sulfoxide rearrangement, the observation of an ionization mechanism for the sulfenate-chloride rearrangement presented above, appears to us to be novel and unique.

EXPERIMENTAL

M.ps and b.ps are uncorrected. IR spectra were recorded on Perkin–Elmer Grating Infrared Spectrophotometer Model 257. NMR Spectra were recorded on Varian HA 100 NMR Spectrometer, and mass spectra on Perkin–Elmer Hitachi RMU 6 Spectrometer. Optical rotations were measured with a Perkin–Elmer 141 Polarimeter. All commercial reagents and materials were distilled or crystallized before use and all solvents employed were carefully purified by standard procedures.[22]

Preparation of the sulfenates. p-Anisyl trichloromethanesulfenate 1. A 10·00 g quantity (0·072 mole) of *p*-anisyl alcohol and 8·00 g (0·1 mole) of pyridine were weighed into a 250 ml round bottom flask. After addition of 100 ml of anhydrous ether, the flask was cooled in a dry ice-acetone bath, and 15 g (0·075 mole) of Cl_3CSCl dissolved in 150 ml of dry ether were added gradually during 45 min, with stirring. The reaction mixture was kept in the cooling bath for an additional hour, and then transfered to a separatory funnel containing 200 ml of ether. The ether solution was washed 3 times with 100 ml portions of water, 3 times with 100 ml of 5% HCl, 3 times with portions of $NaHCO_3$ and again 3 times with 100 ml portions of water. After drying over anhydrous $MgSO_4$, filtration and evaporation of ether, a yellowish product was obtained. This was purified with active carbon and crystallized at 0° from petroleum ether (b.p. 40–60°). M.p. = 27·5–28·5° (85% yield), IR absorption ($CHCl_3$) showed bands at 940 and 910 cm^{-1}, characteristic of sulfenates. The NMR spectrum ($CDCl_3$) showed signals at τ 6·20 (3 H, s), 4·80 (2 H, s), 3·16 (2 H, d, J = 8 Hz), 2·70 (2 H, d, J = 8 Hz). The mass spectrum was also in accord with the assigned structure.[23] Calcd. for $C_9H_9O_2SCl_3$: C, 37·58; H, 3·15. Found: C, 37·80; H, 3·23%.

Benzyl trichloromethanesulfenate 2 was prepared from benzyl alcohol and Cl_3CSCl as described for 1 (yield 80·2%). n_D^{25} = 1·5428, characteristic IR absorption ($CHCl_3$) at 930 and 900 cm^{-1}, NMR ($CDCl_3$) τ 4·70 (2 H, s) and 2·70 (5 H, s). Calcd. for $C_8H_7OSCCl_3$: C, 37·30; H, 2·74. Found: C, 37·43; H, 2·81%.

Benzhydryl trichloromethanesulfenate 3, was prepared from benzhydryl alcohol and Cl_3CSCl as described for 1. Purification by sublimation of the crude product gave a white solid, m.p. 58–60° (yield 60%). IR absorption ($CHCl_3$) showed characteristic bands at 940 and 910 cm^{-1}. The NMR spectrum ($CDCl_3$) showed two singlets at τ 3·60 (1 H, s) and 2·70 (10 H, s). Calcd. for $C_{14}H_{11}OSCl_3$: C, 50·60; H, 3·31; Found: C, 50·38; H, 3·26%.

Furfuryl trichloromethanesulfenate 4 was prepared from furfuryl alcohol and Cl_3CSCl as described for 1, n_D^{25} = 1·5183, characteristic IR bands ($CHCl_3$) at 930 and 910 cm^{-1} and NMR absorption ($CDCl_3$) at τ 2·5 (1 H, d), 3·52 (1 H, d), 3·70 (1 H, q) and 4·78 (2 H, s). Because of the low stability of this ester elemental analysis was not performed.

$(-)$-α-Phenylethyl trichloromethanesulfenate 5 was prepared by reaction of $(-)$-α-phenylethyl alcohol, (obtained by the method described by Isaacs,[24] $[\alpha]_D^{20} = -12°$ (ethanol), lit.[24] $[\alpha]_D = -13°$), with Cl_3CSCl, as described for 1 (yield 80%). $[\alpha]_D^{20} = -20{\cdot}5°$ (ethanol). The IR spectrum ($CHCl_3$) showed a sulfenate characteristic peak at 940 cm^{-1}, and the NMR spectrum ($CDCl_3$) showed signals at τ 8·31 (3 H, d, J = 7 Hz), 4·60 (1 H, q, J = 6 Hz) and 2·60 (5 H, s). Calcd. for $C_9H_9OSCl_3$: C, 39·80; H, 3·33. Found: C, 40·02; H, 3·38%.

Rearrangements of sulfenates to sulfoxides. Rearrangement of p-anisyl trichloromethanesulfenate 1. A solution of 0·500 g of 1 in 10 ml. of hexane was heated in a sealed tube for 3 h at 80°. After cooling and evaporation of the solvent at the water aspirator a solid residue (0·490 g, 98%

yield) was left. Crystallization from pentane gave crystals, m.p. 111·5–112·5°. The IR spectrum ($CHCl_3$) showed characteristic[25] absorption at 1100 cm^{-1}, and the NMR spectrum ($CDCl_3$) displayed three groups of lines. An aromatic AA′BB′ quartet (4 H) centred at τ 2·96 (Δν 0·4 ppm, $J_{AA'} = J_{BB'} = 8$ Hz), an AB quartet (2 H) centred at τ 5·92 (Δν 0·5 ppm, $J_{AB} = 12$ cps) due to the diastereotopic[26] methylenic protons, and a sharp singlet at τ 6·23 (3 H). Calcd. for $C_9H_9O_2SCl_3$: C, 37·58; H, 3·15. Found: C, 37·56; H, 2·96%.

Rearrangement of benzhydryl trichloromethanesulfenate 3. A solution of 1·0 g of 3 in 20 ml of hexane was heated for 10 min at reflux temperature. After evaporation of the solvent and crystallization from pentane 0·9 g (90% yield) of white crystals were obtained, which had m.p. 79°, exhibited the characteristic[25] sulfoxide band at 1085 cm^{-1} in IR, and gave two NMR signals ($CDCl_3$) at τ 2·82 (10 H, s) and 4·74 (1 H, s). Calcd. for $C_{14}H_{11}OSCl_3$: C, 50·60; H, 3·31. Found: C, 50·42; H, 3·27%.

Rearrangement of furfuryl trichloromethanesulfenate 4. A solution of 1·0 g of 4 in 20 ml dioxan was heated for 2 h at reflux temperature. The solution darkened during the heating because of partial decomposition. After dilution with 100 ml of ether, it was washed with three 100 ml portions of water, and dried over anhydrous $MgSO_4$. The black residue obtained after evaporation of the ether, was dissolved in petroleum ether (b.p. 40–60°) and purified with active carbon. After evaporation of the solvent, 0·75 g (75%) of the sulfoxide was obtained as a yellowish liquid, $n_D^{25} = 1{\cdot}5395$. The IR showed characteristic absorption ($CHCl_3$) at 1110 cm^{-1} and the NMR spectrum ($CDCl_3$) showed signals at τ 2·50 (1 H, d, J = 2 Hz), 3·44 (1 H, d, J = 2 Hz), 3·58 (1 H, q, J = 2 Hz), 5·40 (1 H, d, J = 14 HZ), 5·90 (1 H, d, J = 14 Hz).

Rearrangement of (−)*-α-phenylethyl trichloromethanesulfenate* 5. A solution of 1·0 g of (−)-5 in 10 ml of hexane was heated in a sealed tube for an overnight period at 80°. After evaporation of the solvent 0·9 g (90%) of solid material was left, m.p. 120°, $[\alpha]_D^{20} = -17{\cdot}8°$ (ethanol). The IR spectrum ($CHCl_3$) showed characteristic absorption at 1100 cm^{-1}, and the NMR spectrum (CCl_4) displayed three sets of lines, a singlet at τ 2·7 (5 H) two quartets at τ 5·47 (J = 6 Hz) and 5·76 (together 1 H) and two doublets at τ 8·57 (J = 7 Hz) and 8·74 (together 3 H). Calcd. for $C_9H_9OSCl_3$: C, 39·80; H, 3·33. Found: C, 40·12; H, 3·35%.

Attempted rearrangement of benzyl trichloromethanesulfenate 2. A solution of 1·18 g in 10 ml hexane was heated in a sealed tube for 123 h at 80°. After cooling and evaporation of the solvent under reduced pressure, unchanged starting material was obtained as indicated by IR and NMR spectra.

DPPH test. To a solution of 1·00 g (0·003 mole) of 1 in 10 ml of hexane, 0·76 g (0·002 mole) of diphenylpicryl hydrazyl was added. The colored solution was heated in a sealed tube for 10 h at 80°. No change in the intensity of the color was noticed. On cooling, a white solid precipitated which was collected by filtration (0·97 g, 97%) and showed IR and NMR spectral data identical with that of *p*-anisyl trichloromethyl sulfoxide.

Rearrangements of sulfenates to chlorides. Rearrangement of p-anisyl trichloromethanesulfenate 1. A solution of 5·00 g of 1 in 10 ml acetonitrile was heated in a sealed tube for 2 h at 80°. After evaporation of the solvent a liquid residue (4·85 g, 97%) was left. Its IR spectrum ($CHCl_3$) showed peaks at 950, 1050 and 1150 cm^{-1}, characteristic of dichlorosulfine and at 1030, 1170, and 1250, 1510 and 1610 cm^{-1}, due to *p*-anisyl chloride. The crude product was distilled and the fraction boiling at 84–5° (5 mm Hg) was collected (2·3 g, 80%) and identified as *p*-anisyl chloride by its IR spectrum (see above), NMR spectrum ($CDCl_3$): τ 6·20 (3 H, s); 5·46 (2H, s), 3·12 (2 H, d, J = 9 Hz) and 2·70 (2 H, d, J = 9 Hz); as well as by its mass spectrum which showed M^+ peaks at *m/e* 156 and 158 in the ratio of 3 : 1.

Rearrangement of benzyl trichloromethanesulfenate 2. This ester was treated as described for 1, except that heating was continued for 98 h. The IR of the crude material also showed the presence of dichlorosulfine (peaks at 950, 1050 and 1150 cm^{-1}). After distillation (b.p. 57–58° at 8 mm Hg), benzyl chloride was obtained, $n_D^{20} = 1{\cdot}5363$, NMR spectrum ($CDCl_3$): τ 5·42 (2 H, s) and 2·82 (5 H, s), and mass spectrum: M^+ at *m/e* 126 and 128 in the ratio 3 : 1.

Rearrangement of benzhydryl trichloromethanesulfenate 3. This ester was treated as described for 1, except that heating was only for 10 min. The IR spectrum of the crude material also indicated the presence of dichlorosulfine. The isolated benzhydryl chloride was identified by its NMR spectrum ($CDCl_3$) which showed two signals at τ 3·90 (1 H, s) and at 2·70 (10 H, m) and by its M^+ in the mass spectrum at *m/e* 202 and 204 (3 : 1).

Rearrangement of (−)*-α-phenylethyl trichloromethanesulfenate* 5. A 2·0 g quantity of (−)-5 was dissolved in 80 ml of acetonitrile and the solution was heated in a sealed tube at 80° for 6 h. After evaporation of the solvent, the residue showed an NMR spectrum ($CDCl_3$) consistent with α-phenylethyl chloride: τ 2·68 (5 H, s), 4·90 (1 H, q, J = 6·0 Hz) and 8·21 (3 H, d, J = 6 Hz). The mass spectrum exhibited M^+ peaks at *m/e* 140, 142 in the ratio of 1 : 0·3. $[\alpha]_D = 0°$ (ethanol).

Isolation of dichlorosulfine. A 30·0 g quantity of 1 was dissolved in 50 ml of acetonitrile and refluxed for 8 h. After evaporation of the solvent, the crude residue was fractionally distilled, and the fraction boiling at 40–41°/28 mm Hg was collected. This sharp odor material showed characteristic IR absorption ($CHCl_3$) at 950, 1050 and 1150 cm^{-1} and M^+ in the mass spectrum at *m/e* 130, 132, 134 in the ratio 1 : 0·6 : 0·1 (base peak at 82 due to CCl_2^+).

Kinetic measurements. Essentially the same procedure was used for the kinetic runs of both rearrangements described above. A quantity of the ester was weighed into a volumetric flask and the appropriate solvent was added to the mark. The solution (*ca* 1%) was shaken and transferred to ampoules in 5 ml portions. After the ampoules were sealed and immersed in the constant temperature bath, they were removed at appropriate time intervals and quenched in a cooling bath. The solvent was evaporated under reduced pressure and the NMR spectrum, in $CDCl_3$ using TMS as internal standard, was recorded. The rate constants were calculated from the first-order kinetic expression, $k = (2{\cdot}303/t) \log (a/a-x)$. The calculations were based on the intensities of the methylenic signals of the ester and sulfoxide or chloride. For example, in the rearrangement of 1 to the corresponding chloride, a represents the sum of the areas of the peaks at τ 4·80 and 5·46, while a–x represents the area of the peak at τ 4·80, at time t. Plots of log (a/a–x) vs t gave good straight lines for each run. The transition-state enthalpy of activation, $\Delta H^{\neq}$, was obtained from a plot of log k/T vs 1/T. $\Delta H^{\neq} = -\text{slope}.\ 2{\cdot}303\,R$. The entropy of activation was calculated by the Eyring equation; $k = (k'T/h)e^{\Delta S^{\neq}/R}\cdot e^{-\Delta H^{\neq}/RT}$; where *k* is the rate constant, while k′ and h, are the Boltzmann and Planck constants, respectively.

REFERENCES

[1] Presented in part at the 40th Meeting of the Israel Chemical Society, Haifa, October 20–22 (1970); See S. Braverman and B. Sredni, *Proceedings Israel J. Chem.* **8**, 30 (1970); Taken from the M.Sc. Thesis of B. Sredni, Bar-Ilan University, 1972

[2] E. G. Miller, D. R. Rayner and K. Mislow, J. Am. Chem. Soc. **88**, 3139 (1966); K. Mislow, *Rec. Chem. Prog.* **28**, 217 (1967); P. Bickart, F. W. Carson, J. Jacobus, E. G. Miller and K. Mislow, *J. Am. Chem. Soc.* **90**, 4869 (1968); R. Tang and K. Mislow, *Ibid.* **92**, 2100 (1970)

[3a] S. Braverman and Y. Stabinsky, *Chem. Comm.* 270 (1967); [b] S. Braverman and Y. Stabinsky, *Israel J. Chem.* **5**, 71 (1967); [c] *Ibid.* **5**, 125 (1967); [d] S. Braverman and C. Simons, in *Mechanisms of Organic Sulfur Reactions*, Ed. N. Kharasch, Intra-Science Foundation, Santa-Monica, Vol. 2, p. 101 (1968); [e] Y. Stabinsky, M. Sc. Thesis, Bar-Ilan University, 1968; [f] S. Braverman, *Int. J. Sulfur Chem.* (*C*) **6**, 149 (1971)

[4a] D. R. Rayner, E. G. Miller, P. Bickart, A. J. Gordon and K. Mislow, *J. Am. Chem. Soc.* **88**, 3138 (1966); [b] E. G. Miller, D. R. Rayner, H. J. Thomas and K. Mislow, *Ibid.* **90**, 4861 (1968)

[5] T. J. Maricich and C. K. Harrington, *J. Am. Chem. Soc.* **94**, 5115 (1972); T. Numata and S. Oae, *Int. J. Sulfur Chem.* (*A*) **1**, 215 (1971)

[6] D. A. Evans, G. C. Andrews and C. L. Sims, *J. Am. Chem. Soc.* **93**, 4956 (1971); D. A. Evans and G. C. Andrews, *Ibid.* **94**, 3672 (1972); P. A. Grieco, *Chem. Comm.* 702 (1972); D. A. Evans, G. C. Andrews, T. T. Fugimoto and D. Wells, *Tetrahedron Letters* 1385, 1389 (1973)

[7] J. E. Baldwin, R. E. Hackler and D. P. Kelly, *Chem. Comm.* 538 (1968); For other leading references see: A. Jefferson and F. Scheinman, *Quart. Rev.* **22**, 391 (1968); V. Rautenstrauch, *Chem. Comm.* 4 (1970); J. E. Baldwin and J. A. Walker, *Ibid.* 354 (1972); S. Ranganathan, D. Ranganathan, R. S. Sidhu and A. K. Mehrotra, *Tetrahedron letters* 3577 (1973)

[8] S. Braverman, Ph. D. Thesis, University of Alberta, Edmonton, Canada, 1963; D. Darwish and S. Braverman, 48th Chemical Institute of Canada Conference, Montreal, Canada, May 30–June 2, 1965. For the rearrangement of propargyl and furfuryl arenesulfinates, see: S. Braverman and H. Mechoulam, *Israel J. Chem.* **4**, 17 p (1966); **5**, 71 (1967); S. Braverman and T. Globerman, *Tetrahedron Letters* 3023 (1973)

[9] G. Sosnovsky, *J. Chem. Soc.* 3139 (1956)

[10] At a still higher temperature, 140°, rearrangement to benzyl chloride was observed

[11] e.g. [a] G. S. Hammond, C. E. Reeder, F. T. Fang and J. K. Kochi, *J. Am. Chem. Soc.* **80**, 568 (1958); [b] D. Darwish and R. A. McLaren, *Tetrahedron Letters* 1231 (1962); [c] S. Braverman and S. Steiner, *Israel J. Chem.* **5**, 267 (1967); [d] S. Braverman and B. Goldrath, *Int. J. Sulfur Chem.* (*A*) **3**, 55 (1973)

[12] L. A. Spurlock and R. G. Fayter, *J. Org. Chem.* **34** 4035 (1969); A. Fava, A. Iliceto, A. Ceccon and P. Koch, *J. Am. Chem. Soc.* **87**, 1045 (1965); A. Fava, U. Tonellato, and L. Congin, *Tetrahedron Letters* 1657 (1965); A. Fava, in *Organic Sulfur Compounds* Vol II, ed. N. Kharasch and C. Y. Meyers, Pergamon, Oxford, p. 86, 1966

[13] e.g. C. A. Grob and S. Winstein, *Helv. Chim. Acta* **35**, 782 (1952)

[14] For a report on a similar mechanism for the solvolyis of 1, see: S. Braverman and D. Reisman, *Tetrahedron letters* 3563 (1973)

[15] For a review see: E. Kuhle, *Synthesis* 566 (1971)

[16] For leading references on sulfines, see: B. Zwanenburg and J. Strating, *Quart. Repts. Sulfur Chem.* **5**, 79 (1970); B. F. Bonini, G. Maccagnani, L. Thijs and B. Zwanenburg, *Tetrahedron Letters* 3569 (1973)

[17] J. F. King and T. Durst, *Can. J. Chem.* **44**, 819 (1966)

[18] J. Silhanek and M. Zbirovsky, *Chem. Comm.* 878 (1969)

[19] J. Strating, L. Thijs and B. Zwanenburg, *Tetrahedron Letters* 4461 (1969)

[20] S. G. Smith, A. H. Fainberg and S. Winstein, *J. Am. Chem. Soc.* 83, 618 (1961)

[21] R. S. Irwin and N. Kharasch, *Ibid.* **82**, 2502 (1960)

[22] e.g. L. F. Fieser *Experiments in Organic Chemistry*, 3rd Edition D. C. Heath and Co., Boston, 1957; A. I. Vogel *Practical Organic Chemistry*, Longmans, London, 1958

[23] The mass spectral data of this and the other sulfenates as well as sulfoxides will be reported separately because of their fragmentation interest

[24] N. S. Isaacs, *Experiments in Physical Organic Chemistry*, Macmillan London, 1969, p. 184

[25] L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, Wiley, New York, pp. 357–360, 1958; K. Nakanishi, *Infrared Absorption Spectroscopy*, Holden-Day, San Francisco, p. 54, 1962

[26] K. Mislow and M. Raban, *Topics in Stereochemistry*, Vol I, N. L. Allinger and Eliel, ed., Wiley, New York, Chapter 1, 1967