α-Halo Sulfones. XI. The Ramberg–Bäcklund Rearrangement of Trichloromethyl Sulfones[1]

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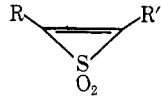
Abstract: Several trichloromethyl sulfones have been subjected to reaction with hydroxide ion in refluxing aqueous tetrahydrofuran in an attempt to elucidate the possible mechanistic pathways involved in the ensuing rearrangement. In particular, sulfones were selected to permit examination of the possible generation and fate of dichloro episulfones and chlorothiirene dioxides. The Ramberg–Bäcklund rearrangement of trichloromethyl sulfones was found to give rise to very small amounts of neutral products, except in those instances in which the dichloro episulfone intermediate was *gem*-dialkyl substituted. Sulfonic acid formation generally predominated and the stated intervention of dichloro episulfones establishes that α-halo sulfones in general are very prone to 1,3 elimination and episulfone formation when exposed to base, regardless of the degree of halogen substitution. On the basis of the available data, it has been inferred that chlorothiirene dioxide formation occurs at a competitive rate only when the dichloro episulfone proton to be abstracted is appreciably acidic; otherwise, hydroxide ion attacks at tetravalent sulfur with ring opening of the strained intermediate.

In earlier papers of this series, we have been concerned with the base-promoted rearrangements of α-halo sulfones. Attention has been focused not only upon the detailed nature of the rearrangement mechanism, but also upon the possible isolation of highly strained and reactive cyclic sulfones. When appropriately constructed α,α-dihalo sulfones are treated with various bases, a marked tendency for consecutive 1,3 and 1,2 eliminations of hydrogen chloride exists, and thiirene 1,1-dioxides (**1**) are generated.[2-4] However, because of their inherent reactivity such unsaturated heterocycles (**1**) are not isolatable under the customary rearrangement conditions; rather, their intervention has been established indirectly.[3,5] The present paper describes the extension of our studies to



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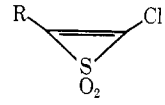

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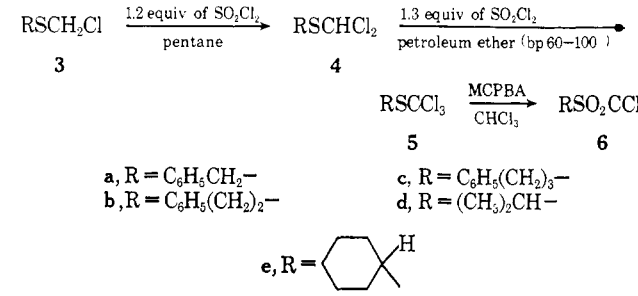
trichloromethyl sulfones in which structural modifications have been made to provide insight into the possible generation and fate of 2,2-dichloro episulfones and chlorothiirene 1,1-dioxide intermediates of type **2**.

Results

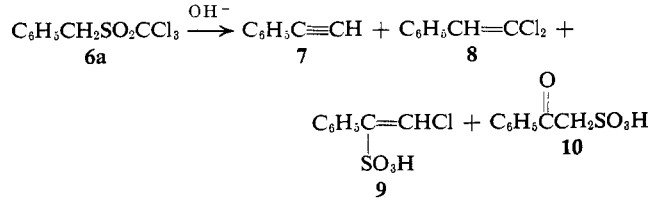
Synthesis. The requisite trichloromethyl sulfones (**6a–e**) were prepared in 37–68% over-all yields by stepwise chlorination of the known[4] chloromethyl sulfides (**3**) and immediate oxidation of the crude[6] trichloromethyl sulfides (**5**) with *m*-chloroperbenzoic acid (MCPBA) in chloroform solution at 0° (Chart I). Dichlorination of **3** in the indicated stepwise manner was found to be superior to the direct addition of 2.5 molar equiv of sulfuryl chloride which consistently

Chart I. Synthetic Scheme for Preparation of Trichloromethyl Sulfones



gave a poorer yields of inferior quality products. No products arising from chlorination of the α′-carbon atom were detected.[7]

Rearrangement Results. The products of the various rearrangements are summarized by the ensuing equations and pertinent comments. Characterization of the products is described in its entirety in the Experimental Section. When benzyl trichloromethyl sulfone (**6a**) was gently refluxed (65°) with 6 molar equiv of 2.0 *N* sodium hydroxide–tetrahydrofuran (1:1) for periods up to 8 hr, a neutral fraction was obtained which contained phenylacetylene (**7**, 2%), 1,1-dichloro-2-phenylethene (**8**, <1%), and trace amounts of two very minor products which were not present in quantities sufficient for identification. However, it was



(1) For the previous paper in this series, see A. L. Paquette and L. S. Wittenbrook, *J. Am. Chem. Soc.*, **90**, 6783 (1968).

(2) L. A. Paquette and L. S. Wittenbrook, *Chem. Commun.*, 471 (1966).

(3) L. A. Paquette and L. S. Wittenbrook, *J. Am. Chem. Soc.*, **89**, 4483 (1967).

(4) L. A. Paquette, L. S. Wittenbrook, and V. V. Kane, *ibid.*, **89**, 4487 (1967).

(5) Recently, a modified procedure has been employed successfully to provide synthetic entry to the first member of this class of compounds (**1**, R = R′ = C_6H_5) [L. A. Carpino and L. V. McAdams, III, *ibid.*, **87**, 5804 (1965)].

(6) Purification of the trichloromethyl sulfides was not attempted because these compounds were observed to hydrolyze rapidly when exposed to the atmosphere.

(7) This result was anticipated from the work of L. A. Paquette, L. S. Wittenbrook, and K. Schreiber, *J. Org. Chem.*, **33**, 1080 (1968), and pertinent references included therein.

established unequivocally by comparison of vpc retention times on different columns that neither of these two substances was chlorophenylacetylene. Appropriate work-up of the base-soluble fraction led to the isolation of 1-chloro-2-phenylethene-2-sulfonic acid (**9**, 27%) and acetophenone-ω-sulfonic acid (**10**, 39%) as their *p*-toluidine salts.

Reaction of phenethyl trichloromethyl sulfone (**6b**) under similar conditions was found to give only trace quantities of 1-chloro-3-phenyl-1-propene (**11**) and 1,1-dichloro-3-phenyl-1-propene (**12**). Rather, this halo sulfone was converted almost completely into vinylsulfonic acids **13** and **14** which were isolated in

$$\underset{\mathbf{6b}}{C_6H_5CH_2CH_2SO_2CCl_3} \xrightarrow{OH^-} \underset{\mathbf{11}}{C_6H_5CH_2CH{=}CHCl} +$$

$$\underset{\mathbf{12}}{C_6H_5CH_2CH{=}CCl_2} + \underset{\mathbf{13}}{C_6H_5CH_2C(SO_3H){=}CHCl} + \underset{\mathbf{14}}{C_6H_5CH_2C(SO_3H){=}CCl_2}$$

yields of 37 and 22%, respectively. No product analogous to **10** was detected in any of the various rearrangements of **6b**.

In the case of homolog **6c**, clear preference for the formation of vinylsulfonic acids was again demonstrated. Thus whereas minor amounts (approximately 1% each) of neutral substances **15**, **16**, and **17** could be detected, the major product (66% yield) was found to be **18**. A compound that might correspond to **14** was not found, but small quantities of somewhat intractable material were separated which displayed infrared spectra resembling that of **10**. Attempts to purify this material proved futile, and it was not examined further.

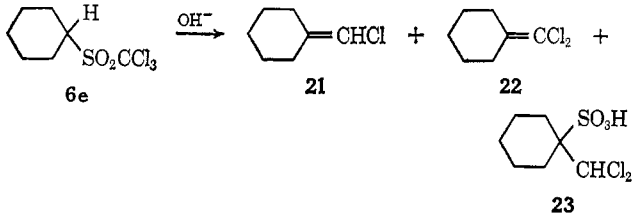
$$\underset{\mathbf{6c}}{C_6H_5(CH_2)_3SO_3CCl_3} \xrightarrow{OH^-} \underset{\mathbf{15}}{C_6H_5(CH_2)_2C{\equiv}CH} +$$

$$\underset{\mathbf{16}}{C_6H_5(CH_2)_2CH{=}CHCl} +$$

$$\underset{\mathbf{17}}{C_6H_5(CH_2)_2CH{=}CCl_2} + \underset{\mathbf{18}}{C_6H_5(CH_2)_2C(SO_3H){=}CHCl}$$

The differing structural elements in **6d** and **6e** obviously do not allow for further dehydrohalogenation of initially formed 2,2-dichloro-3,3-dialkyl episulfone intermediates. This phenomenon was expected to be reflected in a divergent nature of rearrangement products and this expectation was realized. Exposure of **6d** to hydroxide ion in aqueous tetrahydrofuran solution resulted in good conversion to vinyl dichloride **19** (14%) and dichloromethylsulfonic acid **20** (72%). Similarly, **6e** was cleanly rearranged to dichloromethylenecyclohexene (**22**, 51%) and 1-dichloromethylcyclohexylsulfonic acid (**23**, 29%). In addition, the last reaction always yielded a small but reproducible quantity of vinyl chloride **21**. The comparable product was not detected in the case of **6d**. Interestingly, when **6d** was treated with 2 *N* sodium hydroxide solution in the absence of cosolvent (100°), an increase in the yield of **20** to 86% and a concomitant decrease in the amount of **19** (8%) was noted.

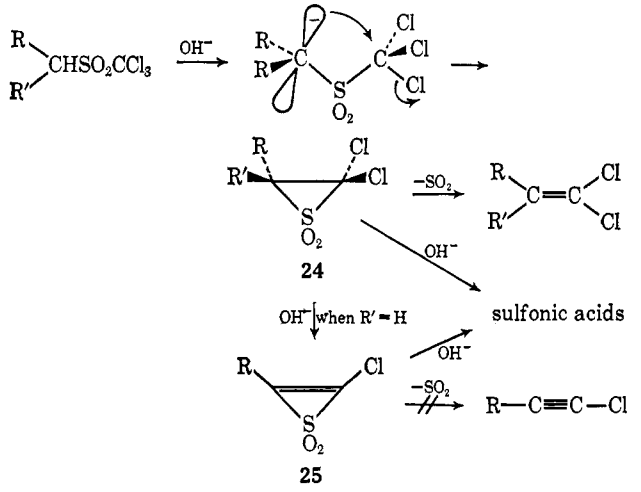
$$\underset{\mathbf{6d}}{(CH_3)_2CHSO_2CCl_3} \xrightarrow{OH^-} \underset{\mathbf{19}}{(CH_3)_2C{=}CCl_2} + \underset{\mathbf{20}}{(CH_3)_2C(SO_3H)CHCl_2}$$



Discussion

Neutral Products. A mechanistic pathway which involves the generation of α-sulfonyl carbanions and subsequent intramolecular 1,3 displacement of chloride ion, presumably *via* semi-W transition states,[1] can be inferred from the above results (Chart II). The dichloro episulfone intermediates (**24**) suffer loss of sulfur dioxide when the R and R′ substituents are other than hydrogen. For instance, isopropyl trichloromethyl sulfone (**6d**) gave rise to dichloride **19** in 14% yield whereas cyclohexyl trichloromethyl sulfone (**6e**) afforded dichloromethylenecyclohexane (**22**) in 51% yield. Interestingly, however, when the three-membered ring bears a hydrogen substituent, very little direct expulsion of sulfur dioxide is observed. This result lies in direct contrast to the general behavior of similarly constructed chloro episulfones, which intermediates in general exhibit a propensity for vinyl chloride formation.[4] Rather, the various product compositions denote that such dichloro episulfones are subject to rapid attack by hydroxide ion. Two competing processes now may intervene; the first involves nucleophilic attack at tetravalent sulfur and ring cleavage to dichloromethyl-substituted sulfonic acids (see subsequent section), while the second centers about the capability of such intermediates for dehydrohalogenation to chlorothiirene dioxides (**25**).

Chart II. Possible Routes to Neutral Products in the Ramberg–Bäcklund Rearrangement of Trichloromethyl Sulfones

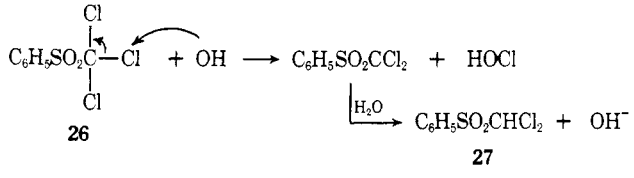


Thiirene dioxides, *e.g.*, **1**, are now recognized to expel sulfur dioxide and give rise to acetylenes in alkaline solution or simply upon warming.[2-5,8,9] Chloroacetylene production was therefore anticipated from intermediates of type **25**. However, they were not found as products in the various rearrangements studied. In the particular case of **6a**, the stability of

(8) L. A. Carpino and R. Y. Rynbrandt, *J. Am. Chem. Soc.*, **88**, 5682 (1966).
(9) L. A. Paquette, *ibid.*, **86**, 4089 (1964).

authentic chlorophenylacetylene toward hydroxide ion was carefully tested; a sample was subjected to the conditions of rearrangement and was recovered unchanged in 91% yield. No minor transformation products were detected. This evidence clearly established that if this product were formed during this particular rearrangement, it would have proven capable of isolation. Although the stabilities of the remaining expected chloroacetylenes were not checked in this manner, the progress of each rearrangement was followed by vpc. In no case was there observed the formation of a transient intermediate which was subsequently destroyed by further chemical change. Thus it appears that chlorothiirene dioxides (**25**), if formed (see below), are less subject to extrusion of sulfur dioxide than their nonchlorinated counterparts.

The isolation of discrete quantities of acetylenes and vinyl chlorides suggests that reduction of the trichloromethyl sulfones to their dichloromethyl congeners is occurring since the latter substrates are known to produce such neutral compounds in alkaline solution.[4] Such rationalization was easily verified by arresting the rearrangements of **6a–c** short of completion, at which point 10–20% yields of the derived dichloromethyl sulfones could be isolated. Sodium sulfite has previously been implicated in the reduction of halo sulfones.[10] However, in the present instance, the major products are sulfonic acids and very little sodium sulfite is generated. It appeared, therefore, that the base was very likely responsible for the trichloro sulfone reduction. To test this concept, phenyl trichloromethyl sulfone (**26**), a system incapable of Ramberg–Bäcklund rearrangement, was heated with 2 *N* sodium hydroxide–tetrahydrofuran for 6 hr; upon work-up, dichloromethyl phenyl sulfone (**27**) was isolated in 15% yield. The exact nature of the reduction process is unknown. However, it appears most



26 **27**

plausible that displacement at a halogen atom occurs to produce an α-sulfonyl carbanion which subsequently is protonated by the medium.[11]

Sulfonic Acids. In the particular case of **6a**, a base-soluble fraction was produced from which could be isolated a 27% yield of 1-chloro-2-phenylethene-2-sulfonic acid (**9**) and a 39% yield of acetophenone-ω-sulfonic acid (**10**) as their *p*-toluidine salts. The unexpected isolation of **10** led to more extensive studies which revealed that wide variations in the duration of reaction did not alter the ratio of **9** to **10**. In addition, submission of **9** to the rearrangement conditions left this sulfonic acid unchanged. These data suggest (but do not prove) that **10** is a primary rearrangement product and we therefore propose that **10** arises directly from chlorothiirene intermediate **28** (Chart III).

A priori, the formation of chlorovinylsulfonic acids **9**, **13**, and **18** can best be rationalized by either of the two mechanisms illustrated in Chart IV. The sequence

(10) F. Scholnick, Ph.D. Dissertation, University of Pennsylvania. Philadelphia, Pa., 1955.

(11) F. G. Bordwell and B. B. Jarvis, *J. Org. Chem.*, **33**, 1182 (1968).

Chart III. Mechanism for the Formation of **10**

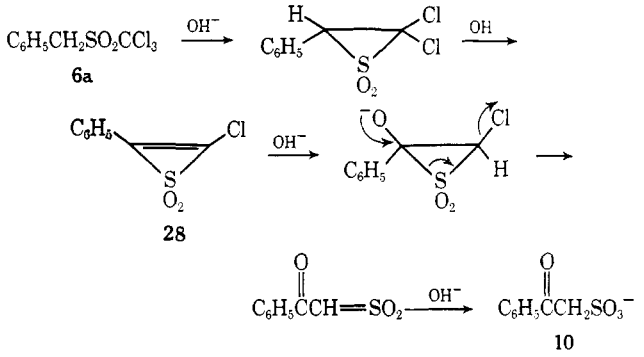
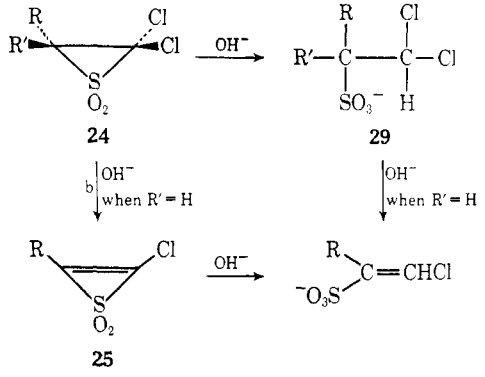


Chart IV. Possible Routes to Chlorovinylsulfonic Acids in the Ramberg–Bäcklund Rearrangement of Trichloromethyl Sulfones



of reactions which culminates in step a uniquely explains the results observed with trichlorosulfones **6d** and **6e**. In these instances, the R and R′ groups of **29** are alkyl in nature and dehydrohalogenation of the derived dichloromethylsulfonic acids (**20** and **23**, respectively) is not possible. By direct analogy, dichloro episulfone formation in the rearrangements of **6a–6c** would be followed by attack of hydroxide ion at tetravalent sulfur with ring opening in the direction of the more stable dichloromethyl anion and subsequent prototropic shift. In the final step, β elimination of the elements of hydrogen chloride from **29** gives rise to the observed chlorovinylsulfonic acids.

Pathway b would be expected to compete favorably in those cases such as **6a** in which the acidity of the α' hydrogen is enhanced. However, in view of the apparent chemical characteristics of **28** (Chart III), it would appear that the propensity of such reactive intermediates for this type of cleavage reaction may be substantially less than expected from the behavior of thiirene dioxides lacking chlorine substitution.[3-5] This result is not too surprising since the chloro derivatives incorporate a substituent which can ultimately serve as a leaving group. Of additional significance is the observation that no ketosulfonic acids of type **10** were isolated in the remainder of the rearrangements. A good case can therefore be made that, with the exception of **6a**, chlorothiirene dioxides are very likely not produced in significant quantities in the rearrangement of trichloromethyl sulfones and that chlorovinylsulfonic acids arise chiefly by cleavage of the less strained dichloro episulfone intermediates. If a mechanism involving chlorothiirene dioxide intermediates is to obtain, it must possess some feature that makes it more favorable energetically than path a of Chart IV Presumably with **6a** (see Chart III) the strain involved in the formation of **30** would be more than offset by

the energy gained in forming the new conjugated styrene type of double bond. Such conjugative stabilization is not available to the remaining examples **6b** and **6c**.

Finally, the demonstrated intervention of dichloro episulfones in the title reaction now permits the conclusion that α-halo sulfones in general display a marked tendency for 1,3 elimination and cyclization to episulfones, irrespective of the degree of halogen substitution.

Experimental Section[12]

Benzyl Trichloromethyl Sulfone (6a). To a stirred solution of 17.3 g (0.10 mol) of benzyl chloromethyl sulfide[4,13] in 150 ml of pentane was added dropwise under a nitrogen atmosphere 16.2 g (0.12 mol) of sulfuryl chloride during 20 min. Vigorous evolution of gas was noted. Upon completion of the addition, the clear yellow solution was refluxed for 1.5 hr. Removal of the solvent *in vacuo* afforded crude benzyl dichloromethyl sulfide as a light yellow liquid. This oil was dissolved in 100 ml of warm (45°) petroleum ether (bp 60–110°) and treated as above with an additional 17.5 g (0.13 mol) of sulfuryl chloride. When the addition was complete, the solution was heated at 80° for 1.5 hr. The solvent was removed *in vacuo*, and the resulting crude benzyl trichloromethyl sulfide was dissolved in chloroform; this solution was added dropwise to a cold (−5°) solution of *m*-chloroperbenzoic acid (43.1 g, 0.25 mol) in 300 ml of the same solvent. The reaction mixture was stirred overnight at room temperature. The insoluble *m*-chlorobenzoic acid was removed by filtration and washed sparingly with cold chloroform. The combined filtrates were washed three times with saturated sodium bicarbonate solution and then water, dried over magnesium sulfate, and evaporated. Trituration of the colorless oil with ether gave 15.2 g (56%) of colorless plates, mp 136–139°. An analytically pure sample of **6a** was obtained by recrystallization from cyclohexane: mp 142°; λ_{max}^{Nujol} 7.42 and 8.63 μ ($-SO_2-$); $\delta_{TMS}^{CDCl_3}$ 4.56 (singlet, 2 H, $C_6H_5CH_2-$) and 7.44 (singlet, 5 H, phenyl group).

Anal. Calcd for $C_8H_7Cl_3O_2S$: C, 35.12; H, 2.58; Cl, 38.88. Found: C, 35.04; H, 2.69; Cl, 38.62.

2-Phenethyl Trichloromethyl Sulfone (6b). In the same manner, 22.4 g (0.12 mol) of chloromethyl 2-phenethyl sulfide[4,14] was chlorinated and oxidized to give 23 g (67%) of crude **6b** as a white solid, mp 61–63°. Further recrystallization from cyclohexane–pentane gave pure **6b**: mp 64–65° (lit.[15] mp 65°); λ_{max}^{Nujol} 7.39 and 8.64 μ ($-SO_2-$); $\delta_{TMS}^{CDCl_3}$ 3.1–3.8 (symmetrical multiplet, 4 H, $C_6H_5CH_2CH_2-$) and 7.20 (5 H, singlet, phenyl protons).

3-Phenylpropyl Trichloromethyl Sulfone (6c). Chlorination and oxidation of 20.1 g (0.10 mol) of chloromethyl 3-phenylpropyl sulfide[4] yielded 11.2 g (37%) of crude **6c**, mp 80–84°. Recrystallization of this material from hexane afforded fine white needles: mp 89–90°; λ_{max}^{Nujol} 7.50 and 8.71 μ ($-SO_2-$); $\delta_{TMS}^{CDCl_3}$ 2.3–3.6 (multiplet, 6 H, methylene protons) and 7.22 (singlet, 5 H, phenyl protons).

Anal. Calcd for $C_{10}H_{11}Cl_3O_2S$: C, 39.82; H, 3.67; Cl, 35.26. Found: C, 39.75; H, 3.69; Cl, 35.39.

Isopropyl Trichloromethyl Sulfone (6d). Chlorination and oxidation of 12.5 g (0.10 mol) of chloromethyl isopropyl sulfide[4] gave 15.2 g (68%) of crude **6d**, mp 65–68°. Several recrystallizations from hexane gave long, colorless rods: mp 72–73°; λ_{max}^{Nujol} 7.53 and 8.68 μ ($-SO_2-$); $\delta_{TMS}^{CDCl_3}$ 1.63 (doublet, J = 7 Hz, 6 H, methyl groups) and 4.2 (septuplet, J = 7 Hz, 1 H, $(CH_3)_2CH-$).

Anal. Calcd for $C_4H_7Cl_3O_2S$: C, 21.30; H, 3.13; S, 14.22. Found: C, 21.28; H, 3.12; S, 14.42.

Cyclohexyl Trichloromethyl Sulfone (6e). Treatment of chloromethyl cyclohexyl sulfide[4] (19.8 g, 0.12 mol) in the predescribed manner afforded 22.0 g of crude white solid, mp 63–70°. Chromatography of this material on silica gel (elution with cyclohexane–chloroform 1:1) gave 13.5 g (49%) of colorless needles: mp 71–72° (from hexane); λ_{max}^{Nujol} 7.40 and 8.69 μ ($-SO_2-$); $\delta_{TMS}^{CDCl_3}$ 1.2–2.4 (complex pattern, 10 H, cyclohexyl protons) and 3.9 (multiplet, 1 H, $>CHSO_2-$).

Anal. Calcd for $C_7H_{11}Cl_3O_2S$: C, 31.66; H, 4.17; Cl, 40.05. Found: C, 31.98: H, 4.45; Cl, 39.82.

Rearrangement Experiments.[16] Rearrangement of 6a. To a solution of 3.38 g (15 mmol) of **6a** in 45 ml of purified tetrahydrofuran was added 45 ml of 2 *N* aqueous sodium hydroxide (90 mmol) in one portion. The reaction mixture was refluxed (65°) with vigorous stirring for 6 hr, cooled, and extracted with three 50-ml portions of ether. The combined ether extracts were washed with three 50-ml portions of water, dried, and carefully concentrated *in vacuo* below room temperature to a volume of approximately 50 ml. Further concentration of the ether solution was effected by fractionation at atmospheric pressure through a 6-in. Vigreux column (maximum temperature of 65°). The pale yellow residual oil (1.58 g) was subjected to vpc analysis on column A[16] at 164° with the following results:[17] phenylacetylene (**7**), 2%; 1,1-dichloro-2-phenylethene (**8**), <1%; and two very minor unidentified components.

The aqueous layer was concentrated under reduced pressure to a volume of 20–30 ml. After acidification (pH 3–5) with concentrated hydrochloric acid, the solution was heated to boiling and treated with 2 g (19 mmol) of *p*-toluidine and 4 ml of concentrated hydrochloric acid. The salt which precipitated was filtered, washed sparingly in ice water, and air dried. Occasionally, additional product could be isolated from the mother liquors. This treatment afforded 1.10 g (23%) of **9** as its *p*-toluidine salt, mp 156–164°. Recrystallization from water gave colorless platelets: mp 176–177°; λ_{max}^{Nujol} 8.52, 8.76, and 9.50 μ ($-SO_3^-$), 3.74 μ ($-NH_3^+$); $\delta_{TMS}^{DMSO\text{-}d_6}$ 2.31 (singlet, 3 H, methyl group), 7.14 (singlet, 1 H, $>C{=}CHCl$), 7.29 and 7.38 (singlets, total of 9 H, aromatic protons).

Anal. Calcd for $C_{15}H_{16}ClNO_3S$: C, 55.30; H, 4.95; Cl, 10.88. Found: C, 55.10; H, 4.99; Cl, 10.88.

When all of **9** was removed from the aqueous solution, approximately 1 g of *p*-toluidine hydrochloride was recovered upon further concentration. The aqueous residue was then evaporated to dryness *in vacuo* and the dry solid was extracted with hot acetone to remove organic salts. Evaporation of the combined acetone extracts gave a reddish brown, viscous, semicrystalline material which upon recrystallization from ethanol–ether gave 1.5 g (33%) of **10** as its *p*-toluidine salt: mp 177–178°; λ_{max}^{Nujol} 8.51 and 9.55 ($-SO_3^-$), 3.80 ($-NH_3^+$), and 6.00 μ ($>C{=}O$); $\delta_{TMS}^{DSMO\text{-}d_6}$ 2.31 (singlet, 3 H, methyl group), 4.30 (singlet, 2 H, $ArCOCH_2-$), and 7.28–8.1 (multiplet, 9 H total, aromatic protons).

Anal. Calcd for $C_{15}H_{17}NO_4S$: C, 58.61; H, 5.58; N, 4.55. Found: C, 58.58; H, 5.64; N, 4.38.

1,1-Dichloro-2-phenylethene (8). For comparison purposes, **8** was prepared in 35% yield from benzaldehyde and triphenylphosphine in hot carbon tetrachloride, bp 96° (15 mm) (lit.[18] bp 135–137° (63 mm)).

Acetophenone-ω-sulfonic Acid (10). Sodium acetophenone-ω-sulfonate was prepared by the method of Parkes and Tinsley.[19] A portion of the product was converted to its S-benzylthiuronium salt, mp 151–152° (lit.[20] mp 152°). The remaining portion was

(12) Melting points, determined with a Thomas–Hoover capillary melting point apparatus, are corrected. Infrared spectra were determined with a Perkin–Elmer Infracord Model 137 spectrometer fitted with sodium chloride prisms. Ultraviolet spectra were determined with a Cary Model 14 spectrometer. Nuclear magnetic resonance spectra were obtained with a Varian A-60 spectrometer; tetramethylsilane was employed as internal standard for solutions in organic solvents, while 3-(trimethylsilyl)-1-propanesulfonic acid sodium salt was used for aqueous solutions. The microanalyses were performed by the Scandinavian Microanalytical Laboratory, Herlev, Denmark.

(13) H. Bohme, H. Fischer, and R. Frank, *Ann.*, **563**, 54 (1949).

(14) H. Bohme, L. Tils, and B. Unterhalt, *Chem. Ber.*, **97**, 179 (1964).

(15) W. J. Farrar, *J. Chem. Soc.*, 508 (1956).

(16) The rearrangements of **6a–6e** were carried out in aqueous sodium hydroxide solutions under controlled conditions and worked up according to a standardized procedure which gave reproducible results. The standardized 2 *N* sodium hydroxide stock solution was prepared in CO_2-free water and stored in a tightly stoppered plastic bottle. The tetrahydrofuran was purified by distillation from lithium aluminum hydride. The vpc analyses were obtained with a Varian Aerograph A-90P3 gas chromatographic unit fitted with the following columns: A, 10 ft × 0.25 in. aluminum packed with 2% XF-1150 on Chromosorb P; B, 10 ft × 0.25 in. aluminum packed with 10% XF-1150 on Chromosorb P; C, 10 ft × 0.25 in. aluminum packed with 10% Carbowax 20M on Chromosorb W.

(17) Tetrahydrofuran excluded; percentages refer to over-all yields from the trichloro sulfones. Values in the text have been corrected for amount of reduction.

(18) R. Rabinowitz and R. Marcus, *J. Am. Chem. Soc.*, **84**, 1312 (1962).

(19) C. D. Parkes and S. G. Tinsley, *J. Chem. Soc.*, 1861 (1934).

(20) W. E. Truce and C. C. Alfieri, *J. Am. Chem. Soc.*, **72**, 2740 (1950).

transformed into its *p*-toluidine salt, colorless needles from ethanol–ether, mp 177–179°. This solid gave spectra superimposable upon those of the material isolated above.

Rearrangement of 6b. In the manner described above, 4.31 g (15 mmol) of **6b** in 45 ml of tetrahydrofuran was refluxed with 45 ml of 2 *N* sodium hydroxide solution (90 mmol) for 8 hr. The neutral, methylene chloride solution portion yielded trace quantities of two products. Sufficient material was rearranged subsequently to permit preparative vpc separation (column B[16]) of samples for infrared examination. The more rapidly eluted material was characterized as 1,1-dichloro-3-phenyl-1-propene (**12**) on the basis of the resemblance of its infrared spectrum with that of **8**. The less rapidly eluted material was identified as 1-chloro-3-phenyl-1-propene (**11**).[4]

From the aqueous layer there was isolated 2.18 g of a mixture of *p*-toluidine salts, mp 181–210° (nmr ratio 1.7:1). Fractional recrystallization was successfully accomplished from water. The more soluble salt was identified as the *p*-toluide of **13**: colorless needles; mp 192–193°; λ_{max}^{Nujol} 8.13, 8.43, 9.73 ($-SO_3^-$), and 3.82 μ ($-NH_3^+$); $\delta_{TMS}^{DSMO\text{-}d_6}$ 2.24 (singlet, 3 H, methyl group), 3.80 (singlet, 2 H, $C_6H_5CH_2-$), 7.1–7.4 (complex pattern, 10 H, aromatic and vinyl protons).

Anal. Calcd for $C_{16}H_{18}ClNO_3S$: C, 56.55; H, 5.34; N, 4.12. Found: C, 56.33; H, 5.22; N, 4.13.

The less soluble component was assigned structure **14**: colorless needles, mp 252–253° dec; λ_{max}^{Nujol} 8.44, 9.66 ($-SO_3^-$), and 3.82 μ ($-NH_3^+$); $\delta_{TMS}^{DMSO\text{-}d_6}$ 2.32 (singlet, 3 H, methyl group), 3.88 (singlet, 2 H, $C_6H_5CH_2-$), and 7.30 (broad singlet, 9 H, aromatic protons).

Anal. Calcd for $C_{16}H_{17}Cl_2NO_3S$: C, 51.34; H, 4.57; Cl, 18.92; N, 3.74. Found: C, 51.56; H, 4.59; Cl, 18.59; N, 3.86.

When the above experiment was repeated but stopped after 4 hr, the neutral portion was found to contain 0.4 g of α,α-dichloromethyl 2-phenethyl sulfone, mp 51–52° (lit.[4] mp 49–50°), but no **6b**. A 40% yield of the *p*-toluidine salt mixture was obtained on work-up of the aqueous solution.

Rearrangement of 6c. A 2.80-g (9 mmol) sample of **6c** was refluxed for 8 hr with 28 ml of tetrahydrofuran and 28 ml of 2 *N* sodium hydroxide solution (56 mmol). From the neutral fraction (column C,[16] 139°), there was isolated acetylene **15** (1%),[4] vinyl chloride **16** (1%),[4] and a third component (1%) assigned structure **17** on the basis of its infrared spectrum.

The aqueous portion yielded a total of 1.84 g (56%) of the *p*-toluidine salt of **18** as colorless needles: mp 148.5–149.5° (from water); λ_{max}^{Nujol} 8.50, 9.67 ($-SO_3^-$), and 3.80 μ ($-NH_3^+$); $\delta_{TMS}^{DMSO\text{-}d_6}$ 2.30 (singlet, 3 H, methyl group), 2.6–2.9 (broad multiplet, 4 H, $C_6H_5(CH_2)_2-$), 6.90 (broad singlet, 1 H, >C=C*H*Cl), 7.2 and 7.3 (overlapping singlets, 9 H, aromatic protons).

Anal. Calcd for $C_{17}H_{20}ClNO_3S$: C, 57.70; H, 5.70; N, 3.96. Found: C, 57.42; H, 5.71; N, 3.97.

The above experiment was repeated with a reflux period of 3 hr. Evaporation of the neutral fraction gave 1 g of α,α-dichloromethyl 3-phenylpropyl sulfone[4] and no **6c**. In addition, a 49% yield of the salt of **18** was isolated.

Rearrangement of 6d. In the manner described above, 3.38 g (15 mmol) of **6d** in 45 ml of tetrahydrofuran was refluxed with 45 ml of 2 *N* sodium hydroxide solution (90 mmol) for 4 hr. From the neutral fraction (column C,[16] 132°), there was isolated a 14% yield of **19**, identical in all respects with an authentic sample.[21]

From the aqueous portion of the reaction mixture, there was obtained 3.38 g (72%) of the *p*-toluidine salt of **20**: white needles from water; mp 176.5–177.5° dec; λ_{max}^{Nujol} 8.41, 9.66 ($-SO_3^-$), and 3.78 μ ($-NH_3^+$); $\delta_{TMS}^{DMSO\text{-}d_6}$ 1.34 (singlet, 6 H, $(CH_3)_2C<$), 2.32 (singlet, 3 H, *p*-toluidine methyl group), 6.22 (singlet, 1 H, $-CHCl_2$), and 7.29 (singlet, 4 H, phenyl protons).

Anal. Calcd for $C_{11}H_{17}Cl_2NO_3S$: C, 42.04; H, 5.45; N, 4.46. Found: C, 41.86; H, 5.50; N, 4.43.

In a similar experiment, **6d** was rearranged without cosolvent. In order to collect volatile vapors, nitrogen was passed through the system at a slow rate and exit gases were routed into a trap cooled in Dry Ice–isopropyl alcohol. This condensate was added to the usual neutral organic layer. Such treatment gave rise to an 86% yield of **20** and an 8% yield of **19**.

Rearrangement of 6e. In the manner described above, 3.98 g (15 mmol) of **6e** in 45 ml of tetrahydrofuran was refluxed with 45 ml of 2 *N* sodium hydroxide solution (90 mmol) for 4 hr. Vpc analysis of the ether-soluble portion (column C,[16] 130°) permitted the isolation of **21** (1%)[4] and **22** (51%); bp 61–62° (1.8 mm); λ_{max}^{neat} 6.17 μ (>C=C<).

Anal. Calcd for $C_7H_{10}Cl_2$: C, 50.93; H, 6.11. Found: C, 51.04; H, 6.24.

Upon work-up of the aqueous portion, there was isolated 1.55 g (29%) of the *p*-toluidine salt of **23**, white platelets from water: mp 176–177° dec; λ_{max}^{Nujol} 8.52, 9.63 ($-SO_3^-$), and 3.83 μ ($-NH_3^+$); $\delta_{TMS}^{DMSO\text{-}d_6}$ 2.32 (singlet, 3 H, methyl group), 1.3–2.6 (complex pattern, 10 H, cyclohexyl protons), 6.21 (singlet, 1 H, $-CHCl_2$), and 7.31 (singlet, 4 H, phenyl protons).

Anal. Calcd for $C_{14}H_{20}ClNO_3S$: C, 47.46; H, 5.97; Cl, 20.01; N, 3.95. Found: C, 47.58; H, 5.98; Cl, 20.05; N, 3.86.

Reaction of Phenyl Trichoromethyl Sulfone with Hydroxide Ion. A solution of 0.91 g (3.5 mmol) of **26**,[22] 10.5 ml of 2 *N* sodium hydroxide, and 10.5 ml of purified dioxane was refluxed for 5.5 hr and worked up in the above manner. This treatment yielded 0.75 g of white solid, careful chromatography of which on silica gel (elution with 4:1 hexane–chloroform) gave 0.49 g of recovered **26**, mp 84–87°, and 0.11 g (14% conversion) of dichloromethyl phenyl sulfone (**27**), mp 55–57°. The spectra of **17** were superimposable upon those of an authentic sample.[22]

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