was added dropwise to a stirred slurry of 82 g (0.38 mole) of *m*-chloroperbenzoic acid (80% active ingredient) in 380 ml of chloroform previously cooled to 0° in an ice bath. The rate of addition was controlled to maintain the reaction temperature at 0°. When the addition was completed, the reaction mixture was allowed to stand overnight at room temperature. The insoluble *m*-chlorobenzoic acid was removed by filtration and was washed with a small amount of cold chloroform. The combined filtrates were washed three times with saturated sodium bicarbonate solution, three times with water, dried over magnesium sulfate, and evaporated. Recrystallization of the crude oxidation product from hexane–benzene gave 6.0 (13%) of **13**, mp 120–135°. Three recrystallizations from cyclohexane afforded pure white crystals, mp 144–145°; $\nu_{\max}^{\text{Nujol}}$ 7.51 and 8.77 μ (SO_2); $\tau_{\text{TMS}}^{\text{CDCl}_3}$ 7.65 (singlet, 3 H, CH_3Ar), 5.39 (singlet, 2 H, $PhCH_2SO_2$), and 2.1–2.9 (multiplet, 9 H, aromatic protons).

Anal. Calcd for $C_{15}H_{14}Cl_2O_2S$: C, 54.72; H, 4.29; Cl, 21.54. Found: C, 54.77; H, 4.36; Cl, 21.37.

α,α-Dichlorobenzyl 4-Methylbenzyl Sulfone (10). In a procedure identical with that described above, 17.0 g (0.16 mole) of benzaldehyde was condensed with 20.7 g (0.15 mole) of 4-methylbenzyl mercaptan.[34] The crude α-chloro sulfide was chlorinated and oxidized, and the crude α,α-dichloro sulfone was recrystallized from benzene–hexane. There was obtained 13.5 g (27%) of white solid, mp 137–140°. Several recrystallizations from cyclohexane gave pure **10** as white needles, mp 148–149°; $\nu_{\max}^{\text{Nujol}}$ 7.52 and 8.73 μ (SO_2); $\tau_{\text{TMS}}^{\text{CDCl}_3}$ 7.66 (singlet, 3 H, CH_3Ar), 5.39 (singlet, 2 H, $ArCH_2SO_2$), and 2.1–2.9 (multiplet, 9 H, aromatic protons).

Anal. Calcd for $C_{15}H_{14}Cl_2O_2S$: C, 54.72; H, 4.29; Cl, 21.54. Found: C, 54.50; H, 4.33; Cl, 21.64.

Rearrangement of 10. A solution of 4.94 g (15.0 mmoles) of **10** in 45 ml of 2.0 *N* sodium hydroxide solution (90 mmoles) and 45 ml of dioxane was refluxed for 4 hr. Work-up of the reaction mixture afforded a neutral, ether-soluble fraction and an aqueous solution. Vpc analysis of the neutral residue indicated the presence of 19% phenyl *p*-tolylacetylene (**16**) and 4% of a *cis*- and *trans*-vinyl chloride mixture. A sample of **16** was collected by preparative vpc, mp 72–73° (from ethanol) (lit.[35] mp 78–79°). The infrared and nmr spectra were entirely consistent with the structural assignment.

The aqueous portion was concentrated to a volume of about 40 ml, acidified, and treated with *p*-toluidine. A brownish solid was obtained which weighed 4.10 g (72%), mp 160–175°. Recrystallization of this mixture of sulfonic acid salts from water gave an analytical sample as colorless needles, mp 169–172° (partial liquefaction) and 194–197° (clear melt); $\nu_{\max}^{\text{Nujol}}$ 3.80 (NH_3^+), 8.33, 8.60, and 9.46 (SO_3).

Anal. Calcd for $C_{22}H_{23}NO_3S$: C, 69.26; H, 6.08; N, 3.68. Found: C, 69.63; H, 6.22; N, 3.85.

Rearrangement of 13. A solution of 1.48 g of **13** in 13.5 ml of 2.0 *N* sodium hydroxide solution (27 mmoles) and 13.5 ml of dioxane was refluxed for 4 hr. There was isolated a 23% yield of **16**, a 6% yield of a vinyl chloride mixture, and a 68% yield of the vinylsulfonic acid mixture (**14** and **15**) as their *p*-toluidine salts, mp 160–175°, identical in all respects with the crude salt obtained from **10**.

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[34] J. von Braun, W. May, and R. Michaelis, *Ann.*, **490**, 189 (1931).

[35] G. Driefahl and G. Plotner, *Chem. Ber.*, **91**, 1274 (1958); our sample was found by vpc to contain approximately 3% of vinyl chloride impurity.

α-Halo Sulfones. VII. The Ramberg–Bäcklund Rearrangement of α,α-Dichloromethyl Sulfones[1-3]

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Contribution from the Department of Chemistry, The Ohio State University, Columbus, Ohio 43210. Received March 9, 1967

Abstract: Several α,α-dichloromethyl sulfones have been subjected to treatment with various bases in an attempt to elucidate the possible mechanistic pathways involved in the ensuing rearrangement. In particular, the selection of sulfones was designed to allow an examination of the possible generation and fate of monosubstituted thiirene dioxides and spirochloro episulfones, two intermediates anticipated from earlier results. The Ramberg-Bäcklund rearrangement of the dichloromethyl sulfones was found to give rise to acetylenes, vinyl chlorides, and α,β-unsaturated sulfonic acids. The mode of formation of these products is discussed. 2-Chlorothiirane 1,1-dioxide, the parent of the chloro episulfone series, has been prepared and its decomposition studied.

In recent years, there has been considerable attention directed toward an elucidation of the mechanistic details involved in the transformation of α-halo sulfones to olefins in the presence of base (the Ramberg–Bäcklund rearrangement).[5] A rate-determining 1,3 elimination of hydrogen halide to give rise to episulfones, followed by their decomposition with expulsion of sulfur dioxide, is now the accepted mechanism. The extension of this reaction to α,α-dichloro sulfones (**1**) was previously demonstrated to proceed in an analogous fashion.[3,6] Products have been shown to result from the formation and subsequent decomposition of chloro episulfones (**2**) and thiirene dioxides (**3**). However, the earlier studies have concentrated exclusively on dihalo sulfones which ultimately could lead only to disubstituted thiirene dioxides (**3**, R = alkyl or aryl).

We wish now to report the results of studies on the base-promoted rearrangement of dichloromethyl sul-

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[1] We thank the National Institutes of Health and the Petroleum Research Fund, administered by the American Chemical Society, for grants used in support of this work.

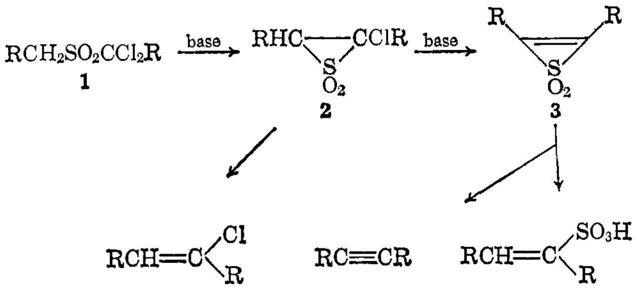
[2] Presented in part at the 151st National Meeting of the American Chemical Society, Pittsburgh, Pa., March 1966.

[3] Paper VI: L. A. Paquette and L. S. Wittenbrook, *J. Am. Chem. Soc.*, **89**, 4483 (1967).

[4] Fellow of the Alfred P. Sloan Foundation.

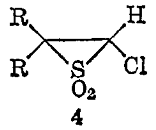
[5] (a) L. Ramberg and B. Bäcklund, *Arkiv Kemi, Mineral. Geol.*, **13A**, No. 27 (1940); *Chem. Abstr.*, **34**, 4725 (1940); (b) F. G. Bordwell and G. D. Cooper, *J. Am. Chem. Soc.*, **73**, 5187 (1951); (c) N. P. Neureiter and F. G. Bordwell, *ibid.*, **85**, 1209 (1963); (d) L. A. Paquette, *ibid.*, **86**, 4053 (1964); (e) L. A. Paquette, *ibid.*, **86**, 4383 (1964); (f) N. P. Neureiter, *J. Org. Chem.*, 30, 1313 (1965); (g) N. P. Neureiter, *J. Am. Chem. Soc.*, **88**, 558 (1966).

[6] (a) L. A. Paquette, *ibid.*, **86**, 4089 (1964); (b) L. A. Carpino and L. V. McAdams, III, *ibid.*, **87**, 5804 (1965); (c) L. A. Paquette and L. S. Wittenbrook, *Chem. Commun.*, 471 (1966).



fones designed to provide evidence for the possible generation of monosubstituted derivatives of **3** and to determine the effect of monosubstitution on chemical behavior, if any.[7]

The second goal of the present investigation was to learn of the fate of disubstituted chloro episulfones such as **4** when generated in the alkaline medium required for



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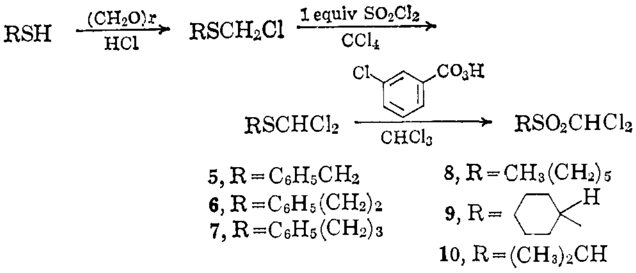
the Ramberg–Bäcklund rearrangement process. Such intermediates are not convertible to thiirene dioxides. Therefore they must react further by a process unique to this class of compounds, a consequence of significant importance in the product analysis.

Results

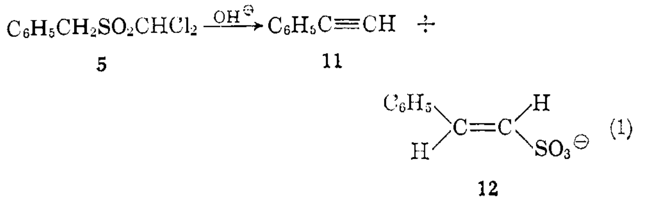
Synthesis. Dichloromethyl sulfones **5–10** were prepared by the general scheme outlined in Chart I. Treatment of the appropriate mercaptan with paraformaldehyde and anhydrous hydrogen chloride at 0° afforded the respective chloromethyl sulfides in good yield.[8] Chlorination of these materials with approximately 1 equiv of sulfuryl chloride proved to be quite efficacious. The resulting α,α-dichloro sulfides were not isolated, but were directly oxidized to the corresponding sulfones with *m*-chloroperbenzoic acid in chloroform solution.

Chart I

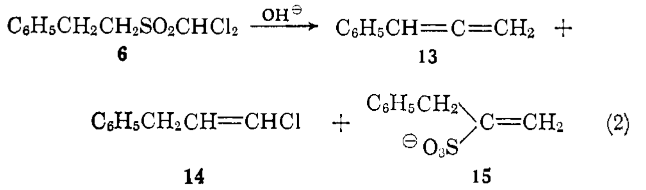


In all of the examples studied, sulfuryl chloride was found to introduce a second chlorine atom exclusively at the site of the original chloromethyl group, even when the R group was benzyl.[9] These results are in accord with earlier observations[6a,10] and provide further support for an ionic mechanism in which the more acidic hydrogen is abstracted from the initially formed chlorosulfonium chloride.[6a,11]

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 α,α-dichloromethyl sulfone (**5**) was gently refluxed (87°) with 2.0 *N* sodium hydroxide–dioxane (1:1) solution for 4 hr, the sole neutral product was shown to be phenylacetylene (**11**), whereas the base-soluble fraction contained only *trans*-β-styrenesulfonic acid (**12**) (eq 1), isolated as its *p*-toluidine salt. Clear preference for the formation of the acetylene was observed, and this propensity was found to persist with differing concentrations of hydroxide ion (Table I); however, with potassium *t*-butoxide as the base, phenylacetylene was the exclusive product. This disappearance of vinylsulfonic acid,[12] accompanied by an increase in alkyne production, has been found to be quite general (Table I).



In the case of the less fully studied reaction of **6**, the expected principal neutral reaction product, benzylacetylene, was found not be be stable to the conditions of rearrangement (2 *N* NaOH–aqueous dioxane). Rather, this acetylene was rapidly converted into phenylallene (**13**) which was isolated in low yield; the remainder was presumably destroyed by further reactions.[13] A 17% yield of 3-phenyi-1-chloropropene (**14**, *cis*:*trans* ratio of 2.8:1) was also noted (eq 2). As expected, a vinylsulfonic acid (**15**) likewise did result but, in contrast to the behavior of **5**, the sulfonate residue was not bonded to the carbon atom to which the chlorine atoms were originally attached.



Because this study of **6** did not permit a quantitative evaluation of the amount of acetylene produced, we were led to a consideration of **7** and **8** in order to gain further insight into the chemical characteristics of monosubstituted thiirene dioxides in which aromatic rings were not conjugated with the olefinic linkage of the strained three-membered ring intermediate. Both of these dichloromethyl sulfones underwent smooth rearrangement in the presence of hydroxide ion to give similar products which included the appropriate acetylenes, vinyl chlorides, and vinylsulfonic acids (eq

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[7] For a preliminary communication of these results, see ref 6c.

[8] This synthetic approach to α-chloro sulfides has served previous utility: see footnote 20 of ref 3.

[9] Further details of the directive influence of the chloromethyl group in this reaction will be reported shortly: K. Schreiber and L. S. Wittenbrook, unpublished observations.

[10] W. E. Truce, G. H. Birum, and E. T. McBee, *J. Am. Chem. Soc.* 74, 3594 (1952).

[11] D. L. Tuleen and V. C. Marcum, *J. Org. Chem.*, 32, 204 (1967).

[12] We have observed that sulfonic acids will not result as long as the KO-*t*-Bu–*t*-BuOH solution is completely devoid of moisture. When moisture is present, quantities of sulfonic acids have been isolated.

[13] M. V. Yen, *Ann. Chim.* (Paris), 7, 785 (1962).

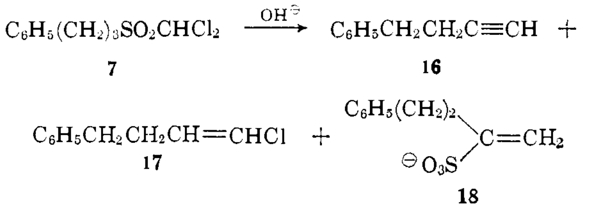
Table I. Base-Promoted Rearrangements of Dichloromethyl Sulfones **5–10**

Compd	Base	Molar equiv of base	Solvent	Temp, °C	Products (%)
5	2.0 *N* NaOH	6	H_2O–dioxane (1:1)	87	**11** (56), **12** (31)
	1.0 *N* NaOH	6	H_2O–dioxane (1:1)	87	**11** (53), **12** (28)
	0.5 *N* NaOH	3	H_2O–dioxane (1:1)	87	**11** (37), **12** (20)[a]
	2.0 *N* KOH	6	H_2O–dioxane (1:1)	87	**11** (61), **12** (28)
	1.06 *M* KO-*t*-Bu	6	*t*-BuOH	84	**11** (76)
6	2.0 *N* NaOH	6	H_2O–dioxane (1:1)	87	**13** (3), **14** (17), **15** (17)
7	2.0 *N* NaOH	6	H_2O–dioxane (1:1)	87	**16** (50), **17** (14), **18** (19)
	1.06 *M* KO-*t*-Bu	6	*t*-BuOH	84	**16** (2.5), **17** (0.6), $C_6H_5(CH_2)_2$-$CH{=}CH_2$ (9)[b]
8	2.0 *N* NaOH	6	H_2O	100	**19** (39), **20** (30), **21** (20)
	1.06 *M* KO-*t*-Bu	6	*t*-BuOH	84	**19** (46)
9	2.0 *N* NaOH	6	H_2O–dioxane (1:1)	87	**22** (60), **23** (20)
	1.06 *M* KO-*t*-Bu	6	*t*-BuOH	84	**22** (60)
10	2.0 *N* NaOH	6	H_2O	100	**24** (44), **25** (37)

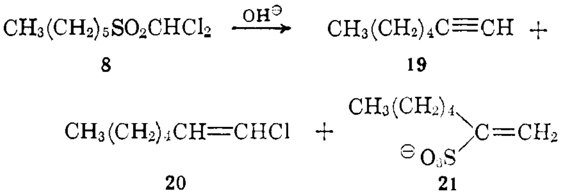
[a] The lower yields in this run are attributable to incomplete consumption of **5**, a portion of which was recovered from the neutral layer.

[b] Much tar formation was observed.

3 and 4). As with **6**, the ratio of *cis*- and *trans*-vinyl chlorides in the reaction products favored the *cis* isomers, but to the increased extent of 4.2:1 and 4.3:1 for **7** and **8**, respectively. The sulfonic acids were structurally analogous to **15** in that the sulfur-containing substituent was again bonded to C_2.



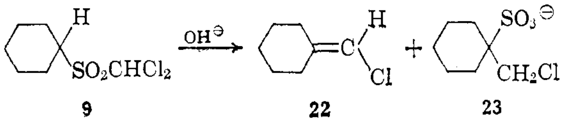
$$\underset{7}{C_6H_5(CH_2)_3SO_2CHCl_2} \xrightarrow{OH^\ominus} \underset{16}{C_6H_5CH_2CH_2C{\equiv}CH} + \underset{17}{C_6H_5CH_2CH_2CH{=}CHCl} + \underset{18}{(C_6H_5(CH_2)_2)(^\ominus O_3S)C{=}CH_2} \quad (3)$$

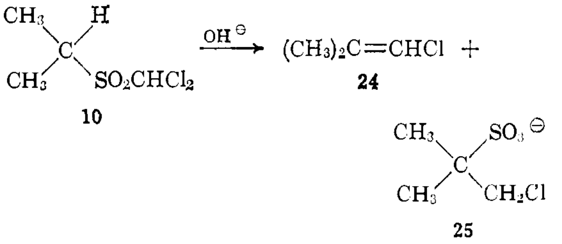


$$\underset{8}{CH_3(CH_2)_5SO_2CHCl_2} \xrightarrow{OH^\ominus} \underset{19}{CH_3(CH_2)_4C{\equiv}CH} + \underset{20}{CH_3(CH_2)_4CH{=}CHCl} + \underset{21}{(CH_3(CH_2)_4)(^\ominus O_3S)C{=}CH_2} \quad (4)$$

When **7** was treated with potassium *t*-butoxide in *t*-butyl alcohol (identical conditions were employed throughout), a vigorous reaction ensued and large amounts of a dark polymer were formed. Work-up of the reaction indicated that only small amounts of **16** and **17** were present. In fact, the major product (9% yield) was shown to be 4-phenyl-1-butene; this olefin probably arises by initial reduction of the dichloromethyl sulfone to the chloromethyl sulfone followed by a normal Ramberg–Bäcklund rearrangement.[14] In contrast, **8** was cleanly rearranged to 1-heptyne (**19**) in good (but probably not optimal) yield when submitted to such strongly basic conditions.

Exposure of **9** and **10** to aqueous hydroxide solution resulted in good conversion to vinyl chlorides **22** and **24**, respectively. In both cases, sulfonic acids containing the chloromethyl group were the only other products; the presence of this differing structural element in **23** and **25** can adequately be attributed to the initial formation of 2,2-dialkylchloro episulfone intermediates (see Discussion).


(5)



$$\underset{10}{(CH_3)_2CHSO_2CHCl_2} \xrightarrow{OH^\ominus} \underset{24}{(CH_3)_2C{=}CHCl} + \underset{25}{(CH_3)_2C(SO_3^\ominus)CH_2Cl} \quad (6)$$

Discussion

Neutral Products. The formation of acetylenes and vinyl chlorides in the rearrangement of α,α-dichloromethyl sulfones demands that bonding of the α-sulfonyl carbon to its α′ counterpart occur at some stage of the transformation. The four most reasonable pathways which may account for such bond formation, all of which proceed by initial formation of the chloro episulfone intermediate, are outlined in Chart II. This beginning point is quite consistent with the results of earlier mechanistic studies.[3,6] Equation a, Chart II, is precisely the mechanism established for acetylene formation in the case of disubstituted thiirene dioxides,[3] and therefore must be considered highly plausible. Another indication of the feasibility of this process has been found in the ease with which 2-methylthiirene 1,1-dioxide undergoes decomposition to give methylacetylene and sulfur dioxide.[15] Alternatively, acetylenes could result from a base-promoted loss of sulfur dioxide as outlined in eq b, Chart II.[16] The extrusion

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(14) Reductions of α,α-dibromo sulfones are known to take place under relatively mild conditions (later in this work and D. Scholnick, Ph.D. Thesis, University of Pennsylvania, 1955). It is therefore not totally unexpected that α,α-dichloro sulfones undergo a similar reaction under certain conditions.

(15) L. A. Carpino and R. H. Rynbrandt, *J. Am. Chem. Soc.*, 88, 5682 (1966).

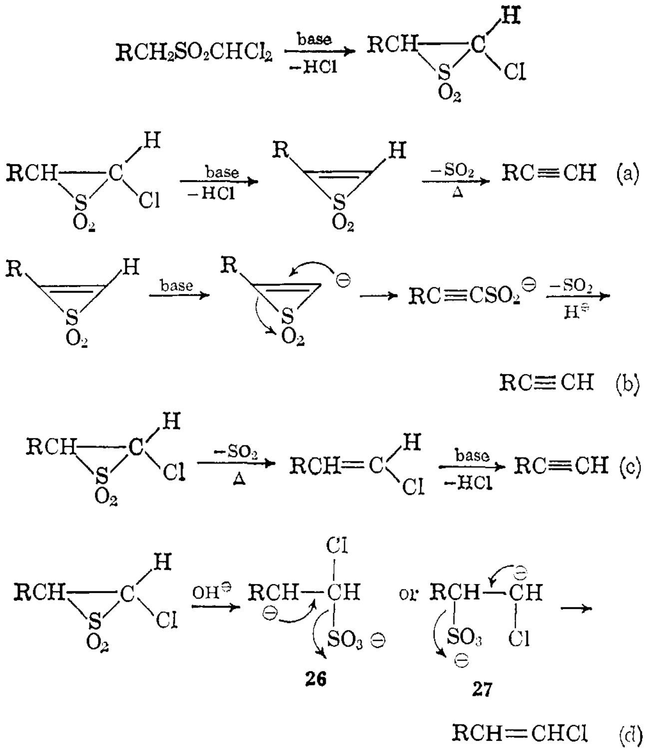
(16) This transformation appears to be operative when 2-methylthiirene 1,1-dioxide is treated with 2 *N* sodium hydroxide at 0°.[15]

Table II. Control Experiments

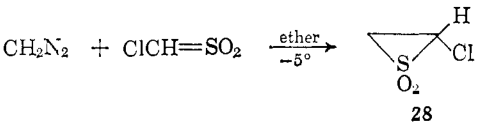
Chloroolefin	Base	Solvent, conditions	Results
$C_6H_5CH{=}CHCl$ *cis*:*trans* ratio 1.2	2.0 *N* NaOH	H_2O–dioxane (1:1), reflux, 4 hr	Recovered intact (*cis*:*trans* ratio 1.2); no **11** detected
	1.06 *M* KO-*t*-Bu	*t*-BuOH, reflux, 0.5 hr	*trans*-β-Chlorostyrene (32%) and **11** (47%); no *cis*-vinyl chloride detected
17	1.06 *M* KO-*t*-Bu	*t*-BuOH, reflux, 0.5 hr	**17** (56%) and **16** (44%)

of sulfur dioxide from chloro episulfones as a route to vinyl chlorides (eq c, Chart II) has been alluded to earlier,[3,6a,c] and has been confirmed in the present study (see below); however, representative vinyl chlorides were shown to be stable under the rearrangement conditions when hydroxide was employed (see Table II), and at least under these circumstances such substrates cannot serve as acetylenic precursors.

Chart II. Possible Routes to Neutral Products in the Ramberg–Bäcklund Rearrangement of α,α-Dichloromethyl Sulfones



In connection with the question of the thermal decomposition of chloro episulfones (eq c, Chart II), the synthesis of the parent molecule of this class of compounds was undertaken. When an ethereal solution of diazomethane was treated at −5° with chlorosulfene (generated *in situ* from chloromethanesulfonyl chloride and triethylamine),[17] 2-chlorothiirane 1,1-dioxide (**28**), mp 53–54° dec, was isolated in 83% yield. Of particular relevance to the above results, **28** was readily decomposed into vinyl chloride and sulfur dioxide on heating to 65° in carbon tetrachloride solution. This substance (**28**) is apparently inert to the action of triethylamine at 0°, and in our hands could not be dehydrochlorinated to thiirene 1,1-dioxide (**29**) under these conditions.[18] When 2 equiv of 2 *N* aqueous sodium hydroxide solution was added to 1 equiv of **28** as the pure solid or when dissolved in dioxane or water, an extremely exothermic reaction was observed which resulted in the vigorous evolution of acetylene and vinyl chloride (trapped as their bromine adducts). Since vinyl chloride was stable to such treatment, acetylene formation testifies to the likely intervention of **29**. Sulfonic acid formation was not observed if the temperature of the exothermic reaction was not controlled. Interestingly, however, when the aqueous sodium hydroxide solution was added to a frozen mixture of **28** and dioxane and the temperature allowed to rise slowly, very little gas evolution was noted and a polymeric sulfonic acid was isolated. Although this gummy substance could be derived from ethylenesulfonic acid, the more reasonable possibility exists that the polymer was formed by reaction of a carbanion intermediate with **29**.[19,20]



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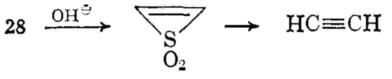

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A final rationalization of the formation of vinyl chlorides involves stepwise cleavage of the chloro episulfone ring by hydroxide ion to give carbanions such as **26** and **27** which would subsequently eject bisulfite (or sulfite) ion (mechanism d, Chart II). The possible intervention of **26** can be ruled out on two counts: first, it is unlikely that the ring would cleave to give the less stable carbanion; second, should **26** be formed, chloride ion is well known to be a better

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[17] L. A. Paquette, *J. Org. Chem.*, **29**, 2854 (1964); for other applications of this reaction to the synthesis of episulfones, see footnote 4 of ref 6c.

[18] It is interesting to compare the inertness of **28** to the relative ease with which 2-bromo-2-methylthiirane 1,1-dioxide may be converted to 2-methylthiirene 1,1-dioxide by means of triethylamine in ether at 3°.[15] The wide variance in the reactivity of these closely related molecules appears to be a further reflection of the greater propensity for elimination of HBr relative to HCl.

[19] The chemistry of vinylsulfonic acid has recently been reviewed: H. Distler, *Angew. Chem. Intern. Ed. Engl.*, **4**, 300 (1965).

[20] In an ancillary study, attempts have been made to rearrange benzyl dibromomethyl sulfone (i) with tertiary amines in order to prepare 2-phenylthiirene 1,1-dioxide. However, treatment of a methylene chloride solution of i with triethylamine for several days at 0°, for example, afforded benzyl bromomethyl sulfone (ii) as the only characterizable product (51% yield). The same reaction in tetrahydrofuran gave back i and 12% of ii (based on recovered i).

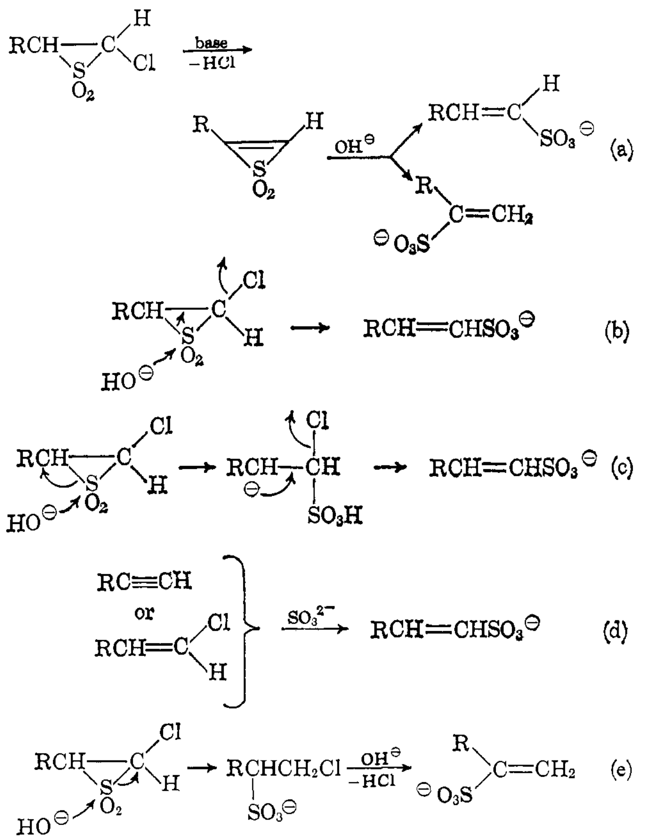
$$\underset{\text{i}}{C_6H_5CH_2SO_2CHBr_2} \xrightarrow[CH_2Cl_2,\ 0^\circ]{(C_2H_5)_3N} \underset{\text{ii}}{C_6H_5CH_2SO_2CH_2Br}$$

leaving group than the sulfur-containing substituent on the basis of the relative ease of cleavage of carbon–sulfur and carbon–chlorine bonds in other displacement reactions.[5b] The intermediacy of **27** also cannot be considered likely because sulfonic acid **23**, a molecule in which the proposed bisulfite (or sulfite) leaving group is linked to a tertiary carbon atom and therefore resides in a favorable environment for elimination, was stable to prolonged reflux in aqueous hydroxide solution.

Therefore, acetylene formation can only be reconciled with the intermediacy of thiirene dioxides (mechanisms a or b, Chart II), whereas vinyl chlorides necessarily result directly from chloro episulfones. In the particular case of dichloromethyl sulfone **5**, no β-chlorostyrene was detected (stable to reaction conditions; see Table II), an observation which suggests that the intermediate chloro episulfone in this case, by virtue of the fact that the α-sulfonyl proton is benzylic, undergoes dehydrochlorination more rapidly than sulfur extrusion.

Sulfonic Acids. The several possible mechanistic pathways which may reasonably be advanced to explain vinylsulfonic acid formation are listed in Chart III. Mechanisms b and c need not be considered further because they require that the sulfonic acid residue necessarily be attached to the terminal olefinic carbon, a fact which is inconsistent, in general, with the above results. Indication that mechanism d, Chart III, was not operative was gained by submitting tolan and β-chlorostyrene to the action of hot aqueous sulfite ion, conditions from which they could be recovered intact.[21]

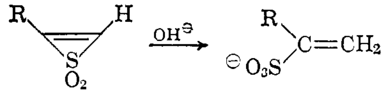
Chart III. Possible Routes to Vinylsulfonic Acids in the Ramberg–Bäcklund Rearrangement of α,α-Dichloromethyl Sulfones



The reasoning expressed in the first step of mechanism e, Chart III, uniquely explains the results derived from dichloromethyl sulfones **9** and **10**. Thus, it is indicated that the rearrangement in these examples proceeds *via* initial 2,2-dialkyl chloro episulfone formation followed by hydroxide attack at tetravalent sulfur with ring opening to produce the more stable carbanion, and terminates with a prototropic shift to carbon.

In turn, the rearrangement of benzyl dichloromethyl sulfone (**5**) can best be rationalized in terms of mechanism a, Chart III;[22] the 2-phenylthiirene 1,1-dioxide intermediate upon attack by hydroxide ion is cleaved in a manner which produces the more stable benzylic carbanion.

However, it is not yet clear which of these two mechanistic patterns is actually operative in the remaining examples. Either pathway is capable of explaining the behavior of **6**, **7**, and **8**. For example, application of mechanism a, Chart III, to these systems demands the formation of a thiirene dioxide intermediate which



would undergo ring rupture again in the direction such as to generate the more stable carbanion, as illustrated. It is to be noted that this product is identical with that required by mechanism e, Chart III. Of special concern is the fact that the latter mechanism derives no importance in the 2,3-diaryl chloro episulfone examples.[3] In such systems, however, the rate of dehydrohalogenation can be expected to exceed the rate of ring cleavage. The precise origin of vinylsulfonic acids which would lead to intermediates lacking this incipient conjugative factor remains, therefore, an open question.

Experimental Section[23]

Benzyl α,α-Dichloromethyl Sulfone (5). To a solution of 20.7 g (0.12 mole) of benzyl α-chloromethyl sulfide[24] [bp 58–60° (0.2 mm)] in 50 ml of carbon tetrachloride was added dropwise with stirring in a nitrogen atmosphere a solution of 17.6 g (0.13 mole) of sulfuryl chloride in 50 ml of the same solvent. The ensuing reaction was mildly exothermic. Upon completion of the addition, which required 40 min, the solution was warmed to 35° and stirred for 1 hr at that temperature. The solvent was removed *in vacuo* at

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(21) These substances were selected in the belief that they could best accommodate the nucleophilic addition and nucleophilic addition–elimination processes implied in mechanism d, Chart IV. The reaction of vinyl halides with sulfite ion has been shown to lead to vinylsulfonic acids in certain cases, but only under considerably more vigorous conditions [W. E. Truce and M. M. Boudakian, *J. Am. Chem. Soc.*, 78, 2752 (1956)].

(22) Pathway b, Chart IV, is not considered likely because this route is not taken in the closely related diphenyl analog.[3]

(23) Melting points, determined with a Thomas-Hoover capillary melting points apparatus, and boiling points are uncorrected. Infrared spectra were determined with a Perkin-Elmer Infracord Model 137 spectrometer fitted with sodium chloride prisms. 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, and by Huffmann Laboratories, Inc., Wheatridge, Colo. The vpc analyses were obtained with an Aerograph A-90P gas chromatograph (helium as the carrier gas) fitted with one of the following three columns: A, 10 ft × 0.25 in. stainless steel packed with 15% Carbowax 20M on Chromosorb W; B, 10 ft × 0.25 in. stainless steel packed with 20% Carbowax 20M on Chromosorb W; C, 10 ft × 0.25 in. aluminum packed with 2% XF1150 on Chromosorb P. Percentage compositions reported refer to the calibrated relative areas observed for the different components.

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

room temperature to afford benzyl α,α-dichloromethyl sulfide as a colorless liquid. This material was not further purified but was taken up in 50 ml of cold chloroform. The resulting solution was added dropwise to a stirred slurry of 51.8 g (0.30 mole) of *m*-chloroperbenzoic acid in 350 ml of chloroform previously cooled to 0° with an ice–salt bath. The rate of addition was controlled to maintain the reaction temperature at 0°. When the addition was completed, the reaction mixture was allowed to stand overnight at room temperature. The insoluble *m*-chlorobenzoic acid was removed by filtration and washed with cold chloroform. The combined filtrates were washed three times with saturated sodium bicarbonate solution and three times with water, dried over magnesium sulfate, and evaporated. One recrystallization of the crude product from carbon tetrachloride–hexane yielded 24 g of a white solid, mp 85–89°. Chromatography of this material on silica gel (250 g) was effected with chloroform–benzene (1:1). The late fractions were combined and recrystallized from cyclohexane to give 7.6 g (30%) of **5** as colorless plates, mp 104°; $\nu_{\max}^{\mathrm{CCl_4}}$ 7.40, 8.71, and 8.87 μ ($\mathrm{SO_2}$); $\tau_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 5.45 (singlet, 2 H, $\mathrm{C}\mathit{H}_2\mathrm{SO_2}$), 3.95 (singlet, 1 H, $\mathrm{SO_2C}\mathit{H}\mathrm{Cl_2}$), and 2.60 (singlet, 5 H, phenyl group).

Anal. Calcd for $\mathrm{C_8H_8Cl_2O_2S}$: C, 40.18; H, 3.38; Cl, 29.65. Found: C, 40.36; H, 3.38; Cl, 29.30.

α,α-Dichloromethyl 2-Phenethyl Sulfone (6). To a stirred mixture of 82.9 g (0.60 mole) of phenethyl mercaptan[25] and 18.0 g (0.20 mole) of paraformaldehyde was introduced anhydrous hydrogen chloride gas at 0° for approximately 1.5 hr. When the mixture was saturated with the gas, it was transferred while still cold to a separatory funnel; the water layer was drawn off and the organic portion was dried over anhydrous calcium chloride. Fractionation of the crude product afforded 57.4 g (52%) of chloromethyl 2-phenethyl sulfide as a colorless, slightly viscous liquid, bp 86–88° (0.25 mm).[26]

In the same manner as described above, 14.9 g (0.11 mole) of sulfuryl chloride was added dropwise to a stirred solution of 18.7 g (0.10 mole) of the chloromethyl sulfide, and the resulting crude α,α-dichloromethyl 2-phenethyl sulfide was oxidized to the sulfone with 43.0 g (0.25 mole) of *m*-chloroperbenzoic acid. One recrystallization of the solid sulfone from carbon tetrachloride–hexane gave 12 g (48%) of a white solid, mp 45°. An analytical sample, which was obtained as long colorless needles, melted at 49–50°; $\nu_{\max}^{\mathrm{CCl_4}}$ 7.44, 8.73, and 8.91 μ ($\mathrm{SO_2}$); $\tau_{\mathrm{TMS}}^{\mathrm{CCl_4}}$ 6.3–6.9 (multiplet, 4 H, aliphatic methylene groups), 3.91 (singlet, 1 H, $\mathrm{SO_2C}\mathit{H}\mathrm{Cl_2}$), and 2.72 (singlet, 5 H, phenyl group).

Anal. Calcd for $\mathrm{C_9H_{10}Cl_2O_2S}$: C, 42.69; H, 3.98; Cl, 28.01. Found: C, 42.61; H, 4.00; Cl, 27.66.

α,α-Dichloromethyl 3-Phenylpropyl Sulfone (7). From 91.4 g (0.60 mole) of 3-phenylpropyl mercaptan and 18.0 g (0.20 mole) of paraformaldehyde, there was obtained upon treatment as above 63.4 g (53%) of chloromethyl 3-phenylpropyl sulfide as a colorless liquid, bp 107–109° (0.2 mm). For purposes of characterization, a small portion of this material was oxidized to its sulfone (83% yield), white solid, mp 75.5–76.5° (from ether–pentane); $\nu_{\max}^{\mathrm{CCl_4}}$ 7.55, 8.71, and 8.98 μ ($\mathrm{SO_2}$); $\tau_{\mathrm{TMS}}^{\mathrm{CCl_4}}$ 7.5–8.1 and 6.6–7.4 (two sets of multiplets, 6 H, aliphatic methylene groups), 5.70 (singlet, 2 H, $\mathrm{SO_2C}\mathit{H}_2\mathrm{Cl}$), and 2.78 (singlet, 5 H, phenyl group).

Anal. Calcd for $\mathrm{C_{10}H_{13}ClO_2S}$: C, 51.61; H, 5.63; Cl, 15.23. Found: C, 51.49; H, 5.61; Cl, 15.24.

Chlorination and oxidation of 20.1 g (0.10 mole) of the chloromethyl sulfide as described above led to the isolation of 15 g (56%) of a low-melting pale yellow solid. Recrystallization from ether–pentane gave the analytical sample as colorless leaflets, mp 46–47°; $\nu_{\max}^{\mathrm{CCl_4}}$ 7.45, 8.73, and 8.89 μ ($\mathrm{SO_2}$); $\tau_{\mathrm{TMS}}^{\mathrm{CCl_4}}$ 6.5–7.9 (series of multiplets, 6 H, aliphatic methylene groups), 3.85 (singlet, 1 H, $\mathrm{SO_2C}\mathit{H}\mathrm{Cl_2}$), and 2.71 (singlet, 5 H, phenyl group).

Anal. Calcd for $\mathrm{C_{10}H_{12}Cl_2O_2S}$: C, 44.95; H, 4.53; Cl, 26.54. Found: C, 45.04; H, 4.57; Cl, 26.67.

α,α-Dichloromethyl *n*-Hexyl Sulfone (8). Chlorination and oxidation of 19.9 g (0.12 mole) of chloromethyl *n*-hexyl sulfide[5e] as described above afforded 5.7 g (25%) of the colorless oily sulfone after repeated chromatography of the crude product on silica gel; $\nu_{\max}^{\mathrm{neat}}$ 7.52, 8.73, and 8.84 μ ($\mathrm{SO_2}$); $\tau_{\mathrm{TMS}}^{\mathrm{CCl_4}}$ 8.56 (multiplet, 11 H, aliphatic methylene groups), 6.75 (triplet, J = 9.0 cps, 2 H, $\mathrm{C}\mathit{H}_2\mathrm{SO_2}$), and 3.66 (singlet, 1 H, $\mathrm{SO_2C}\mathit{H}\mathrm{Cl_2}$).

Anal. Calcd for $\mathrm{C_7H_{14}Cl_2O_2S}$: C, 36.05; H, 6.00; Cl, 30.47. Found: C, 36.33; H, 5.99; Cl, 30.63.

Cyclohexyl α,α-Dichloromethyl Sulfone (9). Chlorination and oxidation of 19.8 g (0.12 mole) of chloromethyl cyclohexyl sulfide[5e] in the customary manner gave rise to 9.1 g (33%) of pure **9** as a colorless crystalline solid, mp 55–56° (from pentane containing a small amount of ether); $\nu_{\max}^{\mathrm{CCl_4}}$ 7.41, 8.79, and 8.95 μ ($\mathrm{SO_2}$); $\tau_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 7.6–8.9 (series of multiplets, 10 H, cyclohexyl ring protons), 6.4 (multiplet, 1 H, $>\mathrm{C}\mathit{H}\mathrm{SO_2}$), and 3.56 (singlet, 1 H, $\mathrm{SO_2C}\mathit{H}\mathrm{Cl_2}$).

Anal. Calcd for $\mathrm{C_7H_{12}Cl_2O_2S}$: C, 36.37; H, 5.23; Cl, 30.68. Found: C, 36.54; H, 5.18; Cl, 30.78.

α,α-Dichloromethyl Isopropyl Sulfone (10). From 76 g (1.0 mole) of 2-propanethiol and 30 g (0.33 mole) of paraformaldehyde, there was obtained in the manner described above 62 g (50%) of chloromethyl isopropyl sulfide, bp 56–58° (30 mm), $n^{25}\mathrm{D}$ 1.4783.

Chlorination and oxidation of 17.4 g (0.14 mole) of this sulfide led to the isolation of 9.3 g (27%) of **10** as a colorless oil after repeated chromatography of the crude product on silica gel; $\nu_{\max}^{\mathrm{neat}}$ 7.46, 8.51, and 8.77 μ ($\mathrm{SO_2}$); $\tau_{\mathrm{TMS}}^{\mathrm{CCl_4}}$ 8.53 (doublet, J = 7.0 cps, 6 H, $(\mathrm{C}\mathit{H}_3)_2\mathrm{CH}$), 6.19 (septet, J = 7.0 cps, 1 H, $(\mathrm{CH_3})_2\mathrm{C}\mathit{H}$), and 3.40 (singlet, 1 H, $\mathrm{SO_2C}\mathit{H}\mathrm{Cl_2}$).

Anal. Calcd for $\mathrm{C_4H_8Cl_2O_2S}$: C, 25.13; H, 4.18; Cl, 37.17. Found: C, 25.34; H, 4.27; Cl, 37.49.

Rearrangement of 5 with Aqueous Sodium Hydroxide. A 3.59-g (15.0 mmoles) sample of **5** in 45 ml of dioxane was refluxed with 45 ml of 2.0 *N* sodium hydroxide (90 mmoles) for 4 hr. The neutral, methylene chloride soluble portion yielded 1.69 g of colorless residual liquid after removal of the solvents. Vpc analysis of this residue on column A[23] at 125° indicated that a 56% yield of phenylacetylene (**11**) has been realized.[27]

From the aqueous layer, there was isolated 1.35 g (31.0%) of **12** as its *p*-toluidine salt. Recrystallization of this material from ethanol–ether provided the analytical sample as small white needles, mp 210–211° dec.[28]

Anal. Calcd for $\mathrm{C_{15}H_{17}NO_3S}$: C, 61.73; H, 5.88; N, 4.81. Found: C, 61.79; H, 5.91; N, 4.70.

The other rearrangements described in Table I were performed in an analogous manner.

Rearrangement of 6 with Aqueous Sodium Hydroxide. In the manner described above, 3.80 g (15.0 mmoles) of **6** in 45 ml of dioxane was refluxed with 45 ml of 2.0 *N* sodium hydroxide solution (90 mmoles) for 1 hr.[30] The neutral, methylene chloride soluble portion yielded 1.39 g of pale yellow residue after removal of the solvents. Vpc analysis of this residue on column B[23] at 170° gave the following results:[27] phenylallene (**13**), 3%; *cis*- and *trans*-1-chloro-3-phenyl-1-propene (**14**), 17%. The various products were separated by preparative gas chromatography. 3-Phenyl-1-propene and phenylallene provided spectra which were identical with those of authentic samples. The *cis* and *trans* isomers of 1-chloro-3-phenyl-1-propene could not be sufficiently well separated from each other. Rather, elemental analysis was obtained on the purified mixture.

Anal. Calcd for $\mathrm{C_9H_9Cl}$: C, 70.82; H, 5.94; Cl, 23.24. Found: C, 70.23; H, 5.84; Cl, 22.20.

From the aqueous layer, there was isolated 0.52 g (17.1%) of the sodium salt of **15**, colorless platelets from ethanol containing small amounts of water, mp >320°;[31] $\nu_{\max}^{\mathrm{Nujol}}$ 8.46 and 9.50 μ ($\mathrm{SO_3^-}$); $\tau_{\mathrm{TPSS}}^{\mathrm{D_2O}}$ 6.32 (singlet, 2 H, $\mathrm{PhC}\mathit{H}_2$), 4.81 (singlet, 1 H, vinyl proton), 4.11 (singlet, 1 H vinyl proton), and 2.86 (singlet, 5 H, phenyl group).

Anal. Calcd for $\mathrm{C_9H_9NaO_3S}$: C, 49.08; H, 4.12; S, 14.56. Found: C, 49.04; H, 4.12; S, 14.02.

Rearrangement of 7 with Aqueous Sodium Hydroxide. In the manner described above, 4.01 g (15 mmoles) of **7** in 45 ml of dioxane was refluxed with 45 ml of 2.0 *N* sodium hydroxide solution (90 mmoles) for 4 hr. The neutral, methylene chloride soluble portion yielded 2.50 g of almost colorless liquid after removal of the major

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(25) Obtained from the Wateree Chemical Co., Lugoff, S. C.

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

(27) Dioxane excluded; percentages refer to over-all yield from the dichloro sulfone.

(28) The structure of **12** was established by conversion of an authentic sample of sodium *trans*-2-phenylethene-1-sulfonate[29] to the identical *p*-toluidine salt. We have established the stereochemistry of this sodium sulfonate by nmr spectroscopy.

(29) F. G. Bordwell, C. M. Suter, J. M. Holbert, and C. S. Rondestvedt, *J. Am. Chem. Soc.*, **68**, 139 (1946). The authors are indebted to Professor Bordwell for a generous sample of this sodium salt.

(30) When the same reaction was allowed to reflux the full 4 hr as in other experiments, no meaningful results were obtained.

(31) Attempts to prepare the *p*-toluidine salt in this instance were thwarted because of the apparent instability of this derivative. Attempts to recrystallize the initially formed pale yellow solid derivative invariably resulted in decomposition to a reddish, ether-soluble liquid.

portion of solvent. Vpc analysis of this residue on column A[23] at 172° gave the following results:[27] **16**, 50% and **17**, 14%.

Anal. Calcd for $C_{10}H_{10}$: C, 92.26; H, 7.74. Found: C, 92.22; H, 7.82. Calcd for $C_{10}H_{11}Cl$: C, 72.07; H, 6.66. Found: C, 72.09; H, 6.76.

From the aqueous layer there was isolated 0.89 g (18.6%) of the *p*-toluidine salt of **18** as a white powder from water, mp 166–167°; $\tau_{\text{TPSS}}^{\text{D}_2\text{O}}$ 6.8–7.5 (multiplet, 4 H, aliphatic methylene groups), 7.79 (singlet, 3 H, CH_3Ar), 4.65 (singlet, 1 H, vinyl proton), 4.15 (singlet, 1 H, vinyl proton), and 2.69 (singlet, 9 H, phenyl protons).

Anal. Calcd for $C_{17}H_{21}NO_3S$: C, 63.92; H, 6.62; N, 4.38. Found: C, 63.84; H, 6.70; N, 4.41.

Rearrangement of 8 with Aqueous Sodium Hydroxide. In the manner described above, 6.99 g (30 mmoles) of **8** in 90 ml of dioxane was refluxed with 90 ml of 2.0 *N* sodium hydroxide solution (0.18 mole) for 4 hr. From the neutral fraction (column A[23] at 110°) there was isolated[27] 1-heptyne (**19**), 39%; *cis*-1-chloro-1-heptene, 24.4%; and *trans*-1-chloro-1-heptene, 5.7%. The various products were separated by preparative gas chromatography. The 1-heptyne proved to be identical in all respects with an authentic sample.[32] The *cis*-vinyl chloride displayed strong infrared absorption (CCl_4) at 6.1 μ (*cis*-substituted olefin).

Anal. Calcd for $C_7H_{13}Cl$: C, 63.40; H, 9.81. Found: C, 63.76; H, 9.86.

The *trans*-vinyl chloride showed a strong infrared band (CCl_4) at 10.7 μ (*trans*-substituted olefin).

Anal. Calcd for $C_7H_{13}Cl$: C, 63.40; H, 9.81. Found: C, 63.25; H, 9.92.

From the aqueous layer, there was isolated 1.23 g (20.4%) of the sodium salt of **21**, small white needles from ethanol–ether, mp 340–342° dec.

Anal. Calcd for $C_7H_{13}NaO_3S$: C, 41.99; H, 6.54; S, 16.01. Found: C, 41.84; H, 6.71; S, 16.29.

The nmr spectrum (D_2O) displayed a series of multiplets in the τ 7.68–8.74 region (11 H, aliphatic groups) and singlets at 4.66 (1 H, vinyl proton) and 4.10 (1 H, vinyl proton).

Rearrangement of 9 with Aqueous Sodium Hydroxide. In the manner described above, 6.94 g (30 mmoles) of **9** in 90 ml of dioxane was refluxed with 90 ml of 2.0 *N* sodium hydroxide solution (0.18 mole) for 4 hr. From the neutral fraction (column A[23] at 125°) there was isolated[27] a 59.7% yield of chloromethylenecyclohexane, bp 158–160°, $n^{25}\text{D}$ 1.4885 (after preparative gas chromatography) (lit.[33] bp 161–162°, $n^{26}\text{D}$ 1.4883).

The aqueous portion yielded a total of 1.88 g (19.6%) of the *p*-toluidine salt of **23** as fine white needles from water, mp 199–201° dec.

Anal. Calcd for $C_{14}H_{22}ClNO_3S$: C, 52.56; H, 6.93; Cl, 11.08; N, 4.38. Found: C, 52.39; H, 7.01; Cl, 11.26; N, 4.29.

The infrared spectrum (Nujol) showed strong bands at 8.46 and 8.62 μ (SO_3^-). The nmr spectrum (dimethyl sulfoxide-d_6) displayed multiplets in the τ 7.3–8.8 region (13 H, cyclohexyl group and C$H_3C_6H_5$) and singlets at 6.20 (2 H, CH_2Cl) and 2.72 (4 H, phenyl protons).

Rearrangement of 10 with Aqueous Sodium Hydroxide. A 5.7-g (30 mmoles) sample of **10** was refluxed for 24 hr with 90 ml of 2.0 *N* sodium hydroxide solution (0.18 mole). Nitrogen was passed over the surface of the hot solution at a slow rate, and the exit gases were passed through a Dry Ice–acetone cooled trap. Examination of the condensate by vpc and preparative vpc denoted the formation of 1-chloro-2-methylpropene (**24**) in 44% yield. Its nmr spectrum was superimposable upon a published curve.[34]

The aqueous portion afforded a total of 2.1 g (37%) of the *p*-toluidine salt of **25** as small white needles from ethanol–ether, mp 208–209°.

Anal. Calcd for $C_{11}H_{18}ClNO_3S$: C, 47.22; H, 6.44; S, 11.44. Found: C, 47.11; H, 6.49; S, 11.46.

The infrared spectrum (Nujol) showed strong bands at 8.40 and 8.53 μ. The nmr spectrum (D_2O) displayed singlets at τ 8.68 (6 H, (CH_3)$_2$C<), 7.68 (3 H, C$H_3C_6H_5$), 6.22 (2 H, CH_2Cl), and 2.75 (4 H, aromatic protons).

General Procedure for Rearrangement with Potassium *t*-Butoxide in *t*-Butyl Alcohol. A 15-mmoles sample of the dichloro sulfone was placed in the reaction flask, and the system was blanketed with nitrogen. With stirring, 85 ml of a 1.06 *M* potassium *t*-butoxide–*t*-butyl alcohol solution (90 mmoles) was added through a syringe, and the resulting solution was refluxed for 0.5 hr. The formation of insoluble potassium chloride was soon in evidence. The reaction mixture was allowed to cool and 50 ml of water was added. The solution was extracted with three 50-ml portions of methylene chloride, and the combined extracts were washed with water, dried, filtered, and concentrated *in vacuo* at room temperature to a volume of approximately 50 ml. Careful fractionation of this solution gave rise to two fractions, bp 42–60 and 60–82°, which were collected, and invariably checked by vpc. The pale yellow liquid residue from the distillation was then carefully analyzed by vpc for the various components.

The aqueous portion of the reaction mixtures when worked up as in the aqueous runs (see above) failed to give any detectable quantities of sulfonic acid (as *p*-toluidine salt). The results of these rearrangements are summarized in Table I.

2-Chlorothiirane 1,1-Dioxide (28). To a vigorously stirred ethereal solution of diazomethane [4.6 g (0.11 mole) by titration] cooled to −10° was added concomitantly in dropwise fashion a solution of 14.9 (0.10 mole) of chloromethanesulfonyl chloride[35] in 40 ml of ether and a solution of 10.1 g (0.10 mole) of triethylamine in 40 ml of the same solvent. Both additions required about 45 min. The combined filtrate and washings were evaporated *in vacuo* at room temperature. A white solid residue, mp 49–51°, weighing 10.5 g (83%), was obtained. Two recrystallizations of the product from ether–hexane at −70° afforded 8.9 g of white platelets, mp 53–54°.[36]

The infrared spectrum (Nujol) showed characteristic peaks at 7.53 and 8.56 μ. The nmr spectrum ($CDCl_3$) displayed a quartet (1 H) at τ 6.83 (*J* = 9.5 and 5.5 cps), a triplet (1 H) at 6.25 (*J* = 9.5 cps), and a quartet (1 H) at 5.15 (*J* = 9.5 and 5.5 cps).

Reaction of 28 with Aqueous Sodium Hydroxide. A solution of 1.26 g (10.0 mmoles) of **28** in 10 ml of 1:1 dioxane–water was placed in a 25-ml one-necked flask modified to accommodate a magnetic stirring bar, a nitrogen inlet tube, a gas exit tube, and a capillary addition tube fitted with a syringe cap. The gas exit tube was connected in series to two traps, each containing a 5% solution of bromine in carbon tetrachloride. To the stirred solution at 25° was rapidly added *via* a syringe 10 ml of 2.0 *N* aqueous sodium hydroxide solution (20 mmoles). The ensuing reaction was very exothermic and a vigorous evolution of gas was observed. After the reaction had subsided, the solution was stirred until the temperature returned to 25°. The combined carbon tetrachloride solutions were washed with 5% sodium bisulfite and water, dried, and filtered. The filtrate, upon submission to vpc analysis, was found to contain 1-chloro-1,2-dibromoethane, *cis*-1,2-dibromoethylene, and *trans*-1,2-dibromoethylene.

Similar results were obtained in dioxane, water, or upon addition of the base to solid **28**. No reaction was evidenced in the presence of triethylamine.

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(32) The authors are indebted to Dr. Kenneth Greenlee for a generous sample of 1-heptyne.

(33) H. Guenther and A. A. Bothner-By, *Ber.*, **96**, 3112 (1963).

(34) Varian Catalog, Varian Associates, Palo Alto, Calif., Spectrum No. 67.

(35) H. Brintzinger, H. Koddebusch, K. Kling, and G. Jung, *Chem. Ber.*, **85**, 455 (1952).

(36) Because of the relative instability of this material and due to the fact that no analytical facilities were immediately accessible, elemental analysis of this compound was not obtained.