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Organic Sulfur Mechanisms. 18. The Sulfo-Cope Rearrangement and Other Thermal Reactions of Unsaturated Sulfonyl Species[1,2]

J. F. King* and D. R. K. Harding

Contribution from the Department of Chemistry, University of Western Ontario, London, Ontario N6A 5B7, Canada. *Received September 12, 1975*

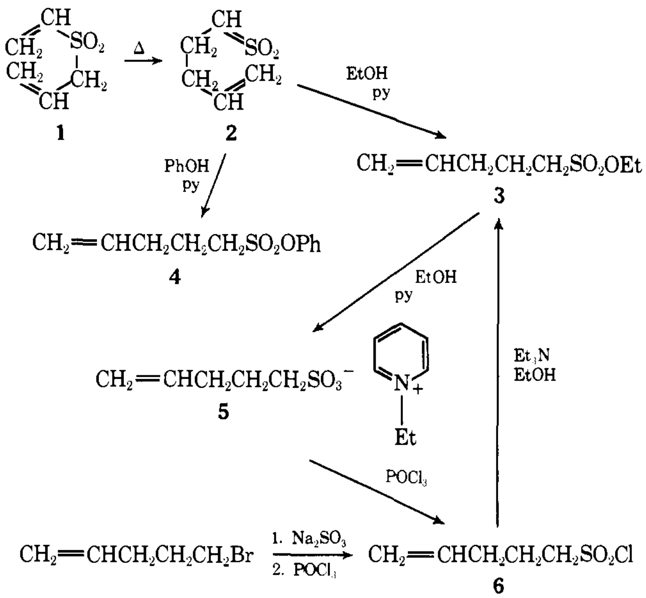
Abstract: The first examples of sulfene formation by thermal rearrangement of allyl vinyl sulfones—the "sulfo-Cope" rearrangement—are described. In ethanol-pyridine solution the *N*-ethylpyridinium salt of the corresponding sulfonic acid is obtained in good yields (70–95%); the reaction is therefore a potentially useful process for making a new carbon-carbon bond. The rearrangement takes place also on flash thermolysis to give a poor yield of the aldehyde, resulting from thermal desulfinylation of the sulfene. Deuterium labeling shows the sulfo-Cope rearrangement to be clearly of the order [3,3] either in the gas or the liquid phase. Flash thermolysis of a series of alkenesulfonyl chlorides has given a new rearrangement to a sulfene and a new desulfonylation rearrangement, as well as an elimination of sulfur dioxide and hydrogen chloride; the origins of this diversity of reaction are discussed.

As part of a systematic study of sulfenes,[3] we wished to see if they could be formed by rearrangement of an allyl vinyl sulfone, e.g., **1** → **2**. Such a process would be one of the family of "hetero-Cope" rearrangements[4] and might be conveniently labeled the "sulfo-Cope" rearrangement. Cope, Morrison, and Field[5] actually explored the possibility of such a reaction in 1950, but they obtained no identified products. We describe herein our observation that allyl vinyl sulfones, either in the liquid phase or upon flash thermolysis,[6] do, in fact, undergo a rearrangement similar to that of 1,5-hexadienes; we report also some related reactions observed on flash thermolysis of unsaturated sulfonyl chlorides.

Results

Sulfo-Cope Rearrangement in the Liquid Phase. Allyl vinyl sulfone (3-ethenesulfonylpropene, **1**), on heating in a pyridine-ethanol solution in a sealed tube at 165–175 °C for 2 h, gave *N*-ethylpyridinium 4-pentene-1-sulfonate (**5**) in about 70% yield. The structure of this product was shown by (a) elemental analysis and spectroscopy and (b) conversion of **5** to 4-pentene-1-sulfonyl chloride (**6**) and comparison of **6** with a specimen synthesized from 5-bromo-1-pentene (Scheme I). Under the conditions of the above rearrangement, authentic ethyl 4-pentene-1-sulfonate (**3**) is converted to **5** in 93% yield. Both this and the formation of **4** (in only 14% yield, however) on heating **1** in phenol-pyridine, are in accord with the pathways shown in Scheme I. A number of other reaction media were tried (see Experimental Section), but gave little or no identified product.

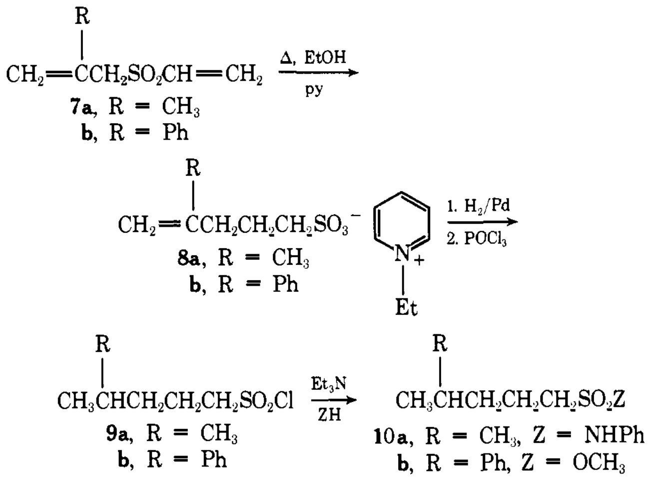
Scheme I



Similar heating of **7a** and **7b** gave the rearranged products **8a** and **8b** in 96 and 81% yields, respectively. The rearrangement of **7b** proceeds also at lower temperatures, a 64% yield of **8b** being obtained after 2 h at 125°. The assignment of structures **8a** and **8b** follows not only from the analogy with **5**, but also from the agreement of analytical and spectroscopic data obtained both from **8a** and **8b** themselves and from the further transformation products shown in Scheme II.

In order to determine if this rearrangement is of the order [3,3] or [1,3] (or both), allyl-α,α-d_2 vinyl sulfone (**11**) was prepared by base-catalyzed deuteration[7] of **1** and rearranged in pyridine-ethanol-*d*. The product (**12**) obtained after reaction with phosphorus oxychloride was exactly that expected for a [3,3] rearrangement: the CD_2 was, within the limits of NMR detection, entirely at the terminal carbon and, in addi-

Scheme II



tion, one deuterium was found on C-1, as required by the sulfene mechanism.

$$\underset{\mathbf{11}}{CH_2{=}CHCD_2SO_2CH{=}CH_2} \xrightarrow[\text{2. POCl}_3]{\text{1. }\Delta\text{,EtOD,py}} \underset{\mathbf{12}}{CD_2{=}CHCH_2CH_2CHDSO_2Cl}$$

Flash Thermolyses. Allyl vinyl sulfone (**1**) and 800° and 20–60 μm in the flash thermolysis apparatus[6,8] gave mostly polymeric product together with small yields of 4-pentenal and acetaldehyde, isolated as the 2,4-dinitrophenylhydrazones (in 9 and 2% yields, respectively); at 950° a lower yield of the aldehydes was obtained and at 620° only recovered starting material was identified. Flash thermolysis of allyl-α,α-d_2 vinyl sulfone (**11**), like the liquid phase reaction, gave the product with the CD_2 group at the terminal position, i.e., $CD_2{=}CHCH_2CH_2CHO$.

For reasons mentioned in the Discussion, a series of homologous alkenesulfonyl chlorides was subjected to flash thermolysis and gave the products shown below:

$$\underset{\mathbf{13}}{CH_2{=}CHSO_2Cl} \xrightarrow[20\text{–}70\ \mu m]{1110°} ClCH_2CHO\ (25\%)$$

$$\underset{\mathbf{14}}{CH_2{=}CHCH_2SO_2Cl} \xrightarrow[20\ \mu m]{700°} ClCH_2CH{=}CH_2\ (>80\%) + SO_2$$

$$\underset{\mathbf{15}}{CH_2{=}CHCH_2CH_2SO_2Cl} \xrightarrow{700°} \text{polymer} + CH_2{=}CHCH{=}CH_2 + SO_2$$

In addition, 1-propene-1-sulfonyl chloride evidently reacted in a qualitatively similar manner to **13**, giving at 950° what appeared to be 1-chloropropionaldehyde. Thermolysis of **14** in a quartz tube at 500–600 °C at ~0.1 mm also gave allyl chloride; when 2-propene-1-sulfonyl-*1-d* chloride ($CH_2{=}CHCHDSO_2Cl$) was so treated, 3-chloropropene-*1-d* ($CHD{=}CHCH_2Cl$) was obtained. 2-Methyl-2-propene-1-sulfonyl chloride on flash thermolysis at 670° gave 3-chloro-2-methylpropene (29% yield), sulfur dioxide, and some cellophane-like polymer. A similar looking polymer, which also showed sulfonyl bands in the infrared, was the major product from **15**; no attempt was made to determine the yields of butadiene and sulfur dioxide, but they were at least 10%. 4-Pentene-1-sulfonyl chloride at 1000° gave mostly a colored polymer plus a very small amount of acetaldehyde, but no sign of any 4-pentenal.

Discussion

The existence of the sulfo-Cope rearrangement is clearly shown by the reaction in the liquid phase of **1**, **7a**, and **7b**. It is likely that reaction is general, provided that appropriate reaction conditions are used. The important factors in choosing these conditions appear to be: (a) the presence of a (weak) base to inhibit acid-catalyzed polymerization[9] and perhaps also to catalyze trapping of the sulfene,[10] and (b) avoidance of species (e.g., primary and secondary amines) which readily add to the ethenesulfonyl group.[11] In the 1:1 pyridine-ethanol mixture, which gave us our best results, the yields ranged from 70 to 96%. Since the reaction is a new carbon-carbon bond-forming process as well as a method of generating a sulfene, this suggests that it ought to find use in synthesis. We have, in fact, already had occasion to make use of this reaction; hydrogenation of a material believed to be methyl 4-phenyl-2,4-pentadiene-1-sulfonate (obtained from photolytic methanolysis of 3-phenyl-2*H*-thiopyran 1,1-dioxide) gave **10b**, thereby providing evidence for the structure of the photolysis product.[1]

The reaction of **1** on flash thermolysis is not nearly as clean as that in the liquid phase, but it is extremely likely that the 4-pentenal is also formed via a sulfo-Cope rearrangement, followed then by thermal desulfinylation[8] (the latter being the normal reaction of sulfenes on flash thermolysis above ~800°). That the sulfo-Cope rearrangement, in either the gas or liquid phase, is a well-behaved [3,3] sigmatropic rearrangement, is shown by the exclusive formation from **11** of products with the terminal CD_2 group.

The most noteworthy feature of the flash thermolysis of the unsaturated sulfonyl chlorides is the fact that they all react differently, as one may see from the following list:

$$CH_3SO_2Cl \rightarrow [CH_2{=}SO_2] + HCl \quad (1)$$

$$CH_2{=}CHSO_2Cl \rightarrow [ClCH_2CH{=}SO_2] \quad (2)$$

$$CH_2{=}CHCH_2SO_2Cl \rightarrow ClCH_2CH{=}CH_2 + SO_2 \quad (3)$$

$$CH_2{=}CHCH_2SO_2Cl \rightarrow CH_2{=}CHCH{=}CH_2 + SO_2 + HCl \quad (4)$$

Included above is the thermolysis of methanesulfonyl chloride,[12] which apparently yields the sulfene which then undergoes desulfinylation. It was the hope of observing the reaction analogous to (1) which prompted our initial experiments with 1- and 2-propenesulfonyl chlorides. It was expected that vinyl sulfene so obtained would either form the five-membered ring sultine or acrolein (depending on the reaction conditions) as has been postulated previously;[8] the observed results were, however, quite different. 1-Propenesulfonyl chloride (like ethenesulfonyl chloride) presumably formed a sulfene, but by rearrangement as in (2), and 2-propenesulfonyl chloride gave allyl chloride and sulfur dioxide. Since the deuterium label initially α to the sulfonyl group was found γ to the chlorine in the product, the latter reaction may therefore be regarded as a six-electron pericyclic fragmentation-rearrangement, as exemplified by the reverse ene reaction and the decarboxylation of β,γ-unsaturated carboxylic acids and the like. Reaction 3 has a very close analogue in the desulfonylation-rearrangement of allylic sulfones, which was discovered and shown to be primarily a cyclic process by La Combe and Stewart.[13] Perhaps still more closely related to (3) is the desulfonylation-rearrangement of allyl chlorosulfites in nonpolar solvents.[14]

Olefin formation by loss of HCl and SO_2, as in (4), has also been observed as the principal reaction in the gas phase flow system thermolysis of 1- and 1-propanesulfonyl chlorides,[15] and can probably be regarded as the normal thermal reaction of a sulfonyl chloride of the type $R^1R^2CHCR^3R^4SO_2Cl$ under circumstances which do not permit a free radical chain process.

In a static gas-phase[16] or liquid-phase[17] thermolysis, a free-radical chain reaction seems to be the preferred process.

In an attempt to find some order in the above multiplicity of reactions, we have made the following very rough estimates of the enthalpies[18] of these reactions: $\Delta H_{(1)} \simeq 17$, $\Delta H_{(2)} \simeq 3$, $\Delta H_{(3)} \simeq -6$, $\Delta H_{(4)} \simeq 9$ kcal/mol, also for the sulfo-Cope rearrangement $\Delta H \simeq 7$ kcal/mol and for the desulfinylation ($>C{=}SO_2 \rightarrow >C{=}O + SO$) $\Delta H \simeq 11$ kcal/mol. We are cautiously gratified to find that the ease of these reactions can be seen to be related to the enthalpy values. Reaction 3 proceeds under the mildest conditions and in good yield; in addition to being exothermic (3) is, of course, also a comfortably allowed pericyclic process. Reaction 2 and the sulfo-Cope rearrangement are next in increasing endothermicity, but, unlike the other reactions (which, as fragmentations, are irreversible under these conditions), are most likely in an unfavorable equilibrium with starting materials. These reactions, then, become detectable in such circumstances only if the sulfene undergoes an irreversible reaction, e.g., desulfinylation; this, however, is also endothermic, and, not surprisingly, neither reaction goes well in the gas phase.[26] In the liquid phase, however, the sulfo-Cope rearrangement can be trapped by ester formation, which is exothermic by an estimated 20 kcal/mol. Of the remaining reactions 1 and 4, the latter is the less endothermic and apparently the normal reaction when the structural requirements are met, and when a free radical chain reaction is precluded by the reaction conditions, as it almost certainly is under flash thermolysis. When a free radical chain is possible, the exothermic conversion to the alkyl chloride and SO_2 (cf. reaction 3) becomes the preferred path, and hence the change in products on changing from a flow to a static gas-phase system found by Geiseler[15,16] with the propanesulfonyl chlorides.

Experimental Section

NMR spectra were obtained with Varian A-60, T-60, and HA-100 spectrometers and ir spectra with Beckman IR-10 and IR-20A instruments using NaCl plates or cells (0.1 mm). Melting points were determined on a Kofler hot stage and are uncorrected. Flash thermolyses were performed as described previously.[8]

Liquid-Phase Thermolysis of Allyl Vinyl Sulfone (3-Ethenesulfonylpropene, 1). Allyl vinyl sulfone (**1**, 0.5 g, 3.79 mmol), prepared as described by Cope et al.,[5] was heated in ethanol (5 ml) and pyridine (5 ml) for 2 h at 160–170 °C in a sealed tube. The reaction mixture was evaporated to a gum that was dissolved in water. The aqueous mixture was washed with ether (2 × 25 ml) and then evaporated to dryness. The residue was dissolved in CH_2Cl_2 and dried over $MgSO_4$. Evaporation gave an oil, 700 mg (72%), that was identical in ir and NMR spectra with the *N*-ethylpyridinium 4-pentene-1-sulfonate (**5**) produced from ethyl 4-pentene-1-sulfonate (see below). A second run gave a 70% yield of **5**.

The *N*-ethylpyridinium salt (**5**, 0.5 g, 1.95 mmol) was treated with phosphorus oxychloride (3 ml) on a steam bath for 2 h. The resulting liquid was poured onto ice and worked up by extraction with ether to yield an oil (235 mg, 70% from **5**) which was identical in ir and NMR spectra with authentic 4-pentene-1-sulfonyl chloride (**6**). A larger scale reaction starting with 5 g of **1** in ethanol (50 ml) and pyridine (50 ml) yielded 3.6 g of **6** (63% from **1**), bp 49–52 °C (0.5 mm).

Allyl vinyl sulfone (**1**) (0.5 g, 3.78 mmol) was heated with pyridine (0.5 g, 6.3 mmol) and phenol (3 g, 31.5 mmol) at 165–170 °C for 2 h in a sealed tube. Removal of the pyridine was followed by partitioning of the residue between ether and water. The usual workup gave a crude product (0.55 g) that was purified by TLC to give **4** as an oil (102 mg, 14%), identified by comparison of the ir and NMR spectra with those of an authentic sample prepared from **6**.

Similar thermolyses (2 h at 165–175 °C) using the following reaction media gave no identified products: aniline, aniline–benzene, phenol–benzene, water, water–dioxane, ethanol, ethanol–water–sodium bicarbonate, pyridine, and pyridine–water.

Allyl-α,α-d_2 Vinyl Sulfone (3-Ethenesulfonylpropene-*3,3*-d_2, 11). Allyl vinyl sulfone (**1**) (4 g, 30 mmol) in a dioxane (8 ml) and deuterium oxide (12 ml) solution was treated with 1 M sodium deuterioxide (1 ml) for 15 min at room temperature. The reaction was then quenched with 3 M hydrochloric acid. The reaction mixture was diluted to 50 ml with water and worked up with methylene chloride to give **11** as an oil (1.7 g, 42%), bp 84–88 °C (1.5 mm). A small sample was redistilled on a cold finger apparatus: NMR ($CDCl_3$) δ 3.65–3.80 (br m, 0.08), 5.35–5.5 (m, 2), 5.55–6.0 (br m, 1), 6.16–6.4 (m, 2), and 6.72 (dd, 1); ν_{max} (film) 2240 (CD), 1635 and 1615 (C=C), and 1310 and 1140 (SO_2) cm^{-1}. For complete α,α-dideuteration: Calcd. 25 atom % excess D. Found: 22.95 atom % excess D (92% dideuteration).

Liquid-Phase Thermolysis of 11. The dideuterated sulfone (**11**). prepared above (0.5 g, 3.7 mmol) in ethanol-*d* (5 ml) and pyridine (5 ml) was heated in a sealed tube and worked up; the product was converted to the sulfonyl chloride (**12**) as with **1**: NMR (of distilled product, $CDCl_3$) δ 2.0–2.4 (m, 4), 3.4–3.8 (m, 1), 4.9–5.2 (d, 0.2), and 5.5–5.9 (m, 1), indicating about 90% dideuteration at C-5 and virtually complete monodeuteration at C-1.

4-Pentene-1-sulfonyl Chloride (6). Sodium sulfite (9 g, 72 mmol) and 5-bromo-1-pentene[28] (8.9 g, 60 mmol) were mixed with water (30 ml), and the entire mixture was refluxed overnight with vigorous stirring. The aqueous layer was cooled, washed with ether, and evaporated to dryness. The residue was treated with phosphorus oxychloride (50 g) and heated at 120–140 °C for 1.5 h with stirring. Workup as before and distillation gave 6.7 g (67%) of **6**, bp 60–66 °C (0.3 mm): NMR ($CDCl_3$) δ 2.0–2.5 (m, 4), 3.5–4.0 (t, 2), 4.9–5.4 (m, 2), and 5.5–6.3 (m, 1); ν_{max} (film) 1640 (C=C) and 1375 and 1170 (SO_2) cm^{-1}. Anal. ($C_5H_9ClO_2S$) C, H, Cl, S.

Phenyl 4-Pentene-1-sulfonate (4). Triethylamine (2.5 ml, 1.8 g, 18 mmol) was added to a stirred solution of **6** (0.5 g, 3 mmol) and phenol (2 g, 21 mmol) in methylene chloride (10 ml). After 0.25 h the solvent was removed, and the product was worked up in the usual way to give an oil (712 mg), which was distilled at 0.05 mm to give 616 mg of crude **4**. The distillate was chromatographed on 0.5 mm silica gel TLC plates with methylene chloride as eluent and redistilled: NMR ($CDCl_3$) δ 1.9–2.5 (m, 4), 3.3 (t, 2), 4.8–5.3 (m, 2), 5.4–6.2 (m, 1), and 7.2–7.6 (m, 5); ν_{max} (film) 1638 (C=C) and 1375 and 1153 (SO_2) cm^{-1}. Anal. ($C_{11}H_{14}O_3S$) C, H, S.

Ethyl 4-Pentene-1-sulfonate (3). Triethylamine (20 ml, 14.6 g, 0.15 mmol) was added to a stirred solution of **6** (3.8 g, 0.023 mol) in ethanol (60 ml). Workup after 2 h at room temperature gave **3** as a colorless oil (3.2 g, 80%), bp 105–108 °C (5 mm): NMR ($CDCl_3$) δ 1.4 (t, 3), 1.8–2.4 (m, 4), 3.2 ("t", 2), 4.3 (q, 2), 4.8–5.4 (m, 2), and 5.5–6.3 (ddt, 1); ν_{max} (film) 1640 (C=C) and 1350 and 1170 (SO_2) cm^{-1}. Anal. ($C_7H_{14}O_3S$) C, H, S.

***N*-Ethylpyridinium 4-Pentene-1-sulfonate (5) from Ethyl 4-Pentene-1-sulfonate (3).** The ester (**3**) (510 mg, 2.86 mmol) was dissolved in pyridine (5 ml) and ethanol (5 ml) and the mixture heated for 2 h at 160–170 °C in a sealed tube. Workup as in the thermolysis of **1** gave **5** (686 mg, 93%), which was recrystallized twice from acetone–ether using an acetone–dry ice bath and working in a cold room (−30°). The resulting crystalline material melted at 40–41 °C and was extremely hygroscopic: NMR ($CDCl_3$) δ 1.7 and 1.8–2.3 (t and m, 7), 2.8 (m, 2), 4.7–5.1 (m, 4), 5.5–6.0 (ddt, 1), 8.2 (t, 2), 8.7 (t, 1), and 9.55 (d, 2); ν_{max} (CH_2Cl_2) 1634 (C=C) and 1190 (SO_3^-) cm^{-1}. Anal. ($C_{12}H_{19}NO_3$) C, H, N, S.

3-Ethenesulfonyl-2-methylpropene (7a).[29] 2-Mercaptoethanol (78 g, 71 ml, 1 mol) was added to a solution of potassium hydroxide (56 g, 1 mol) in ethanol (300 ml). When the mixture had cooled, 3-chloro-2-methylpropene (Eastman, 90.6 g, 98 ml, 1 mol) was added with stirring. The mixture was stirred for 0.5 h and the sodium chloride then removed by filtration. The ethanol was evaporated and the residue worked up by ether extraction and distillation to give β-hydroxyethyl 2-methylallyl sulfide, 118.4 g (90%), bp 60–72 °C (1 mm): NMR ($CDCl_3$) δ 1.83 (d, 3), 2.50 (br s, 1), and 2.63 ppm (t, 2) (addition of D_2O removed the peak at δ 2.5 (br s) and resolved the peak at δ 3.55–3.85 (m) into a triplet at δ 3.68); ν_{max} (film) 3380 (OH) and 1645 (C=C) cm^{-1}; 3,5-dinitrobenzoate, mp 59–60 °C; NMR ($CDCl_3$) δ 1.87 (s, 3), 2.83 (t, 2), 3.20 (s, 2), 4.59 (t, 2), 4.93 (s, 2) and 8.07–8.37 (m, 3); ν_{max} (CH_2Cl_2): 1738 (C=O), 1633 (C=C), and 1548 and 1146 (NO_2) cm^{-1}. Anal. ($C_{13}H_{14}N_2O_6S$) C, H, N, S.

β-Hydroxyethyl 2-methylallyl sulfide (159 g, 1.2 mol) was added at a fast drip to stirred thionyl chloride (200 ml). The mixture was refluxed for 1 h, the thionyl chloride removed, and the mixture worked up with ether extraction and distillation to give an oil, 125.3 g, bp 79–85 °C (10 mm): NMR ($CDCl_3$) δ 1.67 (s), 1.83 (s), 2.6–3.1 (m), 3.18 (s), 3.5–3.8 (m), and 4.95 (s), indicating the product to be a mixture of the desired β-chloroethyl 2-methyl-2-propenyl sulfide and the isomeric β-chloroethyl isobutenyl sulfide; ν_{max} (film) 1635 cm^{-1}. This material was converted to **7a** as described by Cope et al. for the preparation of **1** to give 63 g of **7a**, bp 81–98 °C (1 μ): NMR ($CDCl_3$) δ 1.83–2.03 (m, 3), 3.70 (s, 2), 4.98–5.23 (m, 2), 6.15 (d, 1, J = 10 Hz), 6.34 (d, 1, J = 17 Hz), and 6.73 (dd, 1), as expected for **7a**; ν_{max} (film) 1630, 1597 (C=C), and 1295 and 1100 (SO_2) cm^{-1}. Anal. ($C_6H_{10}O_2S$) C, H, S.

Thermolysis of 3-Ethenesulfonyl-2-methylpropene (7a). Sulfone **7a** (5 g, 34.2 mmol) was dissolved in ethanol (50 ml) and pyridine (50 ml) and the resulting solution heated and worked up as with **1** to yield 8.9 g (96%) of **8a** as sticky crystals: NMR ($CDCl_3$) δ 1.41–2.31 (2m, 10), 2.80 (t, 2), 3.66 (s, 2), 3.92 (q, 2), 8.15 (t, 2), 8.57 (t, 1), and 9.47 (d, 2), consistent with **8a**. This salt (**8a**) was dissolved in ethanol (100 ml) and hydrogenated over platinum oxide (500 mg) at 4 atm in a Parr apparatus; a further portion (250 mg) of catalyst was added after 15 h and then the hydrogenation was continued for another 8 h. The product was 8.6 g of a sticky solid. NMR ($CDCl_3$): δ 0.87 (d, 6), 1.10–2.20 (m, 8), 2.66–3.0 (m, 2), 4.95 (q, 2), 8.19 (t, 2), 8.61 (t, 1), and 9.55 (d, 2). The reduced material was dissolved in phosphorus oxychloride (30 ml) and heated for 1 h on a steam bath as before to give **9a** as an oil, 4.3 g (68% from **7a**) bp 55–62 °C (0.5 mm). Redistillation yielded 2.8 g, bp 56–57 °C (0.3 mm). NMR ($CDCl_3$): δ 0.92 (d, 6), 1.20–1.75 (m, 3), 1.85–2.20 (m, 2), and 3.50–3.75 (m, 2); ν_{max} (film): 1370 and 1160 (SO_2) cm^{-1}. Anal. ($C_6H_{13}ClO_2S$) C, H, Cl, S.

4-Methylpentane-1-sulfonanilide (10a). 4-Methylpentane-1-sulfonyl chloride (**9a**) (1 g, 5.4 mmol) was dissolved in ether (30 ml) and treated with aniline (5 ml) and then with triethylamine (5 ml). The mixture was stirred for 0.25 h and then worked up as usual yielding **10a** (0.95 g, 75%) as a white crystalline solid which was recrystallized twice from ether–petroleum ether (30–60 °C), mp 44–45 °C: NMR ($CDCl_3$) δ 0.71 (d, 6), 0.94–2.10 (m, 5), 2.90–3.30 (m, 2), and 7.00–7.60 (m, 6); addition of D_2O slowly reduced the relative area of the multiplet at δ 7.00–7.60 to 5; ν_{max} (CH_2Cl_2): 3355 (NH) and 1348 and 1148 (SO_2) cm^{-1}. Anal. ($C_{12}H_{19}NO_2S$) C, H, N, S.

3-Ethenesulfonyl-2-phenylpropene (7b).[29] Potassium 2-hydroxyethylthiolate and 3-bromo-2-phenylpropene[30] (estimated by NMR to contain 20–30% 1-bromo-2-phenylpropene) were allowed to react overnight and worked up as in the preparation of **7a**. The distilled product was oxidized with 2 equiv of *m*-chloroperbenzoic acid in refluxing CH_2Cl_2 overnight. The β-hydroxy sulfone so obtained was converted to **7b** by mixing with triethylamine (3 equiv) in CH_2Cl_2 and adding thionyl chloride (1 equiv) in CH_2Cl_2 dropwise; workup and purification by TLC gave **7b** as a pale yellow oil that was used directly for the thermolysis. Further TLC and cold-finger distillation gave an analytical specimen: NMR ($CDCl_3$) δ 4.13 (s, 2), 5.55 (d, 2), 5.91 (dd, 1), 6.20 (dd, 1), 6.47 (dd, 1), and 7.10–7.60 (m, 5); ν_{max} (film) 1300 and 1110 (SO_2) cm^{-1}. Anal. ($C_{11}H_{12}O_2S$) C, H, S.

Thermolysis of 3-Ethenesulfonyl-2-phenylpropene (7b). 2-Phenyl-2-propenyl vinyl sulfone (3.5 g, ca. 17 mmol) was heated for 2 h at 170° in ethanol (35 ml) and pyridine (35 ml) in sealed tubes. The solvent was removed and the residue treated in water with activated charcoal. The water was removed and the material dried further over $MgSO_4$ in methylene chloride, which was evaporated to give **8b** as a sticky material that partially crystallized after drying under vacuum (4.6 g, 81%): NMR ($CDCl_3$) δ 1.58 (t, 3), 1.74–2.20 (m, 2), 2.42–3.10 (m, 4), 4.79 (q, 2), 4.98–5.36 (m, 2), 7.00–7.60 (m, 5), 8.01 (t, 2), 8.38 (t, 1), and 9.35 (d, 2), as expected for **8b**. Conversion of **8b** through **9b** to **10b** is described elsewhere.[1]

Flash Thermolyses. A. Allyl Vinyl Sulfone (1). Allyl vinyl sulfone (**1**) (390 mg, 2.93 mmol) was flash thermolyzed[8] at 800° and 20–60 μm. The volatile products were distilled directly from the cold finger into a flask on the manifold. The flask was quickly removed from the manifold and a solution of 2,4-dinitrophenylhydrazine in phosphoric acid (25 ml) was added as rapidly as possible to the frozen products. After 15 min the mixture was diluted with water (50 ml) and extracted with carbon tetrachloride. The dilution and extraction steps were repeated. The combined organic solutions were dried over $MgSO_4$ and the carbon tetrachloride was removed. The crude hydrazone was purified by TLC (0.5 mm Kieselgel DF-5 plates) with methylene chloride as eluent to give 4-pentenal 2,4-dinitrophenylhydrazone (66 mg, 8.5%) and acetaldehyde 2,4-dinitrophenylhydrazone (16 mg, 2.3%). Two recrystallizations of the 4-pentenal 2,4-dinitrophenylhydrazone from ethanol gave an orange solid, mp 118–119 °C, mmp (with authentic 4-pentenal 2,4-dinitrophenylhydrazone) 117–119 °C; the ir and NMR spectra were identical with those of the material prepared from authentic 4-pentenal.[31]

B. Allyl-α,α,d_2 Vinyl Sulfone (11). Two thermolyses of **11** (513 mg and 516 mg, total 7.67 mmol, 92% dideuterated material prepared as above) were carried out as with **1** giving 18.6 mg (9%) of the deuterated 4-pentenal 2,4-dinitrophenylhydrazone (mp 118–120 °C): NMR ($CDCl_3$) δ 2.2–2.7 (m, 4), 5.0–5.3 (m, 0.3), 5.6–6.1 (br, 1), 7.56 (t, 1), 7.90 (dd, 1), 8.30 (dd, 1), 9.06 (d, 1), and 11.0 (s, 1), showing the D atoms to be at C-5. Found: 15.25 atom % excess D (92% of dideuteration).

C. **Ethenesulfonyl Chloride**[32] **(13).** The volatile products from thermolysis of **13** (256 mg) at 1110° and 20–70 μm were distilled directly onto a frozen mixture of 2,4-dinitrophenylhydrazine (210 mg) and methanol (5 ml). The mixture was warmed to room temperature and concentrated HCl (2 drops) was added; the mixture was refluxed for 0.5 h and chilled, and the hydrazone was filtered to give 94 mg, mp 154–6 °C (lit.[33] mp 158–160 °C for the 2,4-dinitrophenylhydrazone of chloroacetaldehyde); a second crop gave 23 mg, mp 153–154 °C, totaling to a 25% yield of chloroacetaldehyde. The first crop was recrystallized from chloroform, giving fine needles, mp 159–160 °, identified by ir, NMR, and mixed up with an authentic sample prepared from chloroacetaldehyde dimethyl acetal (Eastman). A repeat reaction using 254 mg of ethenesulfonyl chloride and replacing the concentrated hydrochloric acid with gaseous hydrochloric acid (a few bubbles) gave 123 mg (25%), mp 151–154 °C. In another run, spectra of the volatile products were examined directly: NMR ($CDCl_3$) δ 3.98 (d, CH_2) and 9.6 (br s, CHO); ir (CCl_4) 1740 cm^{-1}. Thermolysis at 900–950 °C gave a product with both chloroacetaldehyde and **13** showing in the NMR and ir spectra.

D. **1-Propene-1-sulfonyl Chloride.**[34] Thermolysis at 530–550 °C (40 μm) gave back starting material. The volatile component of the product obtained from thermolysis at 950° (20–50 μm) showed bands at 2840 and 1740 cm^{-1} in the ir and at δ 1.6 (d), 4.2 (m), and 9.5 (d) in the NMR, consistent with formation of 1-chloropropionaldehyde.[35] An attempt to isolate a DNP derivative was unsuccessful.

E. **2-Propene-1-sulfonyl Chloride**[36] **(14).** Thermolysis of two samples of **14** (~250 mg) at 700° and 20 μm gave 81 and 79% yields of allyl chloride as determined by comparison of the NMR spectrum with that of an authentic specimen (BDH) and integration of the NMR signals vs. that of a known amount of dimethyl sulfone added to the sample.

F. **2-Methyl-2-propene-1-sulfonyl Chloride.**[37] Thermolysis at 670° and 10–15 μm gave 3-chloro-2-methylpropene (29%) by qualitative and quantitative NMR as above. Sulfur dioxide (as shown by ir) and a cellophane-like polymer (weight ca. one-third of the starting material) with bands at 1710, 1325, and 1140 cm^{-1} were also formed.

G. **3-Butene-1-sulfonyl Chloride (15).** At 1040° and 20–40 μm, and at 700° and 20–40 μm, two samples (ca. 175 mg each, obtained as described below) gave butadiene, identified by comparison of ir and NMR spectra with those of authentic material (Phillips); SO_2 (identified by ir) and a cellophane-like polymer (about one-half the weight of starting material) with bands at 1295 and 1120 cm^{-1} were also formed.

H. **4-Pentene-1-sulfonyl Chloride.** Thermolysis of 512 mg of this sulfonyl chloride at 1000° and 20–50 μm gave a large amount of colored polymeric material. From the volatile product acetaldehyde 2,4-dinitrophenylhydrazone (56 mg) was prepared; there was no sign of any of the DNP of 4-pentenal.

3-Butene-1-sulfonyl Chloride (15). A mixture of 4-bromobutene[28] (13.6 g, 0.1 mol), Na_2SO_3 (15 g, 0.12 mol), and water (50 ml) was heated at 120–130 °C overnight with vigorous stirring. The water was removed and the residue treated with $POCl_3$ (70 ml) and heated at 120–140 °C for 2 h with vigorous stirring. The mixture was cooled, poured onto ice, and worked up by ether extraction followed by distillation, which gave **15** as a colorless oil (8.6 g, 56%), bp 45–50 °C (0.7 mm): NMR ($CDCl_3$) δ 2.50–3.00 (m, 2), 3.55–3.95 (m, 2), 5.00–5.40 (m, 2), and 5.50–6.20 (m, 1); ν_{max} ($CHCl_3$): 1645 (C=C) and 1378 and 1170 (SO_2) cm^{-1}. Anal. ($C_4H_7ClO_2S$) C, H, S.

2-Propene-1-sulfonyl-*1-d* Chloride. Ordinary 2-propene-1-sulfonyl chloride (**14**) (30 g, 0.205 mol) was mixed with dioxane (125 ml) and D_2O (50 ml), and triethylamine (23 g, 100 ml, 0.73 mol) was added over 20 min with stirring. The mixture was stirred a further 30 min and the solvent was evaporated. The residue was dissolved in CH_2Cl_2 (250 ml), dried further with $MgSO_4$, made up to about 400 ml with more CH_2Cl_2, and treated with PCl_5 (60 g). The mixture was poured onto ice and worked up by extraction with CH_2Cl_2; the product after distillation was a pale yellow oil (22 g, 73%), bp 72-77 °C (10-15 mm): ν_{max} 2160 (CD), 1638 (C=C), and 1370 and 1165 (SO_2) cm^{-1}. A redistilled sample showed 17.05 atom % excess D (85% of monodeuteration).

Thermolysis of 2-Propene-1-sulfonyl-*1-d* Chloride. The chloride (85% monodeuterated, above) was thermolyzed at 600° and 0.1 mm in the quartz tube flow system described elsewhere.[8] The trapped product was distilled (bp 45 °C): 16.50 atom % excess D (82.5% of monodeuteration); NMR ($CDCl_3$) δ 4.05 (d, 2), 5-5.6 (m, 1.2), and 5.6-6.4 ppm (m, 1), showing the product to be principally 3-chloropropene-*1-d*. Flash thermolysis at 660-670 °C and 12-14 μm gave a product with essentially the same NMR spectrum.

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