disappearance of the 675-cm^{-1} band present in the starting material. The presence of iodine in the product was demonstrated by the appearance of a violet color in samples allowed to stand at room temperature and by treating a sample of the material with alcoholic silver nitrate.

2-Methyl-4,6-di-*t*-butylbenzyl Fluoride. To a solution of 10.1 g (40 mmol) of 2-methyl-4,6-di-*t*-butylbenzyl chloride in 50 ml of anhydrous acetonitrile was added 12.7 g (100 mmol) of anhydrous silver (argentous) fluoride (Harshaw). The resulting mixture was stirred without heating for 4 hr, filtered, and poured into cold water. The organic layer was taken up in pentane, washed five times with cold water, dried, and distilled. There was obtained 5.6 g of the desired product, bp 90–94° (3 mm) (methylene doublet at δ 5.85 ppm, J_{HF} = 49 Hz in carbon disulfide relative to TMS internal).

Anal. Calcd for $C_{16}H_{25}F$: C, 81.30; H, 10.66; F, 8.04. Found: C, 81.37; H, 10.60; F, 8.33.

Nmr Measurements. Nmr spectra were measured on a Varian A56-60A spectrometer equipped with a variable-temperature probe. Temperature measurements were accomplished with a thermometer which fitted an nmr tube and which was calibrated at 0° (ice water) and −78° (Dry Ice in acetone) and checked against the chemical shift difference of the methanol signals.

Spectra were obtained on approximately 25 (v/v) solutions in carbon disulfide. Measurement of the coalescence temperatures in chloroform gave the same results within experimental error.

Base-Catalyzed Deuterium Exchange of Acyclic Sulfones

C. D. Broaddus

Contribution from The Procter and Gamble Company, Miami Valley Laboratories, Cincinnati, Ohio 45239.

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Abstract: A series of alkyl and alkenyl methyl sulfones was subjected to deuterioxide-catalyzed exchange in deuterium oxide–dioxane solvent at 25°. The results are summarized in Table I. It was shown that 2-hydroxyhexyl methyl sulfone was stable to these exchange conditions. From these results the following conclusions may be drawn. (1) Increased alkyl substitution at a carbon adjacent to a sulfone substituent strongly retards the rate of carbanion formation relative to similar substitution changes in nitroalkanes and ketones. (2) The rate of exchange of an $-SO_2CH_3$ site is little affected by the other hydrocarbon group attached to a sulfone substituent whether it be alkyl, 1-alkenyl, or 2-alkenyl. (3) Alkyl-substituted allyl anionic species generated adjacent to a sulfone group undergo very specific protonation at the site next to the sulfone group. The difference in activation energies for the two protonation reactions is larger than the difference in ground-state energies of 1- and 2-alkenyl methyl sulfones. (4) Replacement of hydrogen on a carbon adjacent to a sulfone group by a 1-pentenyl substituent increases the rate of base-catalyzed deuterium exchange by a factor of $\sim$10. Replacement of *n*-propyl by 1-pentenyl causes a $\sim 10^4$ increase in rate of exchange. (5) 1-Alkenyl methyl sulfones undergo most rapid exchange at the α-methyl position. The α-vinyl hydrogen is exchanged, by a proton abstraction mechanism, somewhat more rapidly than reaction occurs at the allylic site. (6) Little difference is seen in the reactivities of *cis*- and *trans*-1-alkenyl methyl sulfones or in the reactivities of *cis*- and *trans*-2-alkenyl methyl sulfones.

The subject of carbanionic intermediates adjacent to an activating sulfone substituent has received extensive study.[1] In some recent work it was observed[2] that base-catalyzed deuterium exchange of 2,3-dihydrothiophene 1,1-dioxide resulted in rapid vinyl as compared to allyl proton abstraction. Anionic reactions in unsaturated cyclic sulfones could be influenced by such factors as hybridization changes due to inclusion in a small ring, configurational preferences of the carbanionic species, and ring-strain effects. Therefore, it was felt that a study of acyclic systems should be performed to minimize the number of variables. Since there is little background information in this particular area, the relative reactivities at various positions of saturated, α,β-unsaturated, and β,γ-unsaturated acyclic sulfones have been determined. As described in the Results only three points were taken in each kinetic run and the extent of deuteration was determined from proton magnetic resonance spectra. While this work does not provide precise kinetic data, the observed reactivities allow considerable insight into carbanionic reactions of sulfones.

Results

The results of these base-catalyzed exchange studies are summarized in Table I. The extent and positions of deuterium exchange were determined by removing at least three portions at timed intervals from basic solutions placed in a thermostated bath at 25.0°. The data necessary for construction of Table I were obtained by integration of proton magnetic resonance (pmr) spectra using the terminal methyl of the alkyl chain as an internal standard. Examples of typical runs are presented in Table III of the Experimental Section. First-order rate constants were obtained by plotting the logarithim of the change in relative area of the position undergoing exchange against time. The best straight line was selected visually. Several "one-point" determinations were performed to establish that the concentration of base remained constant during these exchange processes (see Experimental Section). The much more complete kinetic analysis of base-catalyzed deuterium exchange of dimethyl sulfone[3]

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[1] (a) See D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press Inc., New York, N. Y., 1965, pp 71–84; (b) D. J. Cram, R. D. Trepka, and P. St. Janiak, *J. Amer. Chem. Soc.*, **88**, 2749 (1966); (c) S. T. McDowell and C. J. M. Stirling, *J. Chem. Soc.*, *B*, 348 (1967); H. Hogeveen, G. Maccagnani, F. Montanari, and F. Taddei, *ibid.*, 4101 (1964), for leading references.

[2] C. D. Broaddus, *J. Amer. Chem. Soc.*, **88**, 3863 (1966).

[3] J. Hochberg and K. F. Bonhoeffer, *Z. Phys. Chem.*, **A184**, 419 (1939).

Table I. Rates of Deuterioxide-Catalyzed Exchange of Acyclic Sulfones[a,b]

Entry	[OD⁻]	$k_{obsd}/[OD^-]$, l./mol min	Rate relative to $C_3H_7\mathit{CH_2}CO_2CH_3$
1. $C_3H_7\mathit{CH_2}SO_2CH_3$	0.35	4×10^{-4}	1.0
2. $C_3H_7CH_2SO_2\mathit{CH_3}$	0.066	2×10^{-1}	5×10^{2}
3. $trans\text{-}C_3H_7CH_2\overset{H}{C}{=}\overset{H}{C}SO_2\mathit{CH_3}$	0.066	3×10^{-1}	7×10^{2}
4. $cis\text{-}C_3H_7CH_2\overset{H}{C}{=}\overset{H}{C}SO_2\mathit{CH_3}$	0.071	2×10^{-1}	5×10^{2}
5. $C_3H_7\overset{H}{C}{=}\overset{H}{C}—CH_2SO_2\mathit{CH_3}^{c}$	0.066	3×10^{-1}	7×10^{2}
6. $trans\text{-}C_3H_7\mathit{CH_2}\overset{H}{C}{=}\overset{H}{C}SO_2CH_3$	0.92	7×10^{-3}	17
7. $cis\text{-}C_3H_7\mathit{CH_2}\overset{H}{C}{=}\overset{H}{C}SO_2CH_3$	0.685	4×10^{-3}	10
8. $C_3H_7\overset{H}{C}{=}\overset{H}{C}—\mathit{CH_2}SO_2CH_3^{c}$	0.0026	3.0	7×10^{3}
9. $trans\text{-}C_3H_7CH_2\overset{H}{C}{=}\overset{H}{\mathit{C}}SO_2CH_3$	0.92	9×10^{-3}	22
10. $cis\text{-}C_3H_7CH_2\overset{H}{C}{=}\overset{H}{\mathit{C}}SO_2CH_3$	0.685	1×10^{-2}	25

[a] It should be emphasized that these data are not considered to be highly precise. However, they undoubtedly establish the orders of reactivity at these various sites. [b] The position which undergoes exchange at the rate reported is italicized. [c] A mixture of ~15% *cis*- and 85% *trans*-2-hexenyl sulfone was used. The isomers underwent exchange at essentially the same rates.

Table II. Proton Magnetic Resonance Spectra of Acyclic Sulfones[a] in Deuteriochloroform

Compound	Chemical shifts (τ units) A	B	C	D
$CH_3\overset{C}{(CH_2)_2}\overset{B}{CH_2}SO_2\overset{A}{CH_3}$	7.05 (s)	6.95 (t)[b]	8.0–8.7 (m)	
$C_2H_5\overset{D}{CH_2}\overset{C}{CH{=}CH}—\overset{B}{CH_2}SO_2\overset{A}{CH_3}$	7.15 (s)	6.4 (d)[c]	4.0–4.7 (m)	7.95 (m)
$C_3H_7\overset{D}{CH_2}\overset{C}{CH}{=}\overset{B}{CH}—SO_2\overset{A}{CH_3}$ (*trans*)	7.05 (s)	3.55 (d)[d]	2.9–3.2 (m)[e]	7.65 (m)
$C_3H_7\overset{C}{CH_2}—\overset{B}{CH{=}CH}SO_2\overset{A}{CH_3}$ (*cis*)	7.10 (s)	3.6–3.8 (m)	7.25–7.45 (m)	
$C_4H_9\underset{OH}{\overset{C}{CH}}—\overset{B}{CH_2}SO_2\overset{A}{CH_3}$	7.0 (s)	6.9 (m)	5.8 (m)	

[a] The approximate multiplicity is shown in parentheses: s = singlet, d = doublet, t = triplet, and m = multiplet. [b] J_{BC} ~ 8 Hz. [c] This doublet may be attributed to the *trans* isomer. A less intense doublet centered at τ ~6.3 is partially superimposed which may be assigned to the *cis* compound. Comparison of area ratios indicates ~15% *cis*. [d] J_{BC} ≈ 16 Hz. [e] J_{CD} ≈ 6 Hz.

establishes a pseudo-first-order process in this very similar reaction. The second-order constants reported in Table I came from division of the first-order constants by the concentration of deuterioxide. While such factors as the operation of secondary deuterium isotope effects and accumulation of protium in the solvent at high percentages of exchange could affect these rate constants, there should be little effect on the relative rates of exchange. Thus, all runs were conducted at the same concentrations of substrate (0.24 *M*) and were carried out to 50–70% exchange. The pmr spectra of the compounds studied are recorded in Table II with the chemical shifts of the pertinent signals given. It will be noted from Tables I and II that, with the exception of vinylic *vs.* allylic exchange in *cis*- and *trans*-1-hexenyl methyl sulfones, it was possible to observe essentially complete exchange at the more reactive sites of these compounds before any appreciable exchange had occurred at less reactive positions.

In the case of butyl methyl sulfone, the $-SO_2CH_3$ signal at τ 7.05 had completely disappeared before there was any measurable reduction in the methylene signal at τ 6.95 (entry 2, Table I). Furthermore, there was no simplification of the very complex multiplet attributed to the nonactivated methylene protons (τ 8.0–8.7) under these conditions. Using higher concentrations of deuterioxide, exchange was observed at the activated methylene site (entry 1, Table I). Simplification of the complex multiplet was observed under these conditions, as would be expected.

With 2-hexenyl methyl sulfone, it was possible to observe extensive exchange of the allylic position appearing at τ 6.38 (entry 8, Table I) before the occurrence of any reduction in the $-SO_2CH_3$ signal at τ 7.15. It is also significant to point out that the material used in these experiments was ~15% *cis* as evidenced by the area of a doublet centered in the pmr spectrum at τ ~6.3. Qualitatively, this signal of smaller area ratio underwent reduction in area at the same rate as did the doublet attributable to the *trans* compound. The $-SO_2CH_3$ signal disappeared approximately ten times more slowly (entry 5). It should also be noted that there was no reduction in relative area of the vinylic region (τ 4.0–4.7) under the exchange conditions used.

Exchange experiments with 1-hexenyl methyl sulfones were performed with mixtures which were 90:10 *trans* to *cis* and 70:30 *cis* to *trans* by gas–liquid phase chromatography (glpc). While it was possible to observe complete exchange at the $-SO_2CH_3$ sites of these mixtures before any change in the rest of the pmr spectra, reduction in the relative area of the α-vinylic signals and isomerization by abstraction of the allylic protons were more nearly competitive. In the case of the predominantly *trans* mixture, the signals due to the α- and β-vinylic protons are well separated and are easily characterized by their coupling patterns. As mentioned above and shown in Table I (entry 3), it was possible to observe complete disappearance of the $-SO_2CH_3$ signal (τ 7.05) while the rest of the pmr spectrum was unchanged. Using more basic conditions (entries 6 and 9), it was seen that reduction in the area of the α-vinylic signal (τ 3.55) occurred competitively with production of the more stable β,γ-unsaturated compound as evidenced by the appearance of a signal for the vinylic hydrogens of this isomer at τ 4.0–4.7. By comparing the changes in area ratios of the α-vinylic, β-vinylic, and vinylic protons of the β,γ isomer, it was possible to estimate the rates recorded in Table I. Several other points should be made concerning the data. First, reduction in area of the α-vinylic signal was accompanied by simplification in the splitting pattern of the β-vinylic signal. For example, at the point at which comparison of the relative areas of the α- and β-vinylic signals indicated 80% exchange of the α-vinylic position, the β-vinylic signal had undergone transformation from two triplets, the centers of which are separated by 16 Hz, to a single broadened triplet. This is, of course, consistent with obliteration of the *trans*-vinylic coupling constant upon deuterium exchange of the α-vinylic hydrogen. Although it is evident that 2-hexenyl methyl sulfone was formed from the production of a signal at τ 4.0–4.7, due to the vinylic hydrogens of this isomer, no signal was observed at τ 6.38 for the doubly activated allylic position. This is consistent with more rapid deuterium exchange at this site as is recorded in Table I (compare entries 6 and 8). It should also be noted that in these partially isomerized exchanged samples the ratio of the total area of the singly activated allyl sites (τ ~7.5–8.0) to the area of the terminal $C-CH_3$ groups (τ ~9.1) remained constant. From Table II it can be seen that the signal for the allylic site of *trans*-1-hexenyl methyl sulfone occurs as a multiplet centered at τ 7.65 while the singly activated allyl position of 2-hexenyl methyl sulfone is centered at τ 7.95. The ratio of the total area of these two signals to the area of the terminal methyl was not reduced during these experiments, eliminating the possibility that *trans*-1-hexenyl methyl sulfone is converted to either *cis*- or *trans*-2-hexenyl methyl sulfone followed by reversion to the 1 isomer, since reduction in the allylic signal of 1-hexenyl methyl sulfone would accompany such a process.

The observations on deuterioxide-catalyzed exchange of a mixture of ~70% *cis*- and 30% *trans*-1-hexenyl methyl sulfone (by glpc analysis) were very similar to those discussed above and will be briefly outlined. Complete exchange of the $-SO_2CH_3$ hydrogens (entry 4, Table I) occurred more rapidly than reaction at other sites. Reduction in relative area of the vinylic signal proceeded somewhat more rapidly than did isomerization to 2-hexenyl methyl sulfone, although the two processes were more nearly competitive (entries 7 and 10, Table I). With this predominantly *cis* mixture, the α- and β-vinylic protons are not separated in the pmr spectrum (see Table II), and it is assumed that the α-vinylic hydrogen underwent exchange in analogy with *trans*-1-hexenyl methyl sulfone (above) and cyclic unsaturated sulfones.[2] In the case of this sample enriched in the *cis* isomer, it is possible to distinguish the allylic signal of the starting material (τ 7.35) from that of 2-hexenyl methyl sulfone. No reduction in ratio of the total area of the singly activated allylic positions (τ 7.2–8.0) to the area of the terminal methyl group of the alkyl chain was observed, and the reduction in relative area of the *cis*-allylic site (τ 7.2–7.4) was consistent with the extent of isomerization to 2-hexenyl methyl sulfone. These observations establish that *cis*-1-hexenyl methyl sulfone is not converted to either *cis*- or *trans*-2-hexenyl methyl sulfone followed by return to starting material.

Finally, recovery of 2-hydroxyhexyl methyl sulfone from deuterioxide solution showed no generation of hexenyl methyl sulfones by pmr or glpc analysis. These conditions caused very extensive α-vinyl exchange with *cis*- and *trans*-1-hexenyl methyl sulfones and resulted in essentially complete exchange of the $-SO_2CH_3$ position of the hydroxy compound as well as ~50% exchange at the activated methylene position (see Experimental Section).

Discussion

The exchange studies reported in this paper can be separated conveniently into three categories, *i.e.*, exchange at saturated, allylic, and vinylic positions of sulfones, and will be discussed in that order.

Exchange at Saturated Positions. From entries 1 and 2 of Table I, it can be seen that base-catalyzed exchange at a methyl position adjacent to a sulfone group is about 500 times as fast as at an alkyl-substituted methylene position. In contrast, base-catalyzed exchange of ketones is reported to occur at about the same rate at a methyl group as at a more substituted site.[4,5] Also, the deuterioxide-catalyzed exchange of nitroalkanes has been shown to occur about five times faster with nitromethane than with nitroethane.[6] Thus, in these systems an alkyl group either has little effect or retards the rate of exchange by a factor of ~5 while the present sulfone system displays a rate difference of ~5×10^2 with similar substitution changes (eq 1).

$$\underset{\mathbf{1}}{CH_3CH_2CH_2CD_2SO_2CH_3} \xleftarrow[1.0]{A} \underset{\mathbf{2}}{CH_3CH_2CH_2CH_2SO_2CH_3} \xrightarrow[5 \times 10^2]{B} \underset{\mathbf{3}}{CH_3CH_2CH_2CH_2SO_2CD_3} \quad (1)$$

This enhanced alkyl effect can be explained logically by proposing that greater charge density develops at the position of exchange in the case of sulfones than with either ketones or nitroalkanes. Thus, it is generally recognized that retardation of carbanionic reactions by alkyl substituents is a result of increased electron donation, relative to hydrogen, to a center of high electron density. The operation of either of two factors could account for relatively high charge density

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(4) J. Warkentin and O. S. Tee, *J. Amer. Chem. Soc.*, **88**, 5540 (1966).

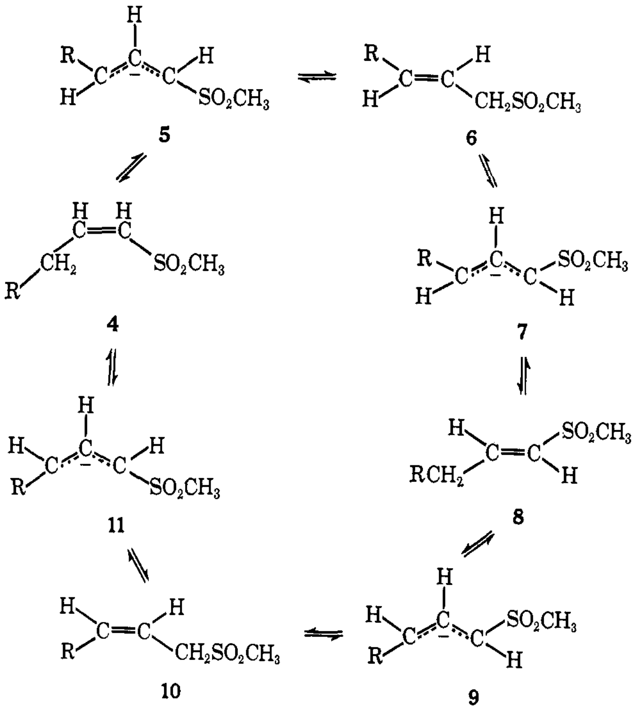
(5) (a) A. A. Bothner-By and C. Sun, *J. Org. Chem.*, **32**, 492 (1967); (b) C. Rappe and W. H. Sachs, *ibid.*, **32**, 4127 (1967).

(6) R. P. Bell, *Discussions Faraday Soc.*, **No. 39**, 16 (1965).

in the case of sulfones. That is, proton removal may be more complete in the transition state for carbanion formation from sulfones[7] resulting in higher charge density at the carbon undergoing exchange, or resonance stabilization may operate more effectively in the ketone and nitroalkane systems. The second alternative implies that d-orbital stabilization of the anionic species derived from sulfones is not as effective as is $p-\pi$ stabilization in the previously reported systems, but does not rule against d-orbital participation as an operating factor. In fact comparison of exchange data for tetramethylammonium[8] ion and dimethyl sulfone[3] suggests that d-orbital participation is quite important. That is, dimethyl sulfone undergoes base-catalyzed exchange readily in comparison to tetramethylammonium ion despite the inductive effect of the ammonium group being larger than that of the sulfone, as measured by σ^* values.[9] This suggests that the transition state for proton removal from dimethyl sulfone is stabilized by overlap with d orbitals of the sulfone group to a significant extent.[10]

Another pertinent observation concerning the effects of substitution patterns on rates of exchange of sulfones is seen by comparing entries 2, 3, 4, and 5 of Table I. No large changes in the rate of exchange of the methyl position with change in the other hydrocarbon group attached to sulfone is observed. Since this series represents attached alkyl, 1-alkenyl, and 2-alkenyl substituents, it appears that the sulfone group effectively insulates the terminal methyl group from the rest of the molecule. This observation rules against an extensive transmission of electronic effects through the sulfone group.

Scheme I



Allylic Exchange. A complete description of allylic exchange in this system would involve four isomeric unsaturated sulfones interconnected by four distinct carbanionic intermediates, as shown in Scheme I. Thus each isomeric sulfone is capable of yielding either of two allyl carbanionic species depending upon the configuration of the alkyl group during the proton abstraction process. However, the observations described in the Results show that this rather complex scheme can be greatly simplified with little loss in depth of understanding of this particular system. First, the data on base-catalyzed deuterium exchange of isomer **6** clearly show that formation of either intermediate **5** or **7** or both is followed by very selective reversion to starting material, *i.e.*, neither isomer **4** nor **8** is formed during the exchange process in any significant concentration nor are they formed transiently to return to starting material. The latter alternative is eliminated by the fact that no reduction in the relative area of the pmr signal due to the vinylic hydrogens (τ 4.0–4.7) is observed during exchange of **6**, which is inconsistent with the intermediacy of isomers **4** and **8**. This then establishes that at least one of these anionic intermediates (**5** or **7**) undergoes very specific protonation at the allylic site adjacent to the sulfone substituent. Next consider the deuterioxide-catalyzed isomerization of isomers **4** and **8** to 2-hexenyl methyl sulfones. As shown in Table I, both these processes occur approximately 10^3 more slowly than does exchange of isomer **6**. The data also clearly indicate that proton loss from either **4** or **8** to produce an allyl anionic species is followed by rapid selective protonation at the allylic position adjacent to the sulfone substituent. Isomerization of **8** can be followed by the appearance of a pmr signal at τ 4.0–4.7 characteristic of the nonconjugated isomers. That protonation at the adjacent position occurs more rapidly than at the position removed from the sulfone substituent is shown by the fact that no change in relative area ratios of the singly activated methylene positions and the terminal methyl of the alkyl chain is observed during the isomerization reaction in the presence of deuterium oxide. Thus if either anionic intermediate **7** or **9** were undergoing protonation to a significant extent at the position removed from the sulfone substituent, to regenerate starting material, a reduction in relative area of the allylic signal at τ 7.6–8.0 (Table II) would be expected, and none is observed. Similarly, during isomerization of isomer **4** no reduction in the signal attributable to the allylic position is observed, indicating specific protonation of intermediates **5** and/or **11**. It should be pointed out that although 2-hexenyl methyl sulfones are obviously formed during isomerization no signal is observed for the doubly activated allylic position at τ 6.4. This is, of course, consistent with the rapid selective exchange at this site observed with isomer **6**. Finally, qualitatively significant data are available for isomer **10**.[11] In experiments conducted to observe exchange of this position using a mixture of $\sim$15% *cis* and $\sim$85% *trans* isomers it was evident that exchange occurred at essentially the same rate at the allylic positions of the two isomers with no change in the rest of the pmr spectrum. Referring then to Scheme I, it appears that either anionic intermediates **9** or **11** or both

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(7) See J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1963, p 158.

(8) W. von E. Doering and A. K. Hoffmann, *J. Amer. Chem. Soc.*, 77, 521 (1955).

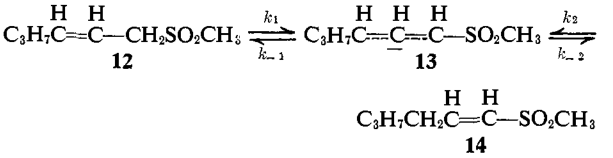
(9) R. W. Taft in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley and Sons, Inc., New York, N. Y., 1956, p 618.

(10) See G. Cilento, *Chem. Rev.*, 60, 147 (1960), for other examples of d orbital effects.

(11) A doublet at $\tau \sim$6.3 was assigned to the doubly activated allylic position of *cis*-2-hexenyl methyl sulfone.

undergo very selective protonation at the allylic position adjacent to the sulfone substituent. This discussion has been based on the assumption that the anionic intermediates maintain their geometrical integrity in line with other work in this area.[12]

Then relating these over-all results to Scheme I, it can be seen that, although all these intermediate anions are not *required* to account for the observations, those allyl anionic species which do intervene must undergo very selective protonation at the allylic site adjacent to the sulfone substituent. Furthermore, there is little difference in behavior of *cis* and *trans* isomers of either 1- or 2-hexenyl methyl sulfones. For these reasons it appears legitimate to represent allylic exchange in this system by the simplified eq 2, in which geometrical isomerism is *not* defined.



$$\underset{\mathbf{12}}{\mathrm{C_3H_7\overset{H}{C}{=}\overset{H}{C}{-}CH_2SO_2CH_3}} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \underset{\mathbf{13}}{\mathrm{C_3H_7\overset{H}{C}{\cdots}\underset{-}{\overset{H}{C}}{\cdots}\overset{H}{C}{-}SO_2CH_3}} \underset{k_{-2}}{\overset{k_2}{\leftrightharpoons}} \underset{\mathbf{14}}{\mathrm{C_3H_7CH_2\overset{H}{C}{=}\overset{H}{C}{-}SO_2CH_3}} \quad (2)$$

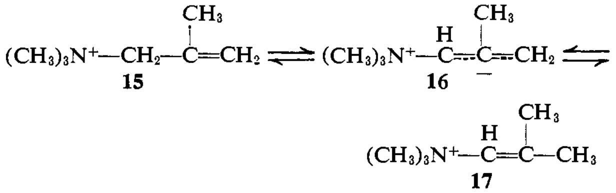
It has been previously established[13] that at equilibrium isomer **12** constitutes >99% of the mixture. This information coupled with the values of k_1 and k_2 given in Table I requires that the ratio of k_{-1}/k_{-2} be quite high. That is, **13** undergoes very specific protonation at the allylic position adjacent to the sulfone group.[14] These observations on allylic reactivity are of interest for several reasons.

As we pointed out in earlier papers[15,16] systems such as this one contradict the Ingold postulate[17] in that the more stable isomer **12** undergoes proton loss more readily than does **14** ($k_1 > k_2$) and is formed more readily on protonation ($k_{-1} > k_{-2}$). These data show that the difference in activation energies for protonation at the two sites of **13** is larger than the difference in ground-state energies of the two isomers. Since $k_{-1} > k_{-2}$, the transition state for proton transfer to the α position of **13** must be of lower energy than the transition state for proton transfer to the γ position. Moreover, for the system to conform to the principle of microscopic reversibility, the difference in energies of these two transition states must offset the difference in ground-state energies of the two isomers. That is, the higher ground-state energy of **14** would contribute to faster proton loss by this isomer. The observed slower rate ($k_1 > k_2$) must then be accounted for by an offsetting higher transition state for proton transfer. This argument is clearly seen by construction of a qualitative reaction coordinate.

Several theories rationalizing unequal rates of protonation at the two sites of electron density in allylic anions have been described.[18] It appears generally accepted that in unsymmetrically substituted systems, such as the present one, these relative reactivities can be related to charge density considerations. For example, Streitwieser[19] and Dewar[20] have discussed the correlation between sites of protonation and relative electron densities in π systems as calculated from molecular orbital theory. In the present case it appears clear that the position adjacent to the sulfone group would have relatively high electron density in the π system, as a result of the inductive effects of both the alkyl and sulfone substituents,[21,22] and would thus be anticipated to be the position of more rapid protonation, as is observed.[23]

Regardless of the controlling factors in the protonation reaction, it must be reemphasized that ground-state energy differences cannot be ignored. In systems such as the present one, wherein the difference in activation energies for protonation is larger than the difference in ground-state energies, the isomer formed faster undergoes proton loss faster. Also, in systems wherein the less stable isomer is formed faster upon protonation, microscopic reversibility requires that the less stable isomer undergoes proton loss more readily.[17] However, systems are known in which the difference in ground-state energies is larger than the difference in transition-state energies.[16,24,25] It should perhaps be restated[16] that all possible combinations of relative exchange rates and relative ground-state energies are now known. It is then apparent that both ground-state energy differences and differences in relative rates of protonation must be considered in any particular system.

Other studies in this general area have been reported recently. The equilibrium and base-catalyzed exchange of alkenyl sulfoxides[15] were quite similar to the present sulfone system. Cram[24] recently published very elegant studies on methyl-substituted allyl anionic intermediates. It was concluded that an alkyl substituent, situated at an allylic site, results in protonation being favored at the site removed from the alkyl substituent by a factor of 30–40. Saunders[25] studied the trimethylammonio-substituted system shown in eq 3. Among other observations **16** was found to protonate at the position adjacent to the nitrogen atom about three times faster than at the position removed from the substituent. The equilibrium ratio of 15:17 was ~60 at 100°.



$$\underset{\mathbf{15}}{\mathrm{(CH_3)_3N^+{-}CH_2{-}\overset{\overset{CH_3}{|}}{C}{=}CH_2}} \rightleftharpoons \underset{\mathbf{16}}{\mathrm{(CH_3)_3N^+{-}\overset{H}{C}{\cdots}\underset{-}{\overset{\overset{CH_3}{|}}{C}}{\cdots}CH_2}} \leftrightharpoons \underset{\mathbf{17}}{\mathrm{(CH_3)_3N^+{-}\overset{H}{C}{=}\overset{\overset{CH_3}{|}}{C}{-}CH_3}} \quad (3)$$

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[12] See (a) R. Hoffmann and R. A. Olofson, *J. Amer. Chem. Soc.*, **88**, 943 (1966); (b) S. Bank, *ibid.*, **87**, 3245 (1965), for leading references.

[13] D. E. O'Connor and W. I. Lyness, *ibid.*, **86**, 3840 (1964).

[14] From an equilibrium distribution of **15**:17 of 100 and the relative rates given in Table I, a ratio of k_{-1}/k_{-2} of ~10^4 is calculated. Although this is only an approximate value, it does give some indication of the very high specificity of the protonation reaction.

[15] D. E. O'Connor and C. D. Broaddus, *J. Amer. Chem. Soc.*, **86**, 2267 (1964).

[16] C. D. Broaddus, *ibid.*, **87**, 3706 (1965).

[17] C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p 565.

[18] See J. Hine, "Physical Organic Chemistry," 2nd ed, McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 238.

[19] A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961, p 418.

[20] M. J. S. Dewar, *Advan. Chem. Phys.*, **8**, 102 (1965).

[21] N. Bouman and G. J. Hoijtink, *Rec. Trav. Chim. Pays Bas*, **76**, 841 (1957).

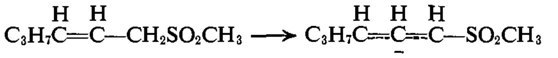
[22] To a first approximation (ref 19, p 418), any participation by d orbitals of the sulfone group would be expected to affect the two allylic positions equally and would therefore not affect the relative electron density.

[23] J. Hine [*J. Org. Chem.*, **31**, 1236 (1966)] recently suggested that the principle of least motion may be an important contributing factor to the relative rates of reaction in allyl anionic species.

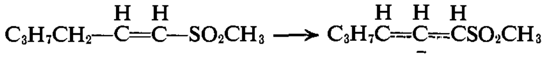
[24] S. W. Ela and D. J. Cram, *J. Amer. Chem. Soc.*, **88**, 5777 (1966).

[25] M. Saunders and E. H. Gold, *ibid.*, **88**, 3376 (1966).

The data of Table I provide interesting information concerning the effect of introducing a double bond on the rates of exchange. The pertinent comparisons are illustrated in eq 1, 4, and 5 which show the rates of base-catalyzed exchange relative to the rate of exchange at the activated methylene position of *n*-butyl methyl sulfone. Comparing path A of eq 1 to eq 4 shows that



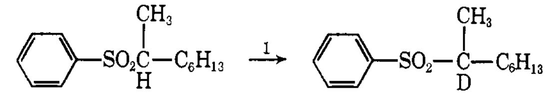
$$C_3H_7\overset{H}{C}{=}\overset{H}{C}{-}CH_2SO_2CH_3 \longrightarrow C_3H_7\overset{H}{C}{\cdots}\overset{H}{\underset{-}{C}}{\cdots}\overset{H}{C}{-}SO_2CH_3 \quad (4)$$



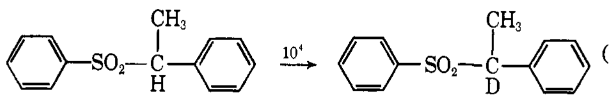
$$C_3H_7CH_2{-}\overset{H}{C}{=}\overset{H}{C}{-}SO_2CH_3 \longrightarrow C_3H_7\overset{H}{C}{\cdots}\overset{H}{\underset{-}{C}}{\cdots}\overset{H}{C}SO_2CH_3 \quad (5)$$

replacement of an *n*-propyl group by 1-pentenyl results in a rate increase of ~10^4 (Table I, entries 1 and 8). Although this is a significant increase, comparison of path B of eq 1 to eq 4 shows that the 1-pentenyl substituent increases the rate by a factor of only ~10 relative to hydrogen (Table I, entries 2 and 8). While more data are needed before separation of inductive and resonance effects of the double bond can be attempted, the fact that the inductive effects of hydrogen and 1-alkenyl are similar[9] (σ^* $CH_3\overset{H}{C}{=}\overset{H}{C} = 0.360$; σ^* H = 0.480) and the exchange rates are not very different suggests that resonance stabilization by the double bond is not a large factor.[26]

These observations are similar to those reported by Corey.[27] As shown in eq 6 and 7, it was found that replacement of alkyl by phenyl resulted in a 10^4 rate increase in base-catalyzed deuterium exchange adjacent to the sulfone substituent. This is very similar to the increase observed upon substitution of alkyl by 1-alkenyl and as discussed above it appears probable that much of the enhancement is due to the difference in polar effects of the two substituents.



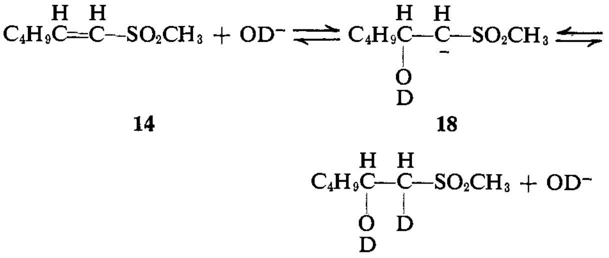
(6)



(7)

Equation 5 depicts allyl proton abstraction from 1-hexenyl methyl sulfone which occurs more slowly than the analogous reaction using the 2-hexenyl isomer. This reduction in rate is most simply viewed as a result of attenuation of the electrostatic effect of the sulfone group in the transition state by the intervening double bond. An apparent consequence of this lowered reactivity is the fact that the α-methyl position of this isomer undergoes reaction more rapidly than does the allylic site (entries 3 and 6 of Table I). This observation supports the foregoing conclusion that resonance stabilization does not play a dominant role during base-catalyzed exchange of these compounds.

Vinyl Proton Abstraction. As discussed in the Results, strong evidence has been obtained that deuterium exchange occurs at the α-vinyl position of both *cis*- and *trans*-1-hexenyl methyl sulfones at a somewhat faster rate than does proton abstraction at the allyl position. Either vinyl proton abstraction or an addition–elimination sequence, as shown in eq 8, could account for this result. In the case of unsaturated ketones it has been postulated[28] that addition of base



14 18

(8)

19

to the activated double bond is followed by rapid reversion to the unsaturated starting material which then contains deuterium at the α-vinyl position. For this mechanism to operate in the present system the equilibrium shown in eq 8 would have to be established rapidly and lie very predominantly toward the unsaturated sulfone. Thus, the pmr evidence shows extensive exchange at the α-vinyl position of **14** under conditions wherein no more than minor amounts of **19** are formed. Synthesis of 2-hydroxyhexyl methyl sulfone and examination of its stability to the exchange conditions show that no[29] hexenyl methyl sulfone is formed under conditions which caused ~90% exchange at the α-vinyl position of **14**. This is taken as conclusive evidence that the addition–elimination sequence is not operative and leads to the conclusion that α-vinyl exchange is occurring by a proton-abstraction mechanism.[30]

The available evidence on base-catalyzed exchange of unsubstituted olefins suggests that reaction occurs more readily at allylic than at vinylic positions.[31,32] Introduction of the sulfone substituent then apparently increases the rate of α-vinyl proton abstraction more than it increases the rate of allyl proton abstraction. A logical explanation for this observation arises from the earlier discussion of allylic reactivity, *i.e.*, positions adjacent to the sulfone group received a much larger electrostatic activation toward carbanion formation than those insulated by a double bond, and it seems reasonable to propose that it is this factor which increases the rate of vinyl proton abstraction relative to allyl abstraction. It should be pointed out that this rationale does not imply that the transition states for vinyl proton removal and allyl proton removal are of similar energy due to similar energies of the carbanions. An equally plausible explanation is that the potential energy curve for vinylic proton abstraction is less steep than that for allylic abstraction and that reaction there-

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(26) Saunders[25] has discussed the possibility of "electrostatic inhibition of resonance-stabilization."

(27) E. J. Corey and T. H. Lowry, *Tetrahedron Lett.*, **13**, 803 (1965).

(28) (a) B. W. Rockett, T. M. Harris, and C. R. Hauser, *J. Amer. Chem. Soc.*, **85**, 3491 (1963); (b) J. Warkentin and L. K. M. Lam, *Can. J. Chem.*, **42**, 1676 (1964).

(29) Not only is *no* hexenyl methyl sulfone formed, but the 2-hydroxy-*n*-hexyl methyl sulfone is stable to these experimental conditions as shown by glpc analysis (see Experimental Section). Deuterium exchange was observed at the SO_2CH_3 position and to some extent at the methylene position adjacent to the sulfone group.

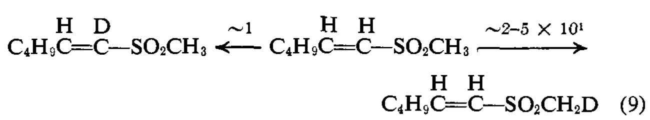
(30) L. DiNunno, G. Modena, and G. Scorrano [*J. Chem. Soc.*, *B*, 1186 (1966), and references therein] report rapid α-vinyl proton abstraction with alkoxides relative to addition using *cis-p*-tolylsulfonylhalogenoethylenes.

(31) See ref 1a, p 23.

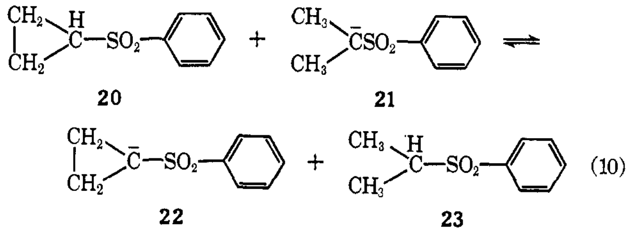
(32) These observations indicate that resonance stabilization of the transition state for proton removal at the allylic position of unsubstituted olefins more than compensates for the difference in hybridization of the two sites. For a discussion of these factors in organometallic systems see C. D. Broaddus, *J. Amer. Chem. Soc.*, **88**, 4174 (1966).

fore occurs more rapidly at the vinylic site.[33,34] In other words, it is not established that the Brønsted catalysis law is obeyed for such widely disparate positions as vinyl and allyl. In fact, if observations on reactivities of amines can be extrapolated to carbanionic reactions, Bell's[35] comparison of substituted pyridines to aniline bases indicates that sp^2-hybridized species react at a faster rate than their basicities would suggest. At the very least it appears premature to conclude that these observations are a reflection of carbanion stabilities. Consideration of the possibility that participation of the d orbitals of the sulfone group causes a greater enhancement of vinyl proton abstraction than of allyl proton removal will be deferred until the observation that vinyl proton abstraction is slower than reaction at the α-methyl position is discussed.

As noted in Table I and shown in eq 9 the rate of base-catalyzed exchange of the SO_2CH_3 position of 1-hexenyl methyl sulfone is $\sim$2-5 × 10 times faster than the rate of vinyl exchange. This observation appears to require not only an important contribution from d-orbital participation but also that this participation be more effective in the transition state for proton removal from the SO_2CH_3 position. Thus, if only inductive effects were operative and were equal for these two positions adjacent to a sulfone group, it might be anticipated that vinyl exchange would be the faster of the two processes on the basis of differences in acidity of sp^3 C–H *vs.* sp^2 C–H positions. Experimental support for the proposal that d-orbital effects can more than counterbalance differences in hybridization is found in the equilibration studies of Zimmerman and Thyagarajan.[36] Although the analytical technique used by these workers has been questioned,[37] the fact that the equilibrium constant for eq 10 is essentially unity has been corroborated[38] recently by nmr studies of dimethyl sulfoxide solutions of these species and seems firmly established. It has long been recognized that C–H positions of cyclopropane possess relatively high s character[39] and there is good evidence that this increase in s character results in increased acidity.[40] From eq 10 it is apparent that the cyclopropyl C–H and a tertiary isopropyl C–H position exhibit the same acidity when adjacent to a sulfone group. This seems most reasonably interpreted as increased d-orbital stabilization of **21** relative to **22**.[36,38] Then the observation that base-catalyzed deuterium exchange at the α-methyl position of 1-hexenyl methyl sulfone proceeds more rapidly than does vinylic exchange points to an important contribution from d-orbital stabilization which operates more effectively in the transition state for proton removal from the SO_2CH_3 site. These observations are in accord with recent studies[41] which indicate increasing effectiveness of d orbital overlap with increasing p character in an orbital containing a free pair of electrons.



$$\mathrm{C_4H_9}\overset{\mathrm{H}}{\mathrm{C}}=\overset{\mathrm{D}}{\mathrm{C}}\mathrm{-SO_2CH_3} \xleftarrow{\sim 1} \mathrm{C_4H_9}\overset{\mathrm{H}}{\mathrm{C}}=\overset{\mathrm{H}}{\mathrm{C}}\mathrm{-SO_2CH_3} \xrightarrow{\sim 2\text{-}5\,\times\,10^1} \mathrm{C_4H_9}\overset{\mathrm{H}}{\mathrm{C}}=\overset{\mathrm{H}}{\mathrm{C}}\mathrm{-SO_2CH_2D} \quad (9)$$



20 **21**

22 **23** (10)

$K \approx 1$

The above comparisons tend to rule out the possibility that the increase in rate of α-vinylic exchange relative to allylic in α,β-unsaturated sulfones could be due to selective d-orbital participation. For such a factor to be important, d-orbital stabilization of an incipient sp^2 hybridized carbanion would have to be greater than that of an incipient allylic species in which negative charge would be contained in either a p–π system or an sp^3 orbital.

A brief consideration of vinylic exchange in the previously reported sulfoxide system is in order. Careful reexamination of the data obtained in that study[14] shows that exchange at the α-vinyl position of 1-dodecenyl methyl sulfoxide can be no more than a very minor factor and probably does not operate, *i.e.*, allylic exchange is more rapid. As described in this paper, vinylic exchange in the sulfone system is thought to be due to the electrostatic effect of the sulfone group. Since this factor would be less important in corresponding sulfoxides, it is perhaps not surprising that vinylic exchange was not observed.

Finally, it should be pointed out that the possible operation of "internal return" mechanisms has been disregarded in this discussion.[42] While this may introduce some ambiguity in the relative rates of carbanion formation, it might be expected[43] that the operation of such processes would result in the observation of relatively rapid exchange at resonance-stabilized sites. This, of course, is not indicated by the present results.

Experimental Section

General. All pmr spectra were obtained on a Varian H-100 spectrometer using approximately 10% solutions in deuteriochloroform. Infrared spectra were recorded on a Perkin-Elmer Infracord spectrophotometer. Gas chromatograms were obtained using an Aerograph 200B apparatus fitted with a 20% SE-30 on Chromosorb W column using helium carrier gas.

Starting Materials. Preparation of Butyl Methyl Sulfone. Oxidation of butyl methyl sulfide using sodium hypochlorite solution[12] provided butyl methyl sulfone in 80% yield after distillation. The pmr characteristics of this compound are recorded in Table II; its infrared spectrum showed strong bands at 7.7 and 8.8 μ indicating the sulfone substituent as well as typical absorptions for the hydrocarbon function. Glpc analysis indicated >98% purity.

Preparation of 1-Hexenyl Methyl Sulfone. Free-radical addition of methyl mercaptan to 1-hexyne provided 1-hexenyl methyl

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[33] See R. P. Bell, "The Proton in Chemistry," Cornell University Press, Ithaca, N. Y., 1959, p 172.

[34] The present data would of course require that the slope of the potential energy curves in the sulfone system differ from those in unsubstituted olefins.

[35] R. P. Bell and G. L. Wilson, *Trans. Faraday Soc.*, **46**, 407 (1950).

[36] H. E. Zimmerman and B. S. Thyagarajan, *J. Amer. Chem. Soc.*, **82**, 2505 (1960).

[37] Reference 1, p 76

[38] A Ratajczak, F. A. L. Anet, and D. J. Cram, *J. Amer. Chem. Soc.*, **89**, 2072 (1967).

[39] L. L. Ingraham in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley and Sons, Inc., New York, N. Y., 1956, p 518, and references therein.

[40] E. J. Lanpher, L. M. Redman, and A. A. Morton, *J. Org. Chem.*, **23**, 1370 (1958).

[41] T. Jordan, H. W. Smith, L. L. Lohr, Jr., and W. N. Lipscomb, *J. Amer. Chem. Soc.*, **85**, 846 (1963).

[42] See ref 1a, pp 38, 97, and 98.

[43] A. Streitweiser, Jr., J. A. Hudson, and F. Mares, *J. Amer. Chem. Soc.*, 90, 648 (1968).

sulfide.[12] Glpc analysis on an SE-30 column at 100° with a helium flow rate of $\sim$75 cc/min indicated a $\sim$1:1 mixture of isomers. Distillation through an 18-in. Nester and Faust spinning-band column provided a lower boiling cut (71–72° (25 mm)) of which 70% was the material with the shorter retention time and a higher boiling cut (73–74° (25 mm)) of which 88% was the material with the longer retention time. The infrared spectrum of the lower boiling material showed a strong absorption at 14.4 μ as well as a double bond stretching absorption at 6.1 μ consistent with *cis*-1-hexenyl methyl sulfide. The infrared spectrum of the high-boiling fraction showed a strong absorption at 10.3 μ and an absorption at 6.1 μ consistent with the *trans* isomer.[44] Oxidation of these fractions using sodium hypochlorite provided the sulfones. Distillation through an 8-in. Vigreux column provided samples (85–89° (0.1 mm)) whose pmr characteristics are recorded in Table II. Glpc analysis of these materials using the SE-30 column at 180° indicated no change in isomer distribution during oxidation.

Preparation of 2-Hexenyl Methyl Sulfone. The isomerization method of O'Connor and Lyness[13] using potassium *t*-butoxide in *t*-butyl alcohol was used. Fair yields ($\sim$60%) of distilled (80–84° (0.05 mm)) material were obtained. Only one peak was observed on glpc; however, the pmr spectrum (Table III) indicates a mixture of $\sim$15% *cis*- and 85% *trans*-2-hexenyl methyl sulfones.

Table III. Deuterium Exchange at the SO_2CH_3 Position of 2-Hexenyl Methyl Sulfone at 25.0°

Concn of base, *M*	Time, min	% exchanged[a]	Area $C\text{-}CH_3/SO_2CH_3$
0.066	10	36	1.57
0.066	30	56	2.29
0.066	60	75	3.95
0.062	10	37	1.59
0.062	30	47	1.89
0.062	60	71	3.45

[a] Determined from the relative areas of the SO_2CH_3 and $C\text{-}CH_3$ pmr signals.

Exchange Studies. All deuterium exchange studies were conducted in a constant-temperature bath thermostated to maintain 25.0°. A solvent mixture consisting of 15 ml of D_2O to 10 ml of dioxane was used throughout. Sodium deuterioxide solutions were prepared by allowing sodium metal, cut under hexane, to react with deuterium oxide. The concentration of these solutions was determined by titration against standard hydrochloric acid solutions using phenolphthalein indicator. Concentration of the basic solution was varied by dilution. The results of typical runs, in which exchange at the SO_2CH_3 position of 2-hexenyl methyl sulfone was observed, are included in Table III. The signal due to the methyl group of the alkyl chain (τ 9.1) was used as an internal standard. The second-order rate constants reported in Table I were obtained by dividing the first-order constants by the concentration of deuterioxide. At least 80% recoveries were obtained in all cases and products were shown to be identical with starting materials by glpc analysis except in the case of 1-hexenyl methyl sulfones which underwent isomerization during exchange. Duplicate runs of entries 2, 3, 5, 6, and 9 of Table I agreed with $\pm$30%.

"One-Point" Determinations. A series of experiments was conducted to establish that the concentration of base remained essentially constant during these exchange reactions. To 25.0 ml of a solution made up of 15.0 ml of 0.1026 *N* deuterium oxide and $\sim$10 ml of dioxane in a bath thermostated to 25.0° was added 1.0 g of 2-hexenyl methyl sulfone. The resulting solution was maintained under nitrogen for 30 min before titration to the phenolphthalein end point with 0.1032 *N* hydrochloric acid solution. Comparison to titration of a blank prepared in an identical manner indicated no change in concentration of base. Recovery of the 2-hexenyl methyl sulfone (95%) and analysis of its pmr spectrum showed the ratio of the areas of the terminal methyl (τ 9.1) to the SO_2CH_3 (τ 7.15) to be 2.47. Although the reaction time is not precise due to the time required for titration, calculation of a second-order rate constant from these data gives a value of 5×10^{-1} l./mol min which is in reasonable agreement with entry 5 of Table I.

A similar run using a 0.0024 *N* solution showed a 5% drop in base concentration after 30 min. The nmr spectrum of recovered material showed 30% exchange of the doubly activated methylene position of 2-hexenyl methyl sulfone. The second-order rate constant from this one point was 5 l./mol min (compare to entry 8 of Table I). Similarly, a 0.061 *N* deuterioxide solution containing 1.0 g of 1-hexenyl methyl sulfone (51% *cis* and 49% *trans* by glpc) showed no change in base concentration after 71% of the SO_2CH_3 position had undergone exchange. The rate constant calculated from this point was 3×10^{-1} l./mol min (compare to entries 3 and 4 of Table I). Also, *n*-butyl methyl sulfone (0.8 g) was subjected to deuterium exchange using a deuterium oxide–dioxane solution which was 0.061 *N* in sodium deuterioxide. A 1% decrease in base concentration was noted after 43% exchange of the SO_2CH_3 position. The second-order rate constant was 3×10^{-1} l./mol min (compare to entry 2 of Table I). Using a 0.707 *N* deuterioxide solution a 2% decrease in base strength was observed after 48% exchange of the methylene position of *n*-butyl methyl sulfone. The second-order rate constant was 5×10^{-4} l./mol min (compare to entry 1 of Table I). A similar experiment in which 1-hexenyl methyl sulfone (51% *cis* and 49% *trans*) was dissolved in deuterium oxide–dioxane solution which was 0.707 *N* in deuterioxide ion showed a 2% decrease in base concentration after 40% isomerization to 2-hexenyl methyl sulfone had occurred. The reaction time was 3 hr. This gives 4×10^{-3} l./mol min for the rate of isomerization of this mixture (compare to entries 6 and 7 of Table I). The work described earlier with samples enriched in *cis* and in *trans* isomers shows that these materials undergo isomerization at similar rates. Inspection of the vinyl proton region of the pmr spectrum of this sample confirmed the α-vinyl proton exchange described above. Thus the relative areas of the τ 3.5–3.8 to τ 2.9–3.2 signals were 3:1 in the starting material and 3:2 after exchange. This establishes approximately 50% exchange of the α-vinyl protons under these conditions.

Preparation of 2-Hydroxyhexyl Methyl Sulfone. Oxidation of 2-hydroxyhexyl methyl sulfoxide[45] using sodium hypochlorite solution gave the sulfone in 95% crude yield. Distillation through an 8-in. Vigreux column provided a material (120° (0.1 mm)) with the following pmr characteristics as a $\sim$10% solution in deuteriochloroform: a multiplet centered at τ 9.1 accounted for three hydrogens; a multiplet centered at τ 8.6 accounted for six hydrogens; a singlet at τ 7.0 superimposed on a multiplet centered at τ 6.9 accounted for five hydrogens; a sharp singlet at τ 6.55 which disappeared upon shaking the sample with D_2O; and a multiplet centered at τ 5.8 accounted for one hydrogen. The infrared spectrum showed strong sulfone bands (7.7 and 8.9 μ) as well as typical alkyl absorptions.[44] Glpc analysis indicated >98% purity.

Stability of 2-Hydroxyhexyl Methyl Sulfone to Exchange Conditions. To a solution of deuterium oxide (10.0 ml) and 1,4-dioxane (10.0 ml) was added 1.0 g of 2-hydroxyhexyl methyl sulfone. The solution was maintained at 25° and 5.0 ml of 1.97 *N* sodium deuterioxide in deuterium oxide was added. Aliquots were taken 1 hr, 4 hr, and 3 days after addition of base and worked up by repeated extractions with chloroform. The chloroform solutions were dried with anhydrous magnesium sulfate and the solvent was removed under reduced pressure. The combined weight of the recovered residues was 0.84 g. The pmr spectra of these samples gave no indication of the formation of either 1- or 2-hexenyl methyl sulfone. Reduction in the relative areas of the signals assigned to the SO_2CH_3 group and the $-CH_2SO_2-$ group (τ 7.0 and τ 6.9; see Table II) was observed. No reduction in the area of the single hydrogen attached to carbon bearing –OH (τ 5.8) relative to the alkyl chain was apparent. No extraneous pmr signals were observed and glpc analysis of the sample recovered after 4 hr indicated $\sim$99% 2-hydroxyhexyl methyl sulfone by comparison of its retention time to that of starting material.

Acknowledgment. The technical assistance of Mr. Jack Wendel is gratefully acknowledged.

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[44] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1958.

[45] A sample of this material prepared by published procedures [G. A. Russell, E. Sabourin, and G. J. Mikol, *J. Org. Chem.*, **31**, 2854 (1966)] was kindly supplied by Dr. D. E. O'Connor.