

OCI. It was stored at 0° in the dark as a dilute solution in carbon tetrachloride. Under these conditions the hypochlorite is stable; about 1% decomposition over a period of 3 months was found by iodometric titration.

**Possible deuterium exchange** during acid hydrolysis of  $C_6H_5C(CH_3)(CD_3)OMgI$  was investigated with cumyl alcohol; 1.5 g. of the alcohol in 12.5 cc. of ether was washed with 0.6 cc. of concentrated sulfuric acid in 18 cc. of  $D_2O$ ; these conditions are similar to those of the hydrolysis of the magnesium salt. The two layers were allowed to remain in contact for 24 hr. at room temperature with occasional shaking; n.m.r. analysis showed no detectable incorporation of deuterium within experimental error,  $\pm 2.5\%$ .

**Standard mixtures** of methyl chloride and methyl- $d_3$  chloride were prepared volumetrically. Some difficulty was encountered because of the solubility of the two gases in stopcock grease, but it was overcome by the use of Cello-grease (Fisher Scientific Co.). Mixtures of varying proportions were made, and the relative sensitivity of the mass spectrometer to the two compounds was found to be independent of the composition of the mixture.

The methyl chloride used (The Matheson Co., Inc.) was purified by g.l.c. on a dinonyl phthalate 2-m. column.

**Methyl- $d_3$  chloride** was prepared from methyl- $d_3$  iodide containing 1.3% methyl- $d_2$  iodide (Merck and Co., Ltd.) by passing over a 50-fold excess of a hot mixture of aluminum chloride, mercuric chloride, and asbestos fiber under reduced pressure at 100°. Thirty passes gave almost complete conversion to the chloride. The material was purified by g.l.c. and mass spectroscopy showed that it contained 1.3% methyl- $d_2$  chloride.

**Determination of the Isotope Effect.**—A typical experiment is described. A solution of hypochlorite (0.5 M) and freshly distilled cyclohexane (1.0 M, Eastman White Label) in freshly distilled carbon tetrachloride (Baker and Adamson) was prepared in the dark. It was placed in a breakseal ampoule, wrapped in black cloth, degassed under high vacuum, sealed, and placed in a  $75 \pm 0.5^\circ$  bath. Ten minutes was allowed for temperature equilibration; then the black cloth was removed and the tube was ir-

radiated with a 200-watt incandescent lamp from a distance of 10 cm. for 24 hr. The tube was frozen with liquid nitrogen, then broken open in a vacuum line system under a pressure of  $10^{-6}$  mm. The reaction products were allowed to warm up to room temperature and the vapors were allowed to expand into a Toepler pump after passing through an efficient spiral trap maintained at  $-20^\circ$ . The contents of the Toepler pump were pushed into a U-tube equipped with stopcocks and the contents of the trap were refrozen into the remaining reaction mixture with liquid nitrogen. This distillation was repeated ten times; then only a trace of methyl chloride could be detected in the distillation residue by g.l.c. The contents of the U-tube were chromatographed on a 2-m. dinonyl phthalate column and the methyl chloride was collected and analyzed by mass spectrometry.

**Treatment of Mass Spectrometric Data.**—The machine was a Consolidated-Nier Isotope Ratio, Model 21-201, with a Gainsville-Philip variable slit leak; an ionizing voltage of about 150 v. and an accelerating voltage of about 900 v. were used. The relative amounts of methyl and methyl- $d_3$  chloride were determined from the 52 and 55 peaks. Corrections for the presence of 1.3% of methyl- $d_2$  chloride were made as follows: The 55 peak was assumed to be due entirely to  $CD_3Cl^{37}$ , an approximation good to high degree (see Table I). The amount of  $CD_2HCl^{37}$  is equal to 1.3% of the 55 peak; the amount of  $CD_2HCl^{38}$  is three times that value and it will contribute to the 52 peak. Therefore, 3.9% of the value of 55 peak was subtracted from the 52. This correction was applied to the relative sensitivity determinations as well. A further subtraction was made from the 52 peak for the amount of natural methyl chloride formed from hypochlorite molecules containing  $-CD_2H$ . This correction amounts to 1.6% of the 55 peak ( $1.3\% \times$  isotope effect in  $-CD_2H$  group). Reproducibility of the ratios obtained in this fashion was good,  $\pm 1\%$ .

**Acknowledgment.**—The authors are indebted to Mr. T. Middleton for mass spectrometric determinations and to Mrs. C. Paul for deuterium analyses.

[CONTRIBUTION FROM THE PROCTER & GAMBLE CO., MIAMI VALLEY LABORATORIES, CINCINNATI 39, OHIO]

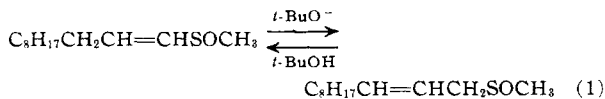
## The Effect of Methylmercapto, Methylsulfinyl, and Methylsulfonyl Groups on the Equilibrium in Three-Carbon Prototropic Systems

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The positions of base-catalyzed equilibrium between the  $\alpha,\beta$ - and  $\beta,\gamma$ -unsaturated isomers of alkenyl methyl sulfides, sulfoxides, and sulfones (eq. 2,  $X = -SCH_3$ ,  $-SOCH_3$ , and  $-SO_2CH_3$ ) have been determined. In the compounds containing an alkyl group attached to the  $\gamma$ -carbon atom, the ratios of  $\beta,\gamma$ - to  $\alpha,\beta$ -unsaturated isomers are: in sulfides ( $X = -SCH_3$ ), 34:66; in sulfoxides ( $X = -SOCH_3$ ), 96:4; in sulfones ( $X = -SO_2CH_3$ ), >99:1. In the allyl-propenyl equilibria the ratios of  $\beta,\gamma$ - to  $\alpha,\beta$ - are: in sulfides, <1:99; in sulfoxides, 20:80; in sulfones, 44:56. The great predominance of  $\beta,\gamma$ -isomers in the alkenyl methyl sulfoxides and sulfones is convincing evidence that ground-state d-orbital resonance contributes little or nothing to the stability of the  $\alpha,\beta$ -double bond. The data are rationalized on the basis that an inductive withdrawal of electrons destabilizes a double bond. Comparison of the case where  $R =$  alkyl with that where  $R = H$  in eq. 2 indicates that the stabilizing effect of the alkyl group is 2.8 kcal.

In an earlier communication,<sup>1</sup> we reported that the  $\beta,\gamma$ -unsaturated isomer is greatly favored over the  $\alpha,\beta$ -unsaturated isomer at equilibrium in the base-catalyzed isomerization of certain alkenyl methyl sulfoxides (eq. 1). Because this was the first case in which the  $\beta,\gamma$ -isomer was found to be favored in an open-chain sys-



tem, we wished to study the more general system (eq. 2) in which R is hydrogen or alkyl and X represents



methylmercapto, methylsulfinyl, and methylsulfonyl groups. The effect of these groupings on the equilibrium is reported herewith.

Linstead and Kon and their co-workers have made a thorough investigation of the effect of certain other substituent groups, X, in the prototropic system depicted in eq. 2. In all such systems which they studied, I is more stable than II.

In esters ( $X = -CO_2R$ ) the ratio of I:II at equilibrium is approximately 92:8<sup>2</sup>; in carboxylic acids ( $X = -CO_2H$ ) or their salts ( $X = -CO_2^-$ ) the ratio is 68-75:32-25<sup>3,4</sup>; in nitriles ( $X = -CN$ ) the ratio is

(2) G. A. R. Kon, R. P. Linstead, and G. W. G. MacLennan, *J. Chem. Soc.*, 2452, 2454 (1932).

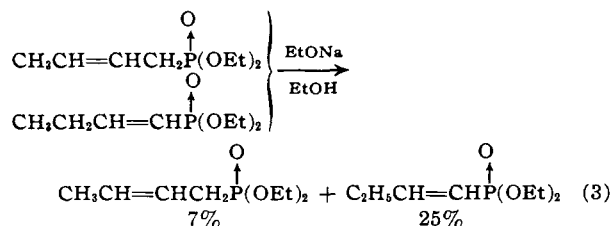
(3) A. A. Goldberg and R. P. Linstead, *ibid.*, 2343 (1928).

(4) R. P. Linstead and E. G. Noble, *ibid.*, 614 (1934).

(1) D. E. O'Connor and W. I. Lyness, *J. Am. Chem. Soc.*, **85**, 3044 (1963).

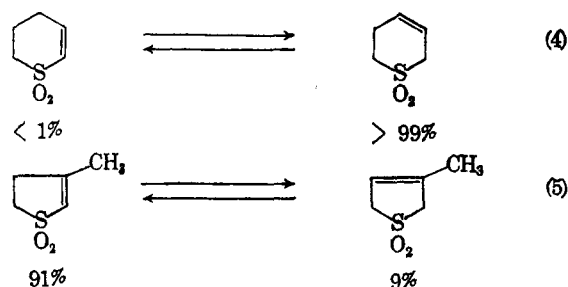
86:14<sup>5</sup>; and in ketones the ratio is 75:25.<sup>6</sup> The presence of a second alkyl group in the  $\alpha$ -,  $\beta$ -, or  $\gamma$ -position has a marked effect on the position of equilibrium: alkyl substituents in the  $\alpha$ -position increase the proportion of I, while alkyl substituents in the  $\beta$ - or  $\gamma$ -position generally increase the proportion of II.<sup>7</sup> The data of Linstead and Kon have been summarized.<sup>8</sup>

In contrast, very little information is available on equilibria in other types of unsaturated compounds. It has recently been reported<sup>9</sup> that treatment with base of either the  $\alpha,\beta$ - or the  $\beta,\gamma$ -unsaturated isomer of diethyl butenylphosphonate gave yields of 7% of the  $\beta,\gamma$ -unsaturated isomer and 25% of the  $\alpha,\beta$ -unsaturated isomer (eq. 3). Much of the other data available concern



allyl-propenyl ( $R = \text{H}$  in eq. 1) equilibria. In ethers,<sup>10</sup> amines,<sup>11</sup> and sulfides,<sup>12,13</sup> the propenyl isomer (I,  $R = \text{H}$ ) is greatly favored over the allyl isomer (II,  $R = \text{H}$ ) at equilibrium.

Equilibria in cyclic unsaturated sulfones have received some attention, but in cyclic systems it is difficult to distinguish between substituent effects and ring effects. For example, in dihydrothiapyran 1,1-dioxide, the  $\beta,\gamma$ -unsaturated isomer is greatly favored (eq. 4),<sup>14</sup> whereas in the next lower cyclic homolog, 3-methyldihydrothiophene 1,1-dioxide, the  $\alpha,\beta$ -unsaturated isomer is favored by a ratio of 91:9 (eq. 5).<sup>15</sup> Other



data on the isomerization of<sup>16</sup> and the equilibrium position in<sup>17,18</sup> various unsaturated sulfones give no indication of the effect produced by the sulfone group.

(5) R. A. Letch and R. P. Linstead, *J. Chem. Soc.*, 443 (1932).

(6) E. N. Eccott and R. P. Linstead, *ibid.*, 905 (1930).

(7) A. E. Abbott, G. A. R. Kon, and R. D. Satchell, *ibid.*, 2514 (1928); A. Kandiah and R. P. Linstead, *ibid.*, 2139 (1929); G. A. R. Kon and E. Leton, *ibid.*, 2496 (1931); G. A. R. Kon and K. S. Nargund, *ibid.*, 623 (1934); A. H. Dickinson, W. E. Hugh, and G. A. R. Kon, *ibid.*, 572 (1929); 1630 (1928).

(8) H. Adkins, "Organic Chemistry," Vol. I, 2nd Ed., H. Gilman, Ed., John Wiley and Sons, Inc., New York, N. Y., 1943, pp. 1041-1043.

(9) B. I. Ionin and A. A. Petrov, *Zh. Obshch. Khim.*, **33**, 432 (1963); *Chem. Abstr.*, **59**, 656d (1963).

(10) T. J. Prosser, *J. Am. Chem. Soc.*, **83**, 1701 (1961).

(11) C. C. Price and W. H. Snyder, *Tetrahedron Letters*, 69 (1962).

(12) C. C. Price and W. H. Snyder, *J. Org. Chem.*, **27**, 4639 (1962).

(13) D. S. Tarbell and W. E. Lovett, *J. Am. Chem. Soc.*, **78**, 2259 (1956).

(14) E. A. Fehnel, *ibid.*, **74**, 1569 (1952).

(15) J. Böeseken and E. de R. van Zuydewijn, *Proc. Acad. Sci. (Amsterdam)*, **40**, 23 (1937); *Chem. Abstr.*, **31**, 4953 (1937).

(16) H. J. Backer and G. J. De Jong, *Rec. trav. chim.*, **67**, 884 (1948).

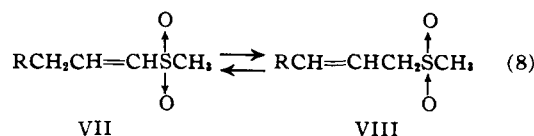
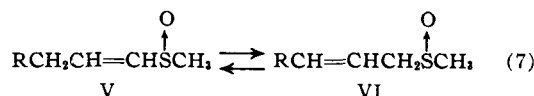
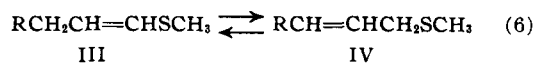
(17) E. Rothstein, *J. Chem. Soc.*, 309 (1937).

(18) A. H. Raper and E. Rothstein, *ibid.*, 1027 (1963).

It is apparent that there is a real need for additional data on the effects of substituents on three-carbon prototropic systems. Our discovery<sup>1</sup> that a  $\beta,\gamma$ -unsaturated sulfoxide was the major product of a base-catalyzed elimination reaction (eq. 10) that should give an equilibrium mixture of  $\alpha,\beta$ - and  $\beta,\gamma$ -unsaturated products led us to study the equilibrium of several unsaturated sulfides, sulfoxides, and sulfones. Our objective was to determine what the effect of the functional group itself was. Hence, we have chosen structures in which other effects should be minimal.

## Results

A number of  $\alpha,\beta$ - and  $\beta,\gamma$ -unsaturated sulfides, sulfoxides, and sulfones have been prepared, and the positions of the equilibria in eq. 6-8 have been established with each pair of isomers.



The results are given in Table I.

TABLE I  
PERCENTAGE COMPOSITION OF EQUILIBRIUM MIXTURES OF  
 $\alpha,\beta$ - AND  $\beta,\gamma$ -UNSATURATED SULFIDES, SULFOXIDES, AND  
SULFONES

		$\xrightleftharpoons{K}$				$\Delta F^\circ_{\text{iso}}$ , kcal.	Remarks
		$\text{RCH}_2\text{CH}=\text{CHX} \rightleftharpoons \text{RCH}=\text{CHCH}_2\text{X}$					
	R	X	% I	% II			
1	$\text{C}_2\text{H}_5\text{--}$	$\text{--SCH}_3$	66	34	$0.39 \pm 0.04$	a, b	
2	$\text{C}_2\text{H}_5\text{--}$		67	33	$0.42 \pm 0.04$	a	
3	H--		>99	<1	>2.7	c	
		$\begin{array}{c} \text{O} \\ \uparrow \end{array}$					
4	$\text{C}_2\text{H}_5\text{--}$	$\text{--SCH}_3$	4	96	$-1.9 \pm 0.15$	d, e	
5	$\text{C}_2\text{H}_5\text{--}$		4	96	$-1.9 \pm .15$	d, f	
6	$\text{C}_2\text{H}_5\text{--}$		4	96	$-1.9 \pm .15$	d	
7	$\text{CH}_3\text{--}$		3	97	-2.1	d	
8	H--		80-83	20-17	$0.9 \pm 0.1$	d	
		$\begin{array}{c} \text{O} \\ \uparrow \\ \text{--SCH}_3 \\ \downarrow \\ \text{O} \end{array}$					
9	$\text{C}_2\text{H}_5\text{--}$	$\text{--SCH}_3$	<1	>99	<-2.7	d	
10	H--		56	44	$0.14 \pm 0.1$	a	

<sup>a</sup> The percentages were determined by g.c. <sup>b</sup> These values were checked by oxidative analysis, which gave 65% I, 34% II, and 1% other isomers, principally  $\gamma,\delta$ -isomer. <sup>c</sup> This value was determined by Price.<sup>12</sup> <sup>d</sup> The percentages were determined by n.m.r. analysis of the vinyl proton region. <sup>e</sup> These values were checked by oxidative analysis, which gave 4% I, 93% II, and 3% other isomers, principally  $\gamma,\delta$ -isomer. <sup>f</sup> These values were checked by oxidative analysis, which gave 5% I, 94% II, and 1% other isomers.

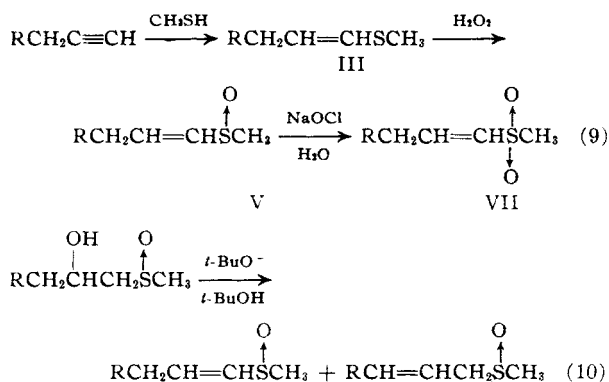
The  $\alpha,\beta$ -unsaturated compounds containing an alkyl group attached to the  $\gamma$ -carbon atom were prepared by the addition of methyl mercaptan to acetylenes<sup>19-21</sup>

(19) A. T. Blomquist and J. Wolinsky, *J. Org. Chem.*, **23**, 551 (1958).

(20) E. P. Kohler and H. Potter, *J. Am. Chem. Soc.*, **57**, 1316 (1935).

(21) H. Bader, L. C. Cross, I. Heilbron, and E. R. H. Jones, *J. Chem. Soc.*, 619 (1949).

to yield III, after which oxidation yielded V and VII (eq. 9). Equilibrium mixtures of the  $\alpha,\beta$ - and  $\beta,\gamma$ -unsaturated sulfoxides were prepared directly by the basic elimination of water from  $\beta$ -hydroxy sulfoxides (eq. 10).<sup>22</sup>



1-Methylmercapto-2-dodecene, containing 4% 1-methylmercapto-1-dodecene, was prepared by reduction of the corresponding sulfoxide with lithium aluminum hydride.

Allyl methyl sulfoxide and allyl methyl sulfone were prepared by oxidation of allyl methyl sulfide. Propenyl methyl sulfoxide and propenyl methyl sulfone were prepared by the oxidation of propenyl methyl sulfide which had been obtained by the basic isomerization of allyl methyl sulfide.<sup>12</sup>

Equilibrium in the sulfoxides and sulfones was established by treating the compounds with a solution of potassium *t*-butoxide in *t*-butyl alcohol at room temperature. The time allowed for equilibrium to be established was normally several hours, although with the allyl and propenyl methyl sulfoxides 1 hr. was sufficient. It is quite likely that the times allowed in the other cases were excessive.

Addition of solvent to the  $\alpha,\beta$ -unsaturated isomers, *via* Michael addition, was no problem, except in the equilibration of allyl and propenyl sulfones. In the sulfoxides and sulfones containing an alkyl group attached at the  $\gamma$ -carbon, the very low concentration of  $\alpha,\beta$ -unsaturated isomer is probably responsible for the lack of addition. Addition of solvent to propenyl methyl sulfoxide did occur but was very much slower than equilibration, so that equilibration could be carried out in alcohol solvent. On the other hand, addition of *t*-butyl alcohol to propenyl methyl sulfone occurred rapidly enough to interfere with the equilibration. The propenyl and allyl sulfones were therefore equilibrated with triethylamine.<sup>16</sup>

Potassium *t*-butoxide in *t*-butyl alcohol was not a strong enough base to effect equilibrium in the unsaturated sulfides in a reasonable length of time at room temperature. For these compounds, it was necessary to use a solution of potassium *t*-butoxide in dimethyl sulfoxide.<sup>23</sup> With this more basic system, equilibrium was established within 0.5 hr., at room temperature. A side reaction also occurred in this system leading to the formation of a diene, probably by 1,4-elimination of methyl mercaptan from the  $\beta,\gamma$ -unsaturated isomer.

(22) An allylic alcohol,  $\text{RCHOHCH}=\text{CH}_2$ , is also formed in this reaction.

(23) C. C. Price and W. H. Snyder, *J. Am. Chem. Soc.*, **83**, 1773 (1961), and D. J. Cram, B. Rickborn, and G. R. Knox, *ibid.*, **82**, 6412 (1960), have reported greatly accelerated rates of base-catalyzed reactions in dimethyl sulfoxide. E. C. Steiner and J. M. Gilbert, *ibid.*, **85**, 3054 (1963), have recently reported that potassium *t*-butoxide in DMSO is  $10^{14}$  more basic when it is alcohol free than it is in the presence of 5% of the alcohol.

At reaction times of 0.5 hr., about 10% of the sulfide was consumed in this manner; after several hours, most of the sulfide was lost. This elimination reaction did not affect the equilibrium; the ratio of isomeric sulfides was the same in aliquots taken at several time intervals.

Proof of equilibrium in the sulfoxides was established in two ways. Treatment of 1-methylsulfinyl-1-dodecene (V,  $\text{R} = \text{C}_9\text{H}_{19}-$ ) with potassium *t*-butoxide in *t*-butyl alcohol for 5 hr. and for 24 hr. gave the same product distribution (96% VI,  $\text{R} = \text{C}_9\text{H}_{19}-$ ; 4% V,  $\text{R} = \text{C}_9\text{H}_{19}-$ ). Further proof was obtained by treating 1-methylsulfinyl-2-undecene (containing 4% 1-methylsulfinyl-1-undecene) with potassium *t*-butoxide in *t*-butyl alcohol-*O-d* at room temperature for 24 hr. Deuterium exchange occurred at both the  $\alpha$ - and the  $\gamma$ -carbons. Thus, a nuclear magnetic resonance spectrum of the starting material had absorption bands centered at 4.4  $\tau$  (area 1.9) due to olefinic protons, at 6.65  $\tau$  (area 2.0) due to doubly activated protons between the double bond and the sulfinyl group, at 7.5  $\tau$  (area 3.0) due to methylsulfinyl protons, at 7.8–8.0  $\tau$  (area 2.0) due to allylic protons, and at 8.7 and 9.1  $\tau$  (area 15) due to alkyl chain protons. After treatment the bands at 6.65 and 7.58  $\tau$  had been reduced to about one-fifth their original area,<sup>24</sup> while the band at 4.4  $\tau$  had been reduced to a relative area of 1.15–1.2. The other bands were unchanged. A control using *t*-butyl alcohol and otherwise identical conditions gave unchanged starting materials. The deuterium in the  $\gamma$ -position must arise by formation of the  $\alpha,\beta$ -unsaturated isomer and conversion to the  $\beta,\gamma$ -unsaturated isomer. The two isomers are therefore readily interconverted in this system.

The allyl-propenyl equilibria (V,  $\text{R} = \text{H}$ ,  $\rightleftharpoons$  VI,  $\text{R} = \text{H}$ , and VII,  $\text{R} = \text{H}$ ,  $\rightleftharpoons$  VIII,  $\text{R} = \text{H}$ ) were approached from each side with both the sulfoxides and sulfones. The equilibrium position of the other sulfone was obtained by basic treatment of 1-methylsulfonyl-1-hexene (VII,  $\text{R} = \text{C}_3\text{H}_7-$ ), and, since the product contained >99% 1-methylsulfonyl-2-hexene (VIII,  $\text{R} = \text{C}_3\text{H}_7-$ ), the equilibrium mixture can contain no less. The dodecenyl methyl sulfide equilibrium (III,  $\text{R} = \text{C}_9\text{H}_{19}-$ ) was approached from each side.

With the sulfoxides and sulfones, the quantity of each isomer present at equilibrium was determined by n.m.r. analysis. The n.m.r. spectra of the  $\alpha,\beta$ - and  $\beta,\gamma$ -unsaturated isomers differ in two respects. The  $\beta,\gamma$ -isomers have an absorption at 6.6  $\tau$  which is not present in the  $\alpha,\beta$ -isomers, and, in addition, the vinyl proton absorptions of the two isomers are well separated. The vinyl protons of the  $\beta,\gamma$ -unsaturated isomers absorb at 4.0–4.8  $\tau$ , while the vinyl protons of the  $\alpha,\beta$ -isomers absorb at 3.5–3.9  $\tau$  in the sulfoxides (the band is at lower field in the sulfones). Since the two bands do not overlap, it is quite simple to measure their relative areas, and thus calculate the proportions of the two isomers.

The proportions of the two unsaturated sulfide isomers were determined by gas chromatographic (g.c.) analysis.<sup>25</sup>

(24) The *t*-butyl alcohol-*O-d* contained a significant amount of *t*-butyl alcohol. Hence, complete exchange of deuterium for hydrogen could not occur.

(25) There were peaks for the *cis*- and *trans*- $\alpha,\beta$ -unsaturated isomers and for one  $\beta,\gamma$ -isomer (probably *trans*). The relative proportions of the three peaks were 27% *cis*- $\alpha,\beta$ , 39% *trans*- $\alpha,\beta$ , and 34%  $\beta,\gamma$ . There was another very small peak which could have been *cis*- $\beta,\gamma$ -isomer.

The accuracy of the n.m.r. analysis of the sulfoxides and sulfones and the g.c. analysis of the sulfides was verified by an oxidative cleavage analysis on the dodecyl sulfide mixture and on the dodecyl and undecyl sulfoxides.<sup>26</sup> The double bonds were cleaved with permanganate-periodate, the resulting acids were converted to their methyl esters, and the esters were determined quantitatively by g.c. This method gave results within 1% of the n.m.r. and g.c. analyses. The close agreement lends considerable confidence to the data listed in Table I.

### Discussion

In the compounds under consideration, there are two groups which can affect the position of equilibrium. These are the alkyl group and the substituent, X.

The length of the alkyl group has little or no effect. Thus, in the sulfoxides, there is essentially no difference in the position of equilibrium where  $R = C_3H_7$  and where  $R = C_9H_{19}$  (entries 4, 5, and 6 in Table I). The constancy of the equilibrium ratio of isomers as R is varied indicates that the length of R is unimportant, so that in their effect on double bond stability,  $R \cong RCH_2$ . Since this is true, the difference in stability between the  $\alpha,\beta$ - and  $\beta,\gamma$ -unsaturated isomers (where  $R = \text{alkyl}$  in eq. 2) is caused solely by the difference in the stabilizing effect of a  $-CH_2X$  group *vs.* that of an X group. A comparison of these two groups appears to be the best approach for considering the effect of the substituent on the equilibrium.

Three ways in which the substituent might affect the equilibrium are: (a) The  $\alpha,\beta$ -double bond can interact with the d-orbitals of sulfur; (b) the  $\alpha,\beta$ -double bond can interact with the filled p-orbital(s) of sulfur in the sulfide and sulfoxide; (c) the inductive effect of the substituent can influence the equilibrium.

A large body of chemical and spectroscopic evidence indicates the possibility of interaction of the d-orbitals of sulfur with adjacent electron-rich centers.<sup>27</sup> Almost all of the examples cited are chemical reactions in which a high-energy intermediate or a transition state is involved. On the other hand, Breslow and Mohacsi have found that d-orbital resonance is not significant in some molecules that are seemingly favorably situated for such resonance.<sup>28</sup>

d-Orbital resonance in these unsaturated sulfur compounds should enhance the stability of the  $\alpha,\beta$ -double bond and should be at least as important in the sulfoxides and sulfones as it is in the sulfides. Since the  $\alpha,\beta$ -unsaturated sulfoxides and sulfones are much less stable than the  $\beta,\gamma$ -unsaturated isomers, it is apparent that d-orbital resonance can play no more than a minor role.

The second type of resonance to be considered is the interaction of the filled p-orbital(s) on sulfur with the  $\pi$ -electrons of the double bond. If  $p-\pi$  resonance were a significant factor in the sulfides and sulfoxides, the  $\alpha,\beta$ -double bond should be stabilized at the expense of the  $\beta,\gamma$ -double bond. The small enhancement of the  $\alpha,\beta$ -isomers in the sulfides (entries 1 and 2 in Table I) could indeed be due to  $p-\pi$  resonance. However, the

energy difference between the two isomers is small. Furthermore, in the sulfoxides  $p-\pi$  resonance cannot be a dominant effect, since the  $\alpha,\beta$ -isomers are considerably less stable than the  $\beta,\gamma$ -isomers. The data are in the proper order for  $p-\pi$  resonance to be operative; *i.e.*, the  $\alpha,\beta$ -double bonds in the sulfides and sulfoxides are relatively more stable than that in the sulfone (entry 9 in Table I) where  $p-\pi$  resonance cannot occur, but the effect cannot account for the great preference for the  $\beta,\gamma$ -isomers in the sulfoxides and sulfones. Hence,  $p-\pi$  resonance can at most be a small effect superimposed on a much larger effect.

The absence of important resonance effects leaves the inductive effect for consideration as a major factor. The order of electron-withdrawing tendency ( $-I$  effect) of the X groups under consideration is  $-SCH_3 < -SOCH_3 < -SO_2CH_3$ . The equilibria will be determined by the differences between the  $-I$  effects of the X and the corresponding  $-CH_2X$  groups ( $I_X - I_{CH_2X}$ ), which should also fall in increasing order as the substituent group is changed from  $-SCH_3$  to  $-SOCH_3$  to  $-SO_2CH_3$ .<sup>29</sup> A comparison of entries 2, 6, and 9 in Table I shows that substantial differences exist and that the order of increasing stability of the  $\beta,\gamma$ -unsaturated isomer follows the same order. The fact that this series does follow the inductive order coupled with the fact that resonance effects cannot be a major factor suggests that in this series of sulfur compounds, inductive effects are quite important. Furthermore, the observed order indicates that an inductive withdrawal of electrons tends to destabilize a double bond.

In considering the effect of substituents upon the relative stabilities of  $\alpha,\beta$ - and  $\beta,\gamma$ -unsaturated isomers which have an alkyl group attached at the  $\gamma$ -carbon, a comparison is required between the combined effects of R and  $-CH_2X$  groups *vs.* those of  $RCH_2$  and X groups. It has already been pointed out that R and  $RCH_2$  have essentially equal effects on double bond stability. This permits a direct comparison of the  $-CH_2X$  and X groups.

The situation is more complex in allyl-propenyl equilibria ( $R = H$  in eq. 1). To compare the effects of  $-SCH_3$ ,  $-SOCH_3$ , and  $-SO_2CH_3$  with that of H requires that the effect of the  $-CH_3$  group be equated with those of the  $-CH_2X$  groups. There is no basis, *a priori*, for equating these effects. Our data, in fact, suggest that  $-CH_2X$  groups, particularly  $-CH_2SOCH_3$  and  $-CH_2SO_2CH_3$ , have destabilizing effects compared to the  $-CH_3$  group. No comparisons of the effects of  $-SCH_3$ ,  $-SOCH_3$ , and  $-SO_2CH_3$  groups with that of H can be drawn, therefore, from the allyl-propenyl equilibria data.

The effect of having an alkyl group attached to the  $\gamma$ -carbon can be seen readily by comparison of the equilibria where  $R = H$  in eq. 1 with those where  $R = \text{alkyl}$  in eq. 1 (*cf.* entries 1 and 3 for the sulfides, entries 4 and 8 for the sulfoxides, and entries 9 and 10 for the sulfones). Assuming that the difference between  $-CH_3$  and long alkyl effects is negligible, replacement of one H on the  $\gamma$ -carbon of the unsaturated sulfoxide by a long alkyl group increases the relative stability of the  $\beta,\gamma$ -unsaturated isomer by 2.8 kcal. (*cf.* entries 4 and

(26) We are indebted to Dr. D. F. Kuemmel of these laboratories for the analyses. The general method has recently been reported (D. F. Kuemmel, *Anal. Chem.*, **36**, 426 (1964)).

(27) G. Cilento, *Chem. Rev.*, **60**, 147 (1960).

(28) R. Breslow and E. Mohacsi, *J. Am. Chem. Soc.*, **84**, 684 (1962); **83**, 4100 (1961).

(29) The relationship  $I_{CH_2X} = I_X/2.8$  is approximately true for a number of substituents, X (R. W. Taft, Jr., "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley and Sons, Inc., New York, N. Y., 1956, p. 592). We assume that it is true in the present case.

8 in Table I). This value is in reasonably good agreement with the *ca.* 2.5 kcal. difference in stability between 1- and 2-olefins.<sup>30</sup>

### Experimental

**General.**—All n.m.r. spectra were obtained on a Varian A-60 spectrometer using approximately 10% solutions in carbon tetrachloride. Infrared spectra were obtained on a Perkin-Elmer Infracord spectrophotometer. Gas chromatograms were obtained on an Aerograph A-90P apparatus using a 20% diethylene glycol succinate (DEGS) on firebrick column, a 10% silicone (SF-96) on Fluoropak column, or an ethylene glycol adipate (AAEG) on Anakrome ABS column. Elemental analyses were performed by the Procter & Gamble Analytical Services Laboratory.

**Preparation of an Equilibrium Mixture of 1-Methylsulfinyl-2-undecene and 1-Methylsulfinyl-1-undecene.**—A solution of potassium *t*-butoxide in *t*-butyl alcohol was prepared from 2.7 g. (0.07 g.-atom) of potassium and 100 ml. of *t*-butyl alcohol, and to the solution was added 11.7 g. (0.5 mole) of 1-methylsulfinyl-2-hydroxyundecane. The reaction mixture was stirred at 60° for 5 hr. and was then poured into 200 ml. of cold water. The mixture was extracted three times with ethyl acetate, the solvent was evaporated and the residue was distilled to yield 7.5 g., b.p. 125–131° (0.5 mm.). Redistillation of this material through a 2 ft. long, 8 mm. diam. spinning band column gave 1.0 g. of 3-hydroxy-1-undecene, b.p. 56° (0.2 mm.).

*Anal.* Calcd. for  $C_{11}H_{22}O$ : C, 77.6; H, 13.0. Found: C, 77.6; H, 13.2.

Further distillation gave 4.9 g. (45% yield) of 1-methylsulfinyl-2-undecene, b.p. 113–114° (0.1 mm.).

*Anal.* Calcd. for  $C_{12}H_{24}OS$ : C, 66.6; H, 11.17; S, 14.81. Found: C, 66.2; H, 11.4; S, 14.4.

An n.m.r. spectrum had absorption bands centered at 4.4 (area 1.95, vinyl protons), 6.6 (area 1.7,  $C=CCH_2SO$ ), 7.55 (area 2.94, methylsulfinyl protons), 7.8–8.0 (area 1.95, allyl protons), and 8.7 and 9.1  $\tau$  (area 15.0, alkyl chain protons). Analysis of the vinyl proton region showed that 4% of this material was  $\alpha,\beta$ -unsaturated. Analysis by oxidative cleavage indicated 5%  $\alpha,\beta$ -unsaturated, 94%  $\beta,\gamma$ -unsaturated, and 1% other isomers.

**Preparation of an Equilibrium Mixture of 1-Methylsulfinyl-2-hexene and 1-Methylsulfinyl-1-hexene.**—The reaction was carried out as described above using 0.1 mole of potassium *t*-butoxide in 200 ml. of *t*-butyl alcohol and 16.4 g. (0.1 mole) of 1-methylsulfinyl-2-hydroxyhexane. Distillation of the residue obtained from the extracts yielded 9.5 g. (65%) of 1-methylsulfinyl-2-hexene, b.p. 71° (0.2 mm.). An n.m.r. spectrum had bands at 4.4 (area 2.3), 6.6 (area 2.1), 7.55 (area 3.0), 7.8–8.0 (area 2.0), 8.5 (area 2.0, methylene adjacent to terminal methyl), and 9.0  $\tau$  (area 3.0, terminal methyl). Analysis of the vinyl proton region indicated 5%  $\alpha,\beta$ -unsaturated material (vinyl proton absorption below 3.9  $\tau$ ).

*Anal.* Calcd. for  $C_7H_{14}OS$ : C, 57.5; H, 8.65; S, 20.9. Found: C, 56.3; H, 9.5; S, 21.7.

**Preparation of an Equilibrium Mixture of 1-Methylsulfinyl-2-butene and 1-Methylsulfinyl-1-butene.**—To a mixture of 0.1 mole of potassium *t*-butoxide in 200 ml. of *t*-butyl alcohol was added 13.6 g. (0.1 mole) of 1-methylsulfinyl-2-hydroxybutane. The reaction mixture was stirred for 3 hr. at 60° and was then poured into 100 ml. of ice-water. The *t*-butyl alcohol was evaporated and the residue was extracted three times with ethyl acetate, the extracts were dried over magnesium sulfate, the solvent was evaporated, and the residue was distilled. There was obtained 5.4 g. (46%) of 1-methylsulfinyl-2-butene, b.p. 62° (0.2 mm.) (lit.<sup>31</sup> b.p. 54–55° (0.02 mm.)). An n.m.r. spectrum had bands at 4.4 (area 1.95), 6.6 (area 1.95), 7.58 (area 3.0), and 8.2–8.3  $\tau$  (area 2.7). Analysis of the vinyl proton region indicated that 3% of the  $\alpha,\beta$ -unsaturated isomer was present.

**Preparation of 1-Methylmercapto-1-dodecene.**—A 300-ml. autoclave was charged with 66.4 g. (0.40 mole) of 1-dodecyne (Farchan Research Labs), 14.4 g. (0.30 mole) of methyl mercaptan (Matheson Co.), and 1.0 g. of azobisisobutyronitrile. The autoclave was pressured to 500 p.s.i. with nitrogen and was heated at 65° for 4 hr. It was then cooled and vented overnight, after which the products were distilled through a 24 in., 8 mm.

diameter spinning band column to yield 41.2 g. (64%) of 1-methylmercapto-1-dodecene, b.p. 84° (0.15 mm.). An n.m.r. spectrum had bands at 4.0–4.9 (area 1.9, vinyl protons), 7.8 (methylmercapto protons), and 7.8–8.1  $\tau$  (alkyl protons) (combined area 5.15), and 8.7 and 9.1  $\tau$  (area 16.0, alkyl chain protons). A g.c. curve indicated that both *cis* and *trans* isomers were present.

*Anal.* Calcd. for  $C_{13}H_{26}S$ : C, 72.8; H, 12.21; S, 14.9. Found: C, 72.6; H, 12.4; S, 14.7.

**Preparation of 1-Methylmercapto-1-hexene.**—A 300-ml. autoclave was charged with 24.6 g. (0.30 mole) of 1-hexyne (Farchan Research Labs), 12.0 g. (0.25 mole) of methyl mercaptan, and 0.6 g. of azobisisobutyronitrile. The autoclave was pressured to 500 p.s.i. with nitrogen, was heated at 65° for 4 hr., and was then cooled and vented overnight. The reaction mixture was distilled to yield 19.1 g. (59%) of 1-methylmercapto-1-hexene, b.p. 75° (25 mm.). An n.m.r. spectrum had bands at 3.9–4.9 (area 1.96), 7.8 and 7.8–8.0 (area 5.27), and 8.5–8.8 and 9.0  $\tau$  (area 7.0).

*Anal.* Calcd. for  $C_7H_{14}S$ : C, 64.5; H, 10.83; S, 24.6. Found: C, 62.3; H, 10.8; S, 24.3.

**Preparation of 1-Methylsulfinyl-1-dodecene.**—A solution of 15 g. (0.065 mole) of 1-methylmercapto-1-dodecene in 100 ml. of ethanol was treated with 8.0 ml. (0.071 mole) of hydrogen peroxide (30% solution in water) at room temperature and the mixture was stirred for 4 hr. A few milligrams of platinum black was then added to destroy any unreacted peroxide and the mixture was allowed to stand overnight. The platinum black was filtered off and the ethanol was evaporated. The residue was distilled to yield 1-methylsulfinyl-1-dodecene, b.p. 132° (0.15 mm.). An n.m.r. spectrum had bands at 3.5–3.9 (area 1.70, vinyl protons), 7.5 (area 3.1, methylsulfinyl protons), 7.6–8.0 (alkyl protons), and 8.7 and 9.1  $\tau$  (area 19.0, alkyl chain protons). Analysis of this material by oxidative cleavage of the double bond indicated that 99% was  $\alpha,\beta$ -unsaturated.

*Anal.* Calcd. for  $C_{13}H_{26}OS$ : C, 67.7; H, 11.37; S, 13.9. Found: C, 67.6; H, 11.6; S, 13.6.

**Preparation of 1-Methylsulfinyl-1-hexene.**—A solution of 9.6 g. (0.074 mole) of 1-methylmercapto-1-hexene in 100 ml. of ethanol was treated with 7.7 ml. of 30% hydrogen peroxide at room temperature. The product was worked up as described above. Distillation yielded 7.0 g. (65%) 1-methylsulfinyl-1-hexene, b.p. 65° (0.2 mm.). An n.m.r. spectrum had bands at 3.6–4.0 (area 1.9, vinyl protons), 7.5 (methylsulfinyl protons) and 7.6–7.9  $\tau$  (alkyl protons) (combined area 5.3), and 8.4–8.8 and 8.9–9.1  $\tau$  (area 7.0, alkyl chain protons).

*Anal.* Calcd. for  $C_7H_{14}OS$ : C, 57.5; H, 9.65; S, 21.9. Found: C, 57.4; H, 10.2; S, 21.9.

**Preparation of 1-Methylsulfonyl-1-hexene.**—To 70 ml. of Clorox (5.25% NaOCl solution) at room temperature was added 2.6 g. (0.02 mole) of 1-methylmercapto-1-hexene. The reaction mixture was stirred for 3 hr., after which the product was extracted with ethyl acetate. The extracts were dried and the solvent was evaporated. Distillation of the residue yielded 2.5 g. (78%) of 1-methylsulfonyl-1-hexene, b.p. 96° (0.1 mm.). An n.m.r. spectrum had bands at 3.0–3.8 (area 1.85, vinyl protons), 7.15 (area 3.1, methylsulfonyl protons), 7.2–8.0 (area 1.95, allyl protons), and 8.4–8.7 and 8.9–9.1  $\tau$  (area 7.0, alkyl chain protons).

*Anal.* Calcd. for  $C_7H_{14}O_2S$ : C, 51.8; H, 8.70; S, 19.7. Found: C, 51.2; H, 9.0; S, 19.3.

**Preparation of Allyl Methyl Sulfoxide.**—To a solution of 44 g. (0.50 mole) of allyl methyl sulfide (Wateree Chemical Co.) in 200 ml. of ethanol was added 57 ml. (0.55 mole) of hydrogen peroxide (30%) and the reaction mixture was stirred for 6 hr. at room temperature. Platinum black was added to destroy any unreacted peroxide. The solvent was evaporated and the liquid residue was distilled to yield 40.8 g. (79%) of allyl methyl sulfoxide, b.p. 48–50° (0.25 mm.) (lit.<sup>32</sup> b.p. 50–60° (0.05 mm.)). An n.m.r. spectrum had bands at 4.0–4.9 (area 2.9, vinyl protons), 6.5–6.7 (area 1.83, doubly activated methylene protons), and 7.5  $\tau$  (area 3.0, methylsulfinyl protons).

**Preparation of Allyl Methyl Sulfone.**—Ten grams (0.096 mole) of allyl methyl sulfoxide was added to excess Clorox, the mixture was stirred for 1 hr. at room temperature and the product was then extracted three times with ethyl acetate. The extracts were dried, the solvent was evaporated, and the residue was distilled to yield 3.6 g. (34%) of allyl methyl sulfone, b.p. 60° (0.1 mm.) (lit.<sup>32</sup> b.p. 80–90° (0.05 mm.), m.p. 87–88°). Our sample was a liquid.

(30) J. E. Kilpatrick, E. J. Prosen, K. S. Pitzer, and F. D. Rossini, *J. Res. Natl. Bur. Std.*, **36**, 559 (1946).

(31) L. Bateman, J. I. Cunneen, and J. Ford, *J. Chem. Soc.*, 3056 (1956).

(32) P. Karrer, N. J. Antia, and R. Schwyzer, *Helv. Chim. Acta*, **34**, 1392 (1951).

Infrared and n.m.r. spectra were, however, consistent with the assigned structure.

**Preparation of Propenyl Methyl Sulfoxide.**—A mixture of 2.0 g. of sodium hydride (53.4% in mineral oil) in 50 ml. of dimethyl sulfoxide was heated at 60° until hydrogen evolution ceased. Then, 18 g. of allyl methyl sulfide was added to the solution and the solution was stirred for 30 min. The reaction mixture was poured into ice-water and the organic layer was separated and dried to yield 12.6 g. of propenyl methyl sulfide. An infrared spectrum of this material had a characteristic *trans* double bond absorption at 10.7  $\mu$ ; the absorption bands at 10.1 and 11.0  $\mu$ , which are present in allyl methyl sulfide, had completely disappeared. The propenyl methyl sulfide was then oxidized with hydrogen peroxide by the procedure described above to yield 10.2 g. (57%) of propenyl methyl sulfoxide, b.p. 49° (0.25 mm.). An n.m.r. spectrum had bands at 3.5–3.9 (area 2.0, vinyl protons), 7.5 (area 3.2, methylsulfinyl protons), and 8.0–8.1  $\tau$  (area 2.9, allylic methyl protons). No evidence for the presence of allyl methyl sulfide could be found in the n.m.r. spectrum.

*Anal.* Calcd. for  $C_4H_8OS$ : C, 46.1; H, 7.75; S, 30.7. Found: C, 45.4; H, 8.25; S, 29.3.

**Preparation of Propenyl Methyl Sulfone.**—Four grams (0.038 mole) of propenyl methyl sulfoxide was added to 65 ml. of Clorox. The mixture was stirred for 4 hr. at room temperature and then the reaction mixture was extracted eight times with ethyl ether. The ether extracts were dried, the ether was evaporated and the residue was distilled to yield 2.0 g. (43%) of propenyl methyl sulfone, b.p. 90° (0.3 mm.). An n.m.r. spectrum had bands at 3.0–3.8 (area 2.25, vinyl protons), 7.1 (area 3.0, methylsulfonyl protons), and 7.8–8.1  $\tau$  (area 3.0, allylic methyl protons).

*Anal.* Calcd. for  $C_4H_8O_2S$ : C, 40.0; H, 6.71; S, 26.6. Found: C, 39.6; H, 6.9; S, 25.9.

**Equilibration of 1-Methylmercapto-1-dodecene.**—A solution 2.0 g. (0.016 mole) of potassium *t*-butoxide in 40 ml. of dimethyl sulfoxide was prepared and to it was added 2.0 g. of 1-methyl mercapto-1-dodecene. Aliquots were taken at 30 min., 1 hr., 1.5 hr., and 2 hr. and were poured into 15 ml. of water containing 2 ml. of HCl. The products were taken up in hexane, dried, and the hexane was evaporated; g.c. analysis (DEGS) indicated that the ratios of unsaturated sulfides were constant in all four samples. There were three peaks, which corresponded to 27% *cis*- $\alpha,\beta$ -, 39% *trans*- $\alpha,\beta$ -, and 34%  $\beta,\gamma$ - (probably *trans*). There was also a lower boiling material present, which increased with increasing reaction time. It had a strong absorption in the infrared at 10.1  $\mu$ , characteristic of dienes. This material is believed to be a mixture of isomeric dienes, but it was not investigated further.

A 30-min. run as described above, followed by distillation to remove dienes, resulted in an 82% recovery of sulfides. Analysis of the distillate by g.c. (DEGS) indicated the composition to be 25% *cis*- $\alpha,\beta$ -, 41% *trans*- $\alpha,\beta$ -, and 34%  $\beta,\gamma$ -. Analysis of the same material by oxidative cleavage of the double bond indicated 65%  $\alpha,\beta$ -unsaturated, 34%  $\beta,\gamma$ -unsaturated, and 1% other unsaturated isomers.

**Equilibration of 1-Methylmercapto-2-dodecene.**—A solution of 1.0 g. of potassium *t*-butoxide in 10 ml. of dimethyl sulfoxide was prepared and to it was added 0.5 g. of 1-methylmercapto-2-dodecene. The reaction mixture was stirred for 30 min. and was then poured into water. The product was extracted twice with hexane, the extracts were dried, and the hexane was evaporated to yield 0.42 g. of recovered material; g.c. analysis (silicone) indicated 16% of the recovered material was a diene and 84% was a mixture of unsaturated sulfides; g.c. analysis (DEGS) indicated the presence of 27% *cis*- $\alpha,\beta$ -, 40% *trans*- $\alpha,\beta$ -, and 33%  $\beta,\gamma$ -unsaturated isomer.

An attempt was also made to establish equilibrium using potassium *t*-butoxide in *t*-butyl alcohol. However, after 24 hr. at room temperature, the starting material was recovered unchanged.

**Equilibration of 1-Methylmercapto-1-hexene.**—A solution of 1.0 g. of potassium *t*-butoxide in 20 ml. of dimethyl sulfoxide was prepared. One gram of 1-methylmercapto-1-hexene was added to the solution and the reaction mixture was stirred at room temperature for 35 min. The reaction mixture was poured into dilute HCl, the solution was extracted twice with hexane, and the extracts were dried. The solvent was evaporated to yield 0.6 g. of recovered material. By g.c. analysis (DEGS), the mixture was determined to consist of about 29% *cis*- $\alpha,\beta$ -, 38% *trans*  $\alpha,\beta$ -, and 33%  $\beta,\gamma$ -unsaturated sulfides. The accuracy of this analysis was rather poor, because the *cis*- $\alpha,\beta$ - and the  $\beta,\gamma$ -isomer peaks overlap.

**Equilibration of 1-Methylsulfinyl-1-dodecene.**—To a solution of 0.0125 mole of potassium *t*-butoxide in 200 ml. of *t*-butyl alcohol (from 0.5 g. of potassium and the alcohol) was added 10.0 g. (0.0435 mole) of 1-methylsulfinyl-1-dodecene. The reaction mixture was stirred for 5 hr. at room temperature and was then poured into 300 ml. of water. The sulfoxide was extracted with ethyl acetate, the extracts were dried, and the solvent was evaporated. Distillation of the residue yielded 8.5 g. of unsaturated sulfoxide, b.p. 131–137° (0.1 mm.). Analysis of the vinyl proton region of the n.m.r. spectrum indicated the material consisted of 4% of  $\alpha,\beta$ -unsaturated isomer and 96% of  $\beta,\gamma$ -unsaturated isomer. Analysis by oxidative cleavage of the double bond indicated 4%  $\alpha,\beta$ -unsaturated isomer, 93%  $\beta,\gamma$ -unsaturated isomer, and 3% of more internal unsaturated isomers, mostly  $\gamma,\delta$ -unsaturated isomer.

**Equilibration of 1-Methylsulfinyl-1-hexene.**—To a solution of 0.0038 mole of potassium *t*-butoxide in 15 ml. of *t*-butyl alcohol was added 1.0 g. (0.0069 mole) of 1-methylsulfinyl-1-hexene. The mixture was stirred for 4 hr. and was then poured into water. The product was extracted three times with ethyl acetate, was dried over 4A molecular sieve, and the solvent was evaporated to yield 0.6 g. of recovered material. Analysis of the vinyl proton region of the n.m.r. spectrum indicated that 4% of  $\alpha,\beta$ -unsaturated sulfoxide and 96% of  $\beta,\gamma$ -unsaturated sulfoxide were present.

**Equilibration of Allyl Methyl Sulfoxide.**—To a solution of 0.0038 mole of potassium *t*-butoxide in 50 ml. of *t*-butyl alcohol was added 10.4 g. (0.10 mole) of allyl methyl sulfoxide. The reaction mixture was stirred for 1 hr. at room temperature and then 10 ml. of water was added. The solution was made acidic and the *t*-butyl alcohol and water were evaporated. The residue was distilled to yield 6.3 g. of unsaturated sulfoxides. Analysis by n.m.r. indicated that the product consisted of 20%  $\beta,\gamma$ -unsaturated isomer and 80%  $\alpha,\beta$ -unsaturated isomer.

**Equilibration of Propenyl Methyl Sulfoxide.**—To a solution of 0.013 mole of potassium *t*-butoxide in 50 ml. of *t*-butyl alcohol was added 4.5 g. of propenyl methyl sulfoxide. The reactants were stirred at room temperature for 1 hr., 5 ml. of water was then added, and the solvents were evaporated. Distillation yielded 2.0 g. (45%) of recovered unsaturated sulfoxides. Analysis of the vinyl proton region of the n.m.r. spectrum indicated that the mixture consisted of 83%  $\alpha,\beta$ -unsaturated sulfoxide and 17%  $\beta,\gamma$ -unsaturated sulfoxide. On the basis of the results in this experiment and the one described above, it appears that the equilibrium mixture of allyl and propenyl sulfoxides contains about 17–20%  $\beta,\gamma$ -unsaturated isomer. Since the recovery of material was rather poor, the values obtained in these two experiments may be inaccurate.

**Equilibration of Allyl Methyl Sulfone.**—To 5 ml. of triethylamine was added 0.3 g. of allyl methyl sulfone. The reaction mixture was heated at reflux for 18 hr., after which the triethylamine was stripped off to leave a dark residue; g.c. (AAEG) indicated that 88% of the material was unsaturated sulfones. The percentages of these materials were 3% *cis*- $\alpha,\beta$ -, 53% *trans*- $\alpha,\beta$ -, and 44%  $\beta,\gamma$ -. An n.m.r. spectrum of the vinyl proton region indicated 57%  $\alpha,\beta$ - and 43%  $\beta,\gamma$ -unsaturated sulfones.

**Equilibration of Propenyl Methyl Sulfone.**—A mixture of 5 ml. of triethylamine and 0.3 g. of propenyl methyl sulfone was heated at reflux for 18 hr., after which the triethylamine was stripped off to leave a dark residue weighing 0.26 g. Analysis of this material by g.c. (AAEG) indicated that 96% consisted of a mixture of allyl and propenyl sulfones. The percentages of the three isomers were 2% *cis*- $\alpha,\beta$ -, 54% *trans*- $\alpha,\beta$ -, and 44%  $\beta,\gamma$ -unsaturated sulfone. An n.m.r. spectrum indicated 67%  $\alpha,\beta$ - and 33%  $\beta,\gamma$ -unsaturated sulfones, a substantial discrepancy. Since the g.c. results were in agreement with those obtained by equilibration of allyl methyl sulfone, they were chosen for use in the table.

**The Reaction of 1-Methylsulfinyl-2-undecene with Potassium *t*-Butoxide in *t*-Butyl Alcohol-O-d.**—To a solution of 1.0 g. (0.0083, mole) of potassium *t*-butoxide in 9 ml. of *t*-butyl alcohol-O-d was added 1.0 g. of 1-methylsulfinyl-2-undecene (containing 4% 1-methylsulfinyl-1-undecene). The mixture was stirred at room temperature for 24 hr., then poured into 100 ml. of water containing 10 ml. of concentrated HCl. The sulfoxide was extracted with hexane, the extracts were dried, and the hexane was evaporated to yield 0.8 g. of recovered material. An n.m.r. spectrum of the recovered material had a band at 4.4  $\tau$  (area 1.15) which had greatly reduced coupling. The bands at 6.6 and 7.5  $\tau$  had been reduced to one-fifth their original area. The allylic proton band at 7.8–8.0  $\tau$  (area 1.9) and the bands for the protons

in the alkyl chain were unchanged. These spectral features indicated that deuteration had occurred at both the  $\alpha$ - and  $\gamma$ -carbons as well as in the methylsulfinyl group. A control reaction was run under identical conditions using *t*-butyl alcohol as solvent. The sulfoxide recovered from this reaction was essentially identical with starting material (n.m.r. and infrared spectra).

**Analysis of Equilibrium Mixtures of the Unsaturated Sulfides and Sulfoxides by Oxidative Cleavage.**—The procedure of Kuemmel<sup>26</sup> was employed using 2–3 times the prescribed amount of

potassium permanganate. The accuracy of the method was verified with samples of pure  $\alpha,\beta$ -unsaturated sulfides and sulfoxides.

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## The Hydrogen Carrier Technique for the Pyrolysis of Toluene

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The only products formed from the pyrolysis of toluene at 750° with a hydrogen or deuterium carrier gas are methane and benzene. The apparent activation energy for toluene consumption is 46.1 kcal./mole (log *A* = 7.87). It is concluded that the effect of the carrier gas is to replace the ordinary nonchain toluene pyrolysis mechanism by a chain reaction with hydrogen atoms as the chain carrier. The isotopic compositions of the products formed when toluene-*d*<sub>8</sub>, ring-deuterated toluene, and methyl-deuterated toluene are pyrolyzed with deuterium or hydrogen as the carrier gas suggest that the difference between C–H and C–D bonds is as important as the difference between ring and side-chain C–H bonds in determining the site of methyl and phenyl radical reactions. Both methyl and phenyl radicals abstract hydrogen preferentially from the toluene ring rather than from the side chain.

### Introduction

It was reported earlier<sup>1</sup> that the pyrolysis products of toluene at 750° are reduced to simply methane and benzene if a hydrogen carrier gas is used. It was proposed that at these temperatures, hydrogen could function as a scavenger for benzyl, methyl, and phenyl radicals. Studies were carried out with deuterated toluenes and deuterium as well as hydrogen carrier. These studies have now been extended to the use of ring-deuterated toluene, with both hydrogen and deuterium carriers. The studies reported earlier have been repeated at a higher degree of toluene conversion in order to measure the effect of this variable on the distribution of deuterium in the pyrolysis products.

In agreement with other literature on this hydrogenolysis,<sup>2</sup> we now believe that the hydrogenolysis proceeds *via* a chain mechanism,<sup>2a</sup> with hydrogen atoms as chain carriers. Our measurement of the over-all apparent activation energy, 46.1 kcal./mole, is in agreement with such a mechanism and with previous measurements of this quantity, 45<sup>2b</sup> and 43<sup>2a</sup> kcal./mole. The isotope data reported in this paper will therefore be discussed in terms of such a mechanism.

### Experimental

**Apparatus.**—The equipment train used is similar to that described earlier<sup>1</sup> but more elaborate. It is shown diagrammatically in Fig. 1.

Temperatures were measured with a thermocouple in a well inserted down the middle of the quartz reactor and read with a potentiometer; the temperature of the furnace was controlled by another thermocouple placed between the quartz reactor and the inner wall of the tube furnace and connected to a temperature controller. This is a more precise way of measuring

and controlling temperature than that used earlier<sup>1</sup> where the thermocouple in the reactor well was attached to the controller, and the temperature was read off of the controller. Inasmuch as the results obtained at an indicated temperature of 750° in the earlier set-up look like the results obtained at about 700° with the present set-up (runs 9 and 19, Table II), we conclude that the indicated temperature in our earlier report<sup>1</sup> was about 50° too high.

**Materials.**—Toluene-*d*<sub>2</sub> and toluene-*d*<sub>4</sub> were from Merck and Co., Canada; the toluene-*d*<sub>3</sub> contained 7.4% toluene-*d*<sub>2</sub> and the toluene-*d*<sub>4</sub> contained 6.1% toluene-*d*<sub>7</sub>. The toluene-*d*<sub>8</sub> was prepared in this laboratory from benzene-*d*<sub>6</sub>. The product was purified gas chromatographically and contained 5.7% toluene-*d*<sub>4</sub> by low voltage mass spectrometry. The mass pattern of the toluene-*d*<sub>8</sub> has points of interest and has been discussed recently.<sup>3</sup>

**Procedures and Analyses.**—The conditions of operation were kept closely similar for all of the runs described here. Weights of toluene (or deuterated toluenes) were very close to 250 mg. (2.6 mmoles). The flow rates of carrier gas ranged from 70–110 ml./min. (except runs 17 and 18 where they were about 150 ml./min.). The gas mixture was introduced at atmospheric pressure into the flow system. The differences in flow rate affected only the contact times and percentage conversions, but did not affect the rates. The total volumes of gas passed were in the range of 2900–3300 ml. It was found that gas flow was considerably slower while the frit was wet with toluene than after the toluene had been evaporated. Duration of a run was measured from the appearance of methane to the disappearance of methane in the effluent gas (15–25 min.). Toluene concentrations in the reaction zone were calculated from the total volume of toluene vapor and the total volume of gas passed, and averaged 6–8% for most runs. Total conversions of toluene were 5–8% for runs at 750°, 2% for the low temperature run (20), and 15% for the high temperature run (21). The recovery of toluene was usually in excess of 90% of the amount charged.

Methane yield was measured by sampling the effluent gas stream approximately every minute with the gas chromatograph. The methane content of the stream thus measured was expressed as  $\mu$ l. of methane per 5-cc. sample, and these numbers were plotted as a function of time (with the injection of toluene into the frit as the zero time). The area under the curve was integrated gravimetrically to calculate the total yield of methane. The chromatograph was calibrated with a 1% blend of methane in hydrogen.

Isotopic composition of the methane was measured by recovering the methane collected in the charcoal trap and analyzing it in a CEC 103 mass spectrometer. The methane was recovered

(1) R. A. Meyer and J. G. Burr, *J. Am. Chem. Soc.*, **85**, 478 (1963).

(2) (a) H. Matsui, A. Amano, and H. Tokuhisa, *Bull. Japan. Petrol. Inst.*, **1**, 67 (1959); (b) R. I. Silsby and E. W. Sawyer, *J. Appl. Chem.*, **6**, 347 (1956); (c) H. Morii, A. Hashimoto, and H. Tominga, *Proc. World Petrol. Congress*, 6th Congress, Section IV, paper 24, June, 1963; British Patent 7,121,440. We regret the neglect of these papers in our earlier communication.<sup>1</sup> (d) Abstracts, 1963 American Chemical Society Summer Symposium on Unimolecular Reactions in the Mass Spectrometer, J. G. Burr and R. A. Meyer, *J. Chem. Phys.*, **40**, 2046 (1964).