Proton nmr (solvent $CDCl_3$) gave a triplet at τ 5.1 for the alcohol CH_2 ($J = 7.7$ cps), a singlet at τ 5.5 (diol CH_2), a singlet at τ 7.90 (acetate CH_3).

Registry No.—IV, 13168-64-4; VII, 13168-65-5; IX, 13168-66-6; X, 13168-67-7; 2,2,2-difluoronitroethanol, 3766-88-9; isopropyl hemiacetal of difluoronitroacetaldehyde, 13168-73-5; methyl difluoronitroacetaldehyde, hemiacetal, 13168-74-6; difluoronitroacetaldehyde diacetate, 13168-75-7; trioxymethylene bis(difluoronitroethyl) ether, 13168-76-8; 1,1,3,3-tetracarboxypropane, 4721-45-3; 2,2-[bis(β,β,β-difluoronitroethyl) carboxylate]propanediol, 13168-77-9.

Acknowledgments.—This work was performed under contract with the U. S. Atomic Energy Commission; technical direction was provided by the Lawrence Radiation Laboratory (LRL). The authors especially appreciate the helpful discussions and suggestions of Dr. E. R. Bissell, LRL, Livermore, Calif.

The Relative Abilities of Methoxy and Methylthio Substituents to Stabilize Double Bonds[1a]

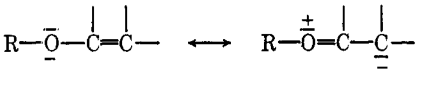
JACK HINE,[1b] LOUIS G. MAHONE, AND CHARLES L. LIOTTA

School of Chemistry, Georgia Institute of Technology, Atlanta, Georgia

Received March 3, 1967

Although the equilibrium between methyl 1-propynyl ether and methyl 2-propynyl ether could not be established, the latter was found to isomerize almost quantitatively to methyl propadienyl ether in the presence of catalytic amounts of strong base. The various 1-methoxy-3-methylthiopropenes and 3-methoxy-1-methylthiopropenes were synthesized; their equilibrium mixture was found to contain about 65% *trans*-1-methoxy-3-methylthiopropene, 32% *cis*-1-methoxy-3-methylthiopropene, 2% *trans*-3-methoxy-1-methylthiopropene, and 1% *cis*-3-methoxy-1-methylthiopropene. The synthesis of 1-methoxy-4-methylthio-2-butene was achieved, but on treatment with base the compound appeared to lose methanol to give 1-methylthio-1,3-butadiene. The equilibrium mixture of the methyl 4-methylthiobutenoates was found to contain about 42% of the *trans*-4-methylthiocrotonate, 34% *trans*-4-methylthio-3-butenoate, and 24% *cis*-4-methylthio-3-butenoate. Methyl *trans*-4-methoxycrotonate isomerized almost quantitatively to *cis*-4-methoxy-3-butenoate, but the equilibrium between this product and its *trans* isomer was not established. It is concluded that methoxy substituents stabilize double bonds better than methylthio substituents do.

It has been pointed out previously, in the case of the formation of a fluoro olefin, that the presence of a highly electronegative atom on an unsaturated carbon atom should tend to destabilize the unsaturated compound, relative to similar saturated compounds.[2,3] Thus, the high electronegativity of oxygen should tend to destabilize vinyl and ethynyl ethers. No equilibrium data seem to be available for ethynyl ethers, but several investigations in which allyl ethers have been isomerized almost quantitatively to vinyl ethers[4-9] show that alkoxy substituents stabilize double bonds better than hydrogen or alkyl substituents do. This fact may be rationalized by the hypothesis that stabilization of the double bond by resonance (1) overwhelms the destabilizing electronegativity



$$R-\underline{\bar{O}}-\overset{|}{C}=\overset{|}{C}- \longleftrightarrow R-\overset{\pm}{\bar{O}}=\overset{|}{C}-\underset{\bar{}}{\overset{|}{\underline{C}}}- \quad (1)$$

effect. We have attempted to determine the effect of alkoxy substituents on triple bonds since the electronegativity effect should be larger (sp carbon is more electronegative than sp^2 carbon) and resonance stabilization would be expected to be smaller.[10-12] We have also attempted to compare the ability of alkylthio substituents to stabilize double bonds with that of alkoxy substituents. This was done in the belief that the resonance effect of an alkylthio group attached to unsaturated carbon is significant, but less than that of alkoxy.[13,14] We hoped to learn more about the relative importance of resonance and electronegativity effects, since the former should cause alkoxy groups to stabilize double bonds, relative to alkylthio groups, and the latter should cause alkoxy groups to destabilize double bonds, relative to alkylthio groups. Several reports of the isomerization of allyl sulfides to vinyl sulfides show that alkylthio substituents stabilize double bonds better than hydrogen or alkyl substituents do.[15-20] However, in most of the studies made with both the ethers and the sulfides, the equilibrium lies so far to the side of the vinyl compound that no reliable equilibrium constant could be obtained. For this and other reasons, there did not seem to be good evidence available as to whether an alkoxy or an alkylthio substituent stabilizes a double bond better.

---

(1) (a) This investigation was supported in part by Grant GP-2002 from the National Science Foundation; (b) to whom all correspondence should be addressed at the Evans Laboratory of Chemistry, The Ohio State University, Columbus, Ohio 43210.

(2) J. Hine and P. B. Langford, *J. Am. Chem. Soc.*, **78**, 5002 (1956).

(3) *Cf.* R. W. Taft, Jr., and M. M. Kreevoy, *ibid.*, **79**, 4011 (1957).

(4) A. J. Birch, *J. Chem. Soc.*, 1642 (1947).

(5) R. Paul, G. Roy, M. Fluchaire, and G. Collardeau, *Bull. Soc. Chim. France*, 121 (1950).

(6) R. Paul, M. Fluchaire, and G. Collardeau, *ibid.*, 668 (1950).

(7) W. H. Watanabe and L. E. Conlon, *J. Am. Chem. Soc.*, **79**, 2828 (1957).

(8) T. J. Prosser, *ibid.*, **83**, 1701 (1961).

(9) C. C. Price and W. H. Snyder, *ibid.*, **83**, 1773 (1961).

(10) There is evidence that carbon–carbon triple bonds interact less with conjugated carbonyl groups, for example, than do carbon–carbon double bonds.[11,12]

(11) R. W. Taft, Jr., and D. J. Smith, *ibid.*, **76**, 305 (1954).

(12) J. Hine and W. C. Bailey, Jr., *ibid.*, **81**, 2075 (1959).

(13) Note, for example, the much larger difference between Hammett's *meta* and *para* substituent constants for methoxy compared with methylthio substituents.[14]

(14) J. Hine, "Physical Organic Chemistry," 2nd ed, McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 87.

(15) D. S. Tarbell and M. A. McCall, *J. Am. Chem. Soc.*, **74**, 48 (1952).

(16) D. S. Tarbell and W. E. Lovett, *ibid.*, **78**, 2259 (1956).

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

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

(19) D. E. O'Connor and C. D. Broaddus, *ibid.*, **86**, 2267 (1964).

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

Results

Attempted Equilibration of Methyl Propynyl Ethers.—Treatment of methyl 2-propynyl ether with sodium methoxide in dimethyl sulfoxide at 90° yielded a colorless liquid, bp 50.8–52.2°. The elemental analysis agrees with the empirical formula C_4H_6O and the volatility of the material shows that this must also be its molecular formula. The reaction is thus an isomerization and in view of the many known examples of base-catalyzed conversions of acetylenes to isomeric allenes and isomeric acetylenes, including isomerizations of 2-propynyl sulfides to propadienyl sulfides,[21,22] it seemed probable that our reaction product was either methyl propadienyl ether or methyl 1-propynyl ether. The latter possibility was ruled out by comparison with a known sample (and in many other ways). The methyl propadienyl ether structure is strongly supported by the nmr spectrum, which consists of a three-proton singlet at τ 6.61 in the region to be expected for a methoxy group, a one-proton triplet at 3.23, and a two-proton doublet at 4.54 (J = 6.0 cps for each). The triplet occurs at a slightly lower field than those (τ 3.6–4.0) found in the present work and elsewhere[23] for hydrogen attached to the same olefinic carbon atom as a methoxy group. The doublet occurs at a slightly lower field than that (τ 5.3) at which allene absorbs.[23] The coupling constant is in the range (6–7 cps) usually found for allenes.[24]

In the sodium methoxide catalyzed formation of methyl propadienyl ether, no methyl 1-propynyl ether was detected as a by-product. In the presence of 0.05 M dimsylsodium (sodium salt of dimethyl sulfoxide) at room temperature, the formation of methyl propadienyl ether from methyl 2-propynyl ether was shown by nmr measurements to be about half complete in 10 hr. With 0.11 M dimsylsodium, the reaction was more than 99% complete in 3 days, but even after 1 week no methyl 1-propynyl ether was detected.

In view of the possibility that methyl propadienyl ether is the most stable of the three possible isomers, an attempt was made to approach the equilibrium from the other direction. Methyl 1-propynyl ether, prepared by a method like that used by Brandsma and Arens for ethyl 1-propynyl ether,[25] was treated with base, first under milder conditions and finally with 0.11 M dimsylsodium in dimethyl sulfoxide at 100° for 85 min. The stronger conditions brought about the decomposition of about half the starting material, but in no case was the formation of any methyl propadienyl ether detected. Nooi and Arens have similarly observed that treatment of alkyl 1-propynyl ethers with powdered potassium hydroxide at 150° results in the formation of no more than trace amounts of alkyl propadienyl ethers.[26]

Thus we may conclude that methyl propadienyl ether is more stable than methyl 2-propynyl ether by at least 2.7 kcal/mole, but we did not succeed in mobilizing the equilibrium between methyl propadienyl ether and methyl 1-propynyl ether and therefore learned nothing

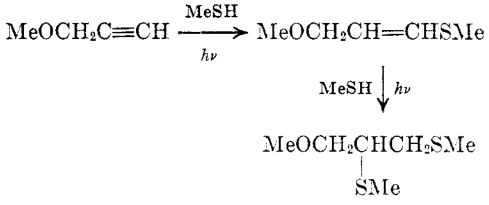
$$\mathrm{MeOCH_2C{\equiv}CH} \rightleftharpoons \mathrm{MeOCH{=}C{=}CH_2} \not\rightleftharpoons \mathrm{MeOC{\equiv}CCH_3} \quad (2)$$

about the stability of the latter compound (eq 2). It would have been desirable to attempt the isomerization of methyl propadienyl ether at higher temperatures.

Arens and co-workers have shown that 1-propynyl ethers may be isomerized using a more strongly basic catalyst, sodium amide in liquid ammonia.[27] Under these conditions, n-butyl 1-propynyl ether is transformed, with the intermediate formation of n-butyl propadienyl ether, no doubt, to n-butyl 2-propynyl ether, present as its sodium salt. The formation of the salt of the 2-propynyl ether makes it clear that this salt is the most stable species under the given conditions, but it gives no new information as to the relative stabilities of the three ethers.

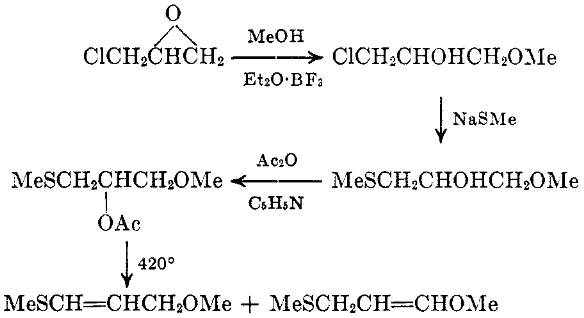
Preparation and Equilibration of the Methoxymethylthiopropenes.—An attempt to prepare 3-methoxy-1-methylthiopropene by the acid-catalyzed decomposition of the dimethyl mercaptal of 3-methoxypropionaldehyde was not successful. The photoaddition of methyl mercaptan to methyl 2-propynyl ether was found to give small amounts of 3-methoxy-1-methylthiopropene, but even at small extents of conversion larger amounts of 1,2-bis(methylthio)-3-methoxypropane appeared to be formed (Scheme I). A better method of synthesis started with epichlorohydrin and followed the course outlined in Scheme II. The first

Scheme I



$$\mathrm{MeOCH_2C{\equiv}CH} \xrightarrow[h\nu]{\mathrm{MeSH}} \mathrm{MeOCH_2CH{=}CHSMe} \xrightarrow[h\nu]{\mathrm{MeSH}} \mathrm{MeOCH_2\underset{\displaystyle SMe}{\underset{|}{C}}HCH_2SMe}$$

Scheme II



step in the sequence is analogous to a known procedure.[28] One could imagine that the second step would proceed *via* an epoxide to give 3-methoxy-2-methylthio-1-propanol rather than the product shown. However, the nmr spectrum shows that this alternative product was not formed. The nmr spectrum of the product contains singlets at τ 6.67 and 7.89, in the ranges (6.0–6.7 and 7.2–7.9, respectively) where methoxy and methylthio hydrogen atoms usually absorb,[29a] and dou-

---

[21] G. Pourcelot, P. Cadiot, and A. Willemart, *Compt. Rend.*, **252**, 1630 (1961).

[22] G. Pourcelot, M. Le Quan, M. P. Simonnin, and P. Cadiot, *Bull. Soc. Chim. France*, 1278 (1962).

[23] N. S. Bhacca, L. F. Johnson, and J. N. Shoolery, "NMR Spectra Catalog," Varian Associates, Palo Alto, Calif., 1962.

[24] S. Sternhell, *Rev. Pure Appl. Chem.*, **14**, 15 (1964).

[25] L. Brandsma and J. F. Arens, *Rec. Trav. Chim.*, **79**, 1275 (1960).

[26] J. R. Nooi and J. F. Arens, *ibid.*, **78**, 284 (1959).

[27] J. J. van Daalen, A. Krauk, and J. F. Arens, *ibid.*, **80**, 810 (1961).

[28] H. Flores-Gallardo and C. D. Pollard, *J. Org. Chem.*, **12**, 831 (1947).

[29] J. R. Dyer, "Applications of Absorption Spectroscopy of Organic Compounds," Prentice-Hall, Inc., Englewood Cliffs, N. J., 1965: (a) pp 84–85; (b) p 99.

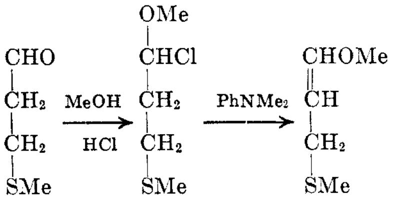
blets at τ 6.85 and 7.43. The latter doublet occurs at too high a field to correspond to the hydrogen atoms of a hydroxylated aliphatic methylene group. The observed chemical shifts, coupling constants, and integrated intensities are in agreement with the 1-methoxy-3-methylthio-2-propanol structure.

The last step of the sequence, an acetate pyrolysis, yielded a product that showed two peaks on gas-liquid partition chromatography but could not be separated cleanly on a spinning-band column. Elemental analysis of fractions rich in each of the two glpc peaks agreed with the molecular formula $C_5H_{10}OS$, corresponding to the loss of the elements of acetic acid from the reactant. Determination of the nmr spectra of samples containing about 95% of the peak with the longer retention time showed that there were singlets of equal intensity at τ 7.78 and 6.76, a doublet (J = 6.0 cps) of doublets (J = 1.0 cps) with about two-thirds the intensity at τ 6.12, and two doublets (J = 15.0 cps for each) of triplets (with J values of 6.0 and 1.0 cps) at 4.61 and 3.72, respectively. From the splitting patterns and relative intensities, it follows that the peaks at τ 7.78, 6.76, and 6.12 are due to methylthio, methoxy, and methylene hydrogen atoms, respectively. These methylene hydrogen atoms must be those of an allyl ether derivative rather than an allyl sulfide derivative, inasmuch as their chemical shift is so much nearer that of diallyl ether (6.03)[23] than that of diallyl sulfide (6.92).[23] The hydrogen atom absorbing at τ 4.61 must be attached to the same carbon atom that the methylene group is or it would not be so strongly (J = 6.0 cps) coupled with the methylene hydrogens. The chemical shift of this hydrogen occurs at too low a field to be plausible for the β hydrogen of an alkenyl ether—the β-hydrogen atom attached to unsaturated carbon in dihydropyran absorbs at τ 5.35;[23] its chemical shift is quite plausible for the β-hydrogen atom of an alkenyl sulfide—the β-hydrogen atoms of the methyl propenyl sulfides absorb at τ 4.46 and 4.60.[30] Therefore it seems clear that the coupound is a 3-methoxy-1-methylthiopropene and the large coupling constant between the two hydrogen atoms attached to unsaturated carbon (15 cps) shows that it must be the *trans* isomer.[29b] This structural assignment is supported by the observation of absorption in the infrared at 940 cm^{-1}, near the frequency range (965–990 cm^{-1}) characteristic of *trans* olefins.[31a,32]

The nmr spectrum of fractions rich in the material with the shorter retention time had strong singlets at τ 6.76 and 7.77, corresponding to methoxy and methylthio groups, a doublet (J = 6.0 cps) of doublets (J = 1.3 cps) at τ 6.07, corresponding to the methylene group, and two doublets (J = 9.8 cps for each) of doublets (with J values of 6.0 and 1.3 cps) at τ 4.43 and 3.95, corresponding to the hydrogen atoms attached to unsaturated carbon β and α, respectively, to the methylthio group. From these assignments, analogous to those described in the preceeding paragraph, and the coupling constant (9.8 cps) between the two hydrogen atoms attached to unsaturated carbon, this compound must be *cis*-3-methoxy-1-methylthiopropene. As in the case of the *trans* isomer, the integrated intensities are consistent with the structure assigned. The presence of an infrared absorption maximum at 670 cm^{-1} in a range usually characteristic of *cis* olefins[31b] and near the frequency (661 cm^{-1}) reported for *cis*-1-propenyl *n*-hexyl sulfide[17] supports the assignment of the *cis* structure to this compound.

Although the product from the acetate pyrolysis showed only two peaks on each of several glpc columns, the nmr spectra taken indicate that the more rapidly eluted peak, largely due to *cis*-3-methoxy-1-methylthiopropene, also contained about 1% *cis*-1-methoxy-3-methylthiopropene, and the more slowly eluted isomer contained about 1% *trans*-1-methoxy-3-methylthiopropene in addition to the principal constituent *trans*-3-methoxy-1-methylthiopropene. These observations may suggest that the pyrolysis of the acetate yielded the vinyl sulfide in preference to the vinyl ether. However, the yield obtained (about 25%) leaves open the possibility that the vinyl ether was formed in yields as high or higher than that of the vinyl sulfide but that its greater reactivity caused most of it to be destroyed subsequently.

Attempts to synthesize 1-methoxy-3-methylthiopropene by the decomposition of 3-methylthiopropionaldehyde dimethyl acetal,[33] in the presence of *p*-toluenesulfonic acid and in its absence, gave low yields of material whose nmr spectra indicated the presence of the desired product, but which could not be obtained in a pure form by fractional distillation. However, the dehydrochlorination of 1-chloro-1-methoxy-3-methylthiopropane, a procedure based on that of Warner and Lands,[34] gave a mixture of the *cis* and *trans* forms of the desired product in 29% yield (based on 3-methylthiopropionaldehyde) (eq 3). Just as in the case of the



$$\begin{array}{c} \mathrm{CHO} \\ | \\ \mathrm{CH_2} \\ | \\ \mathrm{CH_2} \\ | \\ \mathrm{SMe} \end{array} \xrightarrow[\mathrm{HCl}]{\mathrm{MeOH}} \begin{array}{c} \mathrm{OMe} \\ | \\ \mathrm{CHCl} \\ | \\ \mathrm{CH_2} \\ | \\ \mathrm{CH_2} \\ | \\ \mathrm{SMe} \end{array} \xrightarrow{\mathrm{PhNMe_2}} \begin{array}{c} \mathrm{CHOMe} \\ \| \\ \mathrm{CH} \\ | \\ \mathrm{CH_2} \\ | \\ \mathrm{SMe} \end{array} \qquad (3)$$

3-methoxy-1-methylthiopropenes, the *cis* and *trans* isomers could not be separated cleanly by distillation through a spinning-band column. A sample containing about 91% of the isomer with the longer retention time, separated by fractional distillation, and one containing about 89% of the isomer with the shorter retention time, separated by preparative glpc, were each found to have an elemental analysis in agreement with the molecular formula $C_5H_{10}OS$ and their nmr spectra were determined. The nmr spectral data and assignments made are summarized in Table I, with those pertaining to some of the other compounds studied in this investigation. Most of the arguments for the assignments are analogous to those already stated in connection with *trans*-3-methoxy-1-methylthiopropene. In addition, it may be noted that the hydrogen atoms in methoxy and methylthio groups attached to sp^2 carbon have chemical shifts that are at lower fields by 0.26–0.32 ppm than the chemical shifts for the corresponding

---

(30) F. Bohlmann, C. Arndt, and J. Starnick, *Tetrahedron Letters*, 1605 (1963).

(31) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1958: (a) Section 3.4(a); (b) Section 3.4(b); (c) Section 3.2(c).

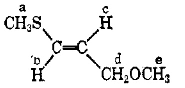
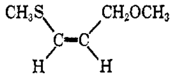
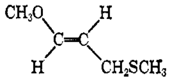
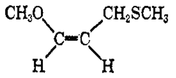
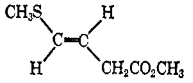
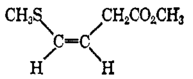
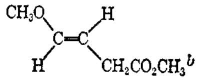
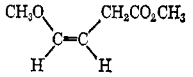
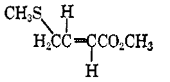
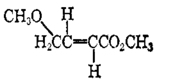
(32) The corresponding absorption in *trans*-1-propenyl *n*-hexyl sulfide is reported to occur at 934 cm^{-1}.[17]

(33) *Cf.* M. G. Voronokov, *J. Gen. Chem. USSR*, **20**, 2060 (1950).

(34) H. R. Warner and W. E. Lands, *J. Am. Chem. Soc.*, **85**, 60 (1963).

Table I

Nmr Data and Assignments

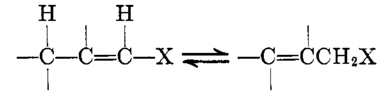
Hydrogen atoms	Chemical shifts, τ					Coupling constants, cps		
	a	b	c	d	e	J_{bc}	J_{bd}	J_{cd}
	7.78	3.72	4.61	6.12	6.76	15.0	1.0	6.0
	7.77	3.95	4.43	6.07	6.76	9.8	1.3	6.0
	6.49	3.64	5.33	7.02	8.04	12.5	~0.8	7.7
	6.44	3.99	5.64	6.93	8.03	6.0	1.0	8.0
	7.84	4.06	4.80	7.06	6.48	14.6	<1.0	6.7
	7.73	3.89	4.36	6.90	6.38	9.5	1.3	6.7
 [b]	6.48[a]	3.67	5.28	7.13	6.36[a]	13	1.2	7.2
	6.42[a]	3.98	5.50	6.95	6.40[a]	6.5	1.6	6.9
	7.99	6.76	3.17	4.13	6.31	7.6	1.0	15.4
	6.63	5.93	3.08	4.00	6.29	4.1	2.0	15.6

[a] It is possible that the chemical shifts assigned to the a-type protons and e-type protons should be reversed in this case. [b] This compound was not obtained in a pure form.

hydrogen atoms in the isomers in which the methoxy or methylthio groups are attached to saturated carbon.

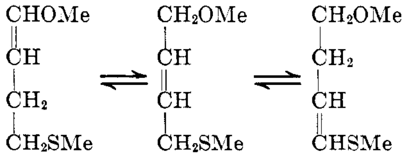
Isomerization of the 3-methoxy-1-methylthiopropenes to the 1-methoxy-3-methylthiopropenes was carried out in dimethyl sulfoxide solution in the presence of potassium *t*-butoxide at 50°. Analysis by nmr showed that the equilibrium mixture contained 32 ± 1% *cis*-1-methoxy-3-methylthiopropene, 65 ± 1% *trans*-1-methoxy-3-methylthiopropene, about 1% *cis*-3-methoxy-1-methylthiopropene, and about 2% *trans*-3-methoxy-1-methylthiopropene. The equilibration of a mixture of *cis*- and *trans*-1-methoxy-3-methylthiopropenes with a *cis–trans* ratio of 1:5.0 and another one with a *cis–trans* ratio of 1:0.67 led to equilibrium mixtures with *cis–trans* ratios of 1:2.07 and 1:2.08, respectively. Apparently the ratio of isomers obtained starting with 3-methoxy-1-methylthiopropenes is the equilibrium mixture and *trans*-1-methoxy-3-methylthiopropene is more stable than the *cis* isomer by 0.47 kcal/mole. The fact that each of these equilibrium mixtures also appeared to contain about 1% *cis*-3-methoxy-1-methylthiopropene and about 2% *trans*-3-methoxy-1-methylthiopropene supports the view that these amounts of the compounds named are indeed present at equilibrium.

Preparation and Attempted Isomerization of 1-Methoxy-4-methylthio-2-butene.—Equilibria of the type shown in eq 4 measure not just the ability of X



$$-\overset{\text{H}}{\underset{|}{\text{C}}}-\overset{\text{H}}{\text{C}}=\text{C}-\text{X} \rightleftharpoons -\text{C}=\underset{|}{\overset{|}{\text{C}}}\text{CH}_2\text{X} \quad (4)$$

to stabilize the double bond but the difference between the abilities of X and CH_2X to stabilize double bonds (plus other such differences depending on the other substituents present). In order to minimize any complications owing to the tendency of the methoxymethyl substituent to destabilize double bonds,[3] we thought it desirable to attempt to equilibrate the 1-methoxy-4-methylthio-1-butenes with the 1-methoxy-4-methylthio-3-butenes *via* the 1-methoxy-4-methylthio-2-butenes (eq 5). In the vinyl sulfide the methoxy group is

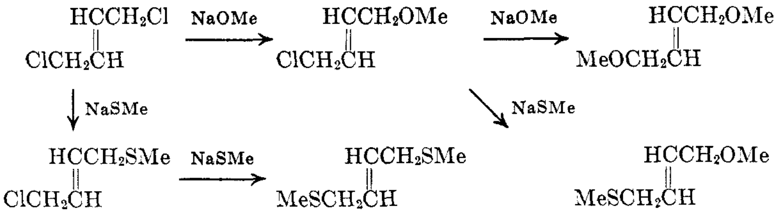


$$\begin{array}{c}\text{CHOMe}\\ \|\\ \text{CH}\\ |\\ \text{CH}_2\\ |\\ \text{CH}_2\text{SMe}\end{array} \rightleftharpoons \begin{array}{c}\text{CH}_2\text{OMe}\\ |\\ \text{CH}\\ \|\\ \text{CH}\\ |\\ \text{CH}_2\text{SMe}\end{array} \rightleftharpoons \begin{array}{c}\text{CH}_2\text{OMe}\\ |\\ \text{CH}_2\\ |\\ \text{CH}\\ \|\\ \text{CHSMe}\end{array} \quad (5)$$

fairly distant from the double bond and in the vinyl ether the methylthio group is rather distant from the double bond.

The reaction of *trans*-1,4-dichloro-2-butene with an equimolar quantity of sodium methoxide gave a mixture of *trans*-1,4-dimethoxy-2-butene, *trans*-1-chloro-4-methoxy-2-butene, and unreacted starting material that we could not separate by fractional distillation. How-

SCHEME III

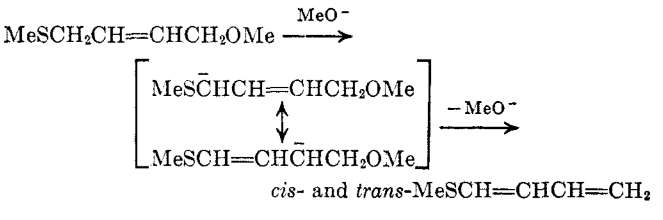


ever, the reaction of this mixture with the sodium salt of methyl mercaptan gave a product that showed three peaks on glpc, corresponding to *trans*-1,4-dimethoxy-2-butene, *trans*-1-methoxy-4-methylthio-2-butene, and, presumably, *trans*-1,4-bis(methylthio)-2-butene which could be separated by fractional distillation (Scheme III).

In an attempt to bring about isomerization, a dimethyl sulfoxide solution was made 0.20 M in sodium methoxide and 0.10 M in *trans*-1-methoxy-4-methylthio-2-butene. Analysis by glpc showed that the starting material (retention time 14.3 min) disappeared, a product with a retention time of 13.7 min appeared and then decreased in concentration, and two products with much shorter retention times (4.6 and 4.7 min) were formed. Distillation of the reaction mixture yielded a mixture of these two more volatile products at 61–65° (48 mm). This boiling point, which is not only about 40° lower than that of the starting material but also considerably lower than that of the methoxymethylthiopropenes, suggests that a smaller molecule has been produced. The material absorbed strongly in the infrared at 1600 cm^{-1}, a frequency characteristic of conjugated dienes.[30c] Its nmr showed singlets of unequal size at τ 7.90 and 7.92 and complex absorption around 5.4 and 6.4. The former are probably due to methylthio groups and the latter to hydrogen on unsaturated carbon.

It thus appears that the base cleaved methanol from the 1-methoxy-4-methylthio-2-butene. Arens, *et al.*, have found that an analogous reaction occurs when 1-alkoxy-2-butynes are treated with sodium amide.[35] It seems probable that the principal reason why methanol was split out rather than methyl mercaptan is the fact that α-methylthio substituents stabilize carbanions much better than α-methoxy substituents do. For this reason, reaction by the mechanism given in Scheme IV is facilitated.

SCHEME IV



Preparation and Equilibration of Methyl 4-Substituted Butenoates.—Methyl 4-bromocrotonate[36] was methanolized to methyl *trans*-4-methoxycrotonate by the procedure of Sultanbawa and Veeravagu[37] and transformed to methyl *trans*-4-methylthiocrotonate by the procedure of Birkofer and Hartwig.[38] The *trans* stereochemistry of these crotonates is confirmed by their nmr spectra in Table I.

Heating methyl *trans*-4-methylthiocrotonate with triethylamine yielded a product mixture that was separated by preparative glpc into the starting material and two more rapidly eluted compounds, whose elemental analyses showed that they were isomers of the starting material. From an interpretation of the nmr spectra of these compounds that is analogous to that described for the 3-methoxy-1-methylthiopropenes, the more rapidly eluted isomer was assigned the structure of methyl *cis*-4-methylthio-3-butenoate, the more slowly eluted isomer that of methyl *trans*-4-methylthio-3-butenoate. The nmr assignments are given in Table I. Various reaction mixtures showed weak nmr bands that may have been due to methyl *cis*-4-methylthiocrotonate, but this compound was not isolated or reliably identified. The nmr singlets owing to the methylthio groups of methyl *trans*-4-methylthiocrotonate and the *cis*- and *trans*-4-methylthio-3-butenoates were separated enough in carbon tetrachloride to permit the analysis of mixtures of the three compounds. In addition, the methoxy singlet of the *trans*-4-methylthiocrotonate was separated from those of the *cis*- and *trans*-4-methylthio-3-butenoates (which overlap strongly) enough to permit an additional method of analysis for this compound. Starting with samples rich in each of the three isomers, essentially identical equilibrium mixtures were obtained. In *t*-butyl alcohol, using triethylamine as a catalyst, this mixture contains 42% methyl *trans*-4-methylthiocrotonate, 34% methyl *trans*-4-methylthio-3-butenoate, and 24% methyl *cis*-4-methylthio-3-butenoate at 35°.

Isomerization of methyl *trans*-4-methoxycrotonate required more strongly basic conditions than did that of the corresponding methylthio compound. Treatment with methanolic sodium methoxide gave a product mixture that showed three new peaks on glpc analysis. The material responsible for the largest of these peaks, the only one with a retention time longer than that of the starting material, was separated by preparative glpc and tentatively assigned the structure of methyl 3,4-dimethoxybutanoate on the basis of nmr spectrum, retention time, and chemical plausibility. A strong nmr singlet at τ 6.60 was attributed to the carbomethoxy group and singlets at τ 6.89 and 6.93 to the other two methoxy groups. Because of the asymmetric β-carbon atom, the other five hydrogen atoms in the ester would all be nonequivalent. For this reason and the fact that some of the absorption appeared to be obscured by the three methoxy peaks, an analysis of

---

[35] L. Brandsma, P. P. Montijn, and J. F. Arens, *Rec. Trav. Chim.*, **82**, 1115 (1963).

[36] H. Schmid and P. Karrer, *Helv. Chim. Acta*, **29**, 573 (1946).

[37] M. U. S. Sultanbawa and P. Veeravagu, *J. Chem. Soc.*, 1262 (1960).

[38] L. Birkofer and I. Hartwig, *Chem. Ber.*, **87**, 1189 (1954).

the spin–spin interactions was not carried out. However there was a one-proton singlet at τ 7.72 and a one-proton apparent doublet at τ 7.83, both in the region where absorption by the two α-hydrogen atoms would be expected. Also present was a one-proton apparent doublet at τ 6.81, about where absorption from the γ-hydrogen atoms would be expected, and complex absorption in the region τ 6.3–6.7, about where absorption from the β-hydrogen atom would be expected.

On the assumption that the equilibrium given in eq 6

$$\mathrm{MeOCH_2CH{=}CHCO_2Me + MeOH \rightleftharpoons MeCH_2CH(OMe)CH_2CO_2Me} \quad (6)$$

had been established, it was reasoned that, if the concentration of methanol were lowered greatly, the complication of the desired isomerization by this equilibrium would be essentially eliminated. Therefore the isomerization of methyl *trans*-4-methoxycrotonate was carried out in *t*-butyl alcohol, which was thought to be so bulky that it would not add readily to an α,β-unsaturated ester. Although a little methanolic sodium methoxide was used to catalyze the isomerization, very little methyl 3,4-dimethoxybutanoate was formed. The principal product was separated by preparative glpc and found to have the proper elemental analysis for an isomer of the starting material. The structure of methyl *cis*-4-methoxy-3-butenoate was assigned to this compound on the basis of an analysis of its nmr spectrum (see Table I) which was analogous to that described for the methoxymethylthiopropenes, except that the signal for the β-hydrogen atom was not a doublet of triplets, but a quartet since its coupling constants with the α- and γ-hydrogen atoms are almost identical. The large glpc peak for the *cis*-4-methoxy-3-butenoate partially overlapped a small peak with a slightly longer retention time. The material responsible for this peak was obtained about 60% pure by preparative glpc and its nmr spectrum determined. From this spectrum (see Table I), it seems very likely that the compound is methyl *trans*-4-methoxy-3-butenoate.

The isomerization of methyl *trans*-4-methoxycrotonate by potassium methoxide in *t*-butyl alcohol solution was most conveniently followed by nmr measurements in carbon disulfide extracts. Starting with essentially pure 4-methoxycrotonate in the presence of 0.2 M potassium methoxide, the half-life for isomerization was about 50 sec at 35°. Between 20 and 60 half-lives, the ratio of the concentration of methyl *cis*-4-methoxy-3-butenoate to that of methyl *trans*-4-methoxycrotonate remained constant within the experimental error at 50:1. During this time, no methyl *trans*-4-methoxy-3-butenoate or methyl *cis*-4-methoxycrotonate was definitely identified in the reaction mixture. Thus, although equilibrium between the *cis*-4-methoxy-3-butenoate and the *trans*-4-methoxycrotonate was probably established, there is no good reason to believe that the equilibria involving the *trans*-4-methoxy-3-butenoate and/or the *cis*-4-methoxycrotonate were established. The equilibrium concentration of *cis*-4-methoxycrotonate should be small, however, Methyl crotonate itself is about 91% *trans* at equilibrium at about 80°.[39]

Discussion

In our systems, methoxy groups were found to stabilize double bonds much more than methylthio groups do. Apparently resonance interactions involving the unshared electron pairs overwhelm any electronegativity effect that may be present. In a study of the isomerization of secondary allyl methyl ethers, Elphimoff-Felkin and Huet have found that equilibria are not always on the side of the vinyl ethers.[40] Apparently other factors (*e.g.*, steric factors) than those that govern the isomerization of primary allyl ethers are important in the case of secondary allyl ethers.

Sodium 4-methoxycrotonate has been reported to be 70% isomerized to sodium 4-methoxy-3-butenoate at equilibrium at 100°[41] in contrast to our observation of about 99% isomerization to the 4-methoxy-3-butenoate in the case of the corresponding methyl esters. Inasmuch as the carboxylate anion group is usually less effective than the carbomethoxy group at stabilizing double bonds,[42] this result was surprising. Our observation that methyl *cis*-4-methoxy-3-butenoate is the kinetically controlled product of the isomerization of methyl *trans*-4-methoxycrotonate is analogous to the reports of other workers.[8,9,43,44] It tells nothing about the relative stabilities of the *cis* and *trans* isomers of the product.

Experimental Section[45]

Methyl Propadienyl Ether.—A mixture of 100 ml of dimethyl sulfoxide and 17 ml of 3 M methanolic sodium methoxide was warmed at reduced pressure to remove most of the methanol. The material was then heated to 90° and 10 ml of methyl 2-propynyl ether was added. After 15 min the system was evacuated through a Dry Ice trap in which product collected. Additional methyl 2-propynyl ether was then added and the process repeated until 40 g (0.57 mole) of the ether had been used. The liquid that had collected in the trap was extracted three times with 10-ml portions of concentrated potassium hydroxide solution to remove methanol and was dried over potassium hydroxide. Distillation under nitrogen through a Todd column yielded 13 g of colorless liquid, bp 50.8–52.2°, $n^{25}\mathrm{D}$ 1.4244. Large amounts of material were lost by evaporation and by polymerization (apparently induced by oxygen). The glpc of this material showed only one peak, using a 2-m diisodecyl phthalate column at 65°. The nmr spectrum of the product showed doublets (J = 6.0 cps) at τ 3.23 and 4.54 and a singlet at 6.61 with relative areas of 1.0, 2.0, and 3.0.

Anal. Calcd for C_4H_6O: C, 68.54; H, 8.63. Found: C, 68.73; H, 8.80.

Methyl 1-Propynyl Ether.—The synthesis of methyl 1-propynyl ether was based on the procedure used by Brandsma and Arens for the synthesis of ethyl 1-propynyl ether.[25] Chloroacetaldehyde dimethyl acetal was treated with excess sodium amide in liquid ammonia to give the sodium salt of methyl ethynyl ether, which was methylated with methyl iodide. When the 600 ml of liquid ammonia used as solvent for the reaction of 0.246 mole of chloroacetaldehyde methyl acetal was allowed to evaporate, the vapors were passed through ether that was kept at −18°. About 1 l. of ether had to be added to make up for losses due to evapora-

---

[39] R. N. Gedye and A. Nechvatal, *J. Chem. Soc.*, 5925 (1964).

[40] I. Elphimoff-Felkin and J. Huet, *Tetrahedron Letters*, 1933 (1966).

[41] L. N. Owen and M. U. S. Sultanbawa, *J. Chem. Soc.*, 3098 (1949).

[42] *Cf.* H. Adkins in "Organic Chemistry," 2nd ed, Vol. I, H. Gilman, Ed., John Wiley and Sons, Inc., New York, N. Y., 1943, pp 1041–1044.

[43] W. O. Haag and H. Pines, *J. Am. Chem. Soc.*, **82**, 387 (1960).

[44] A. Schriesheim, J. E. Hofmann, and C. A. Rowe, Jr., *ibid.*, **83**, 3731 (1961).

[45] All nmr spectra were determined using a Varian A-60 instrument with tetramethylsilane as an internal standard, unless otherwise stated. Analyses were made by Galbraith Laboratories, Inc., Knoxville, Tenn. Boiling points and melting points are uncorrected. The barometer was not read during distillations at atmospheric pressure but the prevailing barometric pressure in Atlanta, Ga., is around 740 mm. Infrared spectra were run using Perkin-Elmer instruments, Model-237B and Model-337.

tion. The ether extract of the residue from the evaporation of ammonia was combined with the ether used to scrub the ammonia vapor and distilled through a 30-cm column packed with glass helices. The fraction boiling at 61–73° weighed 4.1 g and was judged by glpc and nmr measurements to be about 90% pure. Its nmr spectrum showed singlets of equal intensity at τ 4.33 and 8.50. Nooi and Arens reported that methyl 1-propynyl ether boils at 65.7–66.3°.[26] Even poorer yields than the 21% obtained by the procedure described above resulted in earlier runs in which the evaporating ammonia vapor was not scrubbed with ether.

Isomerizations of Methyl Propynyl Ethers.—The use of sodium methoxide in dimethyl sulfoxide (see the section on the preparation of methyl propadienyl ether) was found to be inadequate for the isomerization of methyl 2-propynyl ether past methyl propadienyl ether. Therefore the sodium salt of dimethyl sulfoxide (dimsylsodium) was used. A solution of 0.030 ml of methyl 2-propynyl ether in 1.02 ml of 0.05 *M* dimsylsodium in dimethyl sulfoxide was allowed to stand at room temperature and its nmr spectrum was measured at intervals. After 10 hr, isomerization to methyl propadienyl ether was about half complete and 0.030 ml of 2.3 *M* dimsylsodium in dimethyl sulfoxide was added to speed the reaction. After 3 days the ratio of methyl propadienyl ether to methyl 2-propynyl ether had become greater than 100:1. Even after 1 week, however, no methyl 1-propynyl ether could be detected in the reaction mixture; if its concentration had been as much as 1% that of the methyl propadienyl ether, it would have been detectable.

When 0.030 ml of methyl 1-propynyl ether was dissolved in 1.02 ml of 0.05 *M* dimsylsodium in dimethyl sulfoxide and the solution kept at room temperature for 10 hr and at 100° for 30 min, there was no obvious change in the nmr spectrum. The addition of 0.030 ml of 2.3 *M* dimsylsodium in dimethyl sulfoxide to this reaction solution followed by heating to 100° for 85 min resulted in the destruction of about half the methyl 1-propynyl ether. Very weak broad nmr bands appeared to be formed in several areas but no distinct new bands were found. No evidence for the formation of methyl propadienyl ether could be seen, although as little as 4% should have been detectable.

3-Methoxypropionaldehyde Dimethyl Mercaptal.—A mixture of 30.9 g (0.35 mole) of 3-methoxypropionaldehyde, 38.9 g (0.29 mole) of 3-methoxypropionaldehyde dimethyl acetal, 80 ml (1.41 moles) of methyl mercaptan, and 0.9 ml of 13.5 *M* methanolic hydrogen chloride was kept in Carius tubes at room temperature for 24 hr. The tubes were opened and purged with nitrogen to remove unreacted methyl mercaptan; the contents were made slightly basic with sodium hydroxide. The resultant material was extracted with ether and the ether extract dried over magnesium sulfate and distilled through a 13-cm column packed with glass helices. Between 124.5 and 129° at 42 mm, 42.0 g of product was obtained (40% yield). The nmr spectrum of this material showed triplets at τ 6.17 and 6.51 (J = 7.5 and 6.2 cps, respectively), singlets at 6.72 and 7.95, and a triplet (J = 6.2 cps) of doublets (J = 7.5 cps) at 8.08. The relative areas of these peaks were 1.03, 1.98, 2.98, 5.96, and 2.05, respectively. The glpc of this material showed only one peak, using a 2-m Dow Corning 11 silicone column at 130°.

Anal. Calcd for $C_6H_{14}OS_2$: C, 43.33; H, 8.49; S, 38.56. Found: C, 43.51; H, 8.27; S, 38.67.

Attempts to cleave methyl mercaptan cleanly from 3-methoxypropionaldehyde dimethyl mercaptal by heating with 86% phosphoric acid,[46] vapor phase pyrolysis over glass helices[47] and over alumina, and acid-catalyzed pyrolysis in diphenyl ether solution were unsuccessful. In the latter attempt, a flask was washed with 1 *M* sulfuric acid, dried, charged with 13.8 g of 3-methoxypropionaldehyde dimethyl mercaptal and 20 ml of diphenyl ether, and attached to a 30-cm column packed with glass helices. The solution was kept at 245° for 17 hr and then distilled at reduced pressure until diphenyl ether began to come over. Gas–liquid partition chromatography of the condensate revealed the presence of only one major component, which had a shorter retention time than the reactant. Preparative glpc gave a 0.5-g sample of this component, whose nmr spectrum showed a multiplet at τ 4.4, a doublet (J = 7 cps) at 6.9, and singlets at 7.8 and 8.0, with relative areas of 1.9, 1.9, 3.0, and 3.1. It is possible that this compound is 1,3-bis(methylthio)-propene. No 3-methoxy-1-methylthiopropene was detected.

1-Methoxy-3-methylthio-2-propanol.—A stream of methyl mercaptan was passed into a solution of 50 g (2.17 moles) of sodium metal in 1.0 l. of methanol until the weight increase was 104 g (2.17 moles). After 280 g (2.17 moles) of 1-chloro-3-methoxy-2-propanol (prepared by the method of Flores-Gallardo and Pollard[28]) had been added, the solution was refluxed for 16 hr, concentrated, filtered, and distilled *in vacuo*. The main fraction consisted of 242 g of colorless liquid, bp 100–102° (20 mm) (82% yield). The nmr spectrum of this material consisted of a singlet at τ 6.02, a broad multiplet at about 6.2, a singlet at 6.67 that partially overlaps a doublet ($J \sim 5$ cps) at 6.85, a doublet (J = 6 cps) at 7.43, and a singlet at 7.89, with relative areas of 1.1:0.7:2.8:2.3:1.9:3.0.

Anal. Calcd for $C_5H_{12}O_2S$: C, 44.09; H, 8.88; S, 23.54. Found: C, 44.02; H, 8.96; S, 23.70.

1-Methoxy-3-methylthio-2-propyl Acetate.—To a flask fitted with a drying tube and stirrer were added 47.5 g (0.60 mole) of distilled pyridine, 61.3 g (0.60 mole) of acetic anhydride, and 64.5 g (0.50 mole) of 1-methoxy-3-methylthio-2-propanol. After the mixture had been stirred overnight at 0°, water was added and the mixture extracted with ether. The ether extract was extracted with dilute hydrochloric acid and then with water and dried over Drierite. Finally it was concentrated and distilled through a spinning-band column to give 64.4 g of product, bp 92–93° (3 mm), $n^{27}D$ 1.4587. The glpc of this material showed only one peak, using a 20-ft Carbowax 20 M column at 160°.

Anal. Calcd for $C_7H_{14}O_3S$: C, 47.17; H, 7.92; S, 17.99. Found: C, 46.98; H, 8.04; S, 18.11.

3-Methoxy-1-methylthiopropene.—A solution of 27.2 g (0.158 mole) of 1-methoxy-3-methylthio-2-propyl acetate in 54.3 g of benzene was introduced at a rate of 3 drops/min into a vertical glass tube (2.2 cm × 36 cm), filled with glass helices, and maintained at 420–430°. Movement of the material through the tube was aided by a nitrogen stream flowing at a rate of 120 ml/min. The effluent material (76.9 g) that collected in a series of cold traps was washed with aqueous sodium bicarbonate, then with water, and dried over Drierite. Distillation through a spinning-band column yielded several fractions totalling 4.4 g boiling from 59 to 67° at 16-mm pressure. Analysis of these fractions by glpc on a 0.25 in. × 20 ft Carbowax 20 M column at 160° showed that they all gave rise to only two significant peaks, the same two in all cases. The area under the more rapidly eluted peak decreased steadily from 79% of the total area for the first fraction to 5% of the total area for the last fraction. Analysis on silicone (Dow-Corning 11), phenyldiethanolamine succinate, and Apiezon L columns also showed only two significant peaks. From the nmr spectra of the various fractions, the nmr spectra of the more rapidly eluted material (to which the structure of *cis*-3-methoxy-1-methylthiopropene was assigned) and the more slowly eluted material (*trans*-3-methoxy-1-methylthiopropene) were deduced. These are summarized in Table I. It was analogously deduced that the *cis* compound has infrared maxima (in order of decreasing intensity) at 1110, 2920, 2820, 2890, 1210, 2980, 1440, 950, 1180, 1310, 1430, 1450, 1610, 1380, 750, 910, 1640, 1040, and 670 cm^{-1} and the *trans* compound at 1120, 940, 2920, 1080, 2820, 1060, 1180, 1670, 2890, 1430, 1370, 2980, 800, 1620, and 1720 cm^{-1}.

Anal. Calcd for $C_5H_{10}OS$: C, 50.81; H, 8.53; S, 27.13. Found (for fraction with 77% of the more rapidly eluted material): C, 50.61; H, 8.67; S, 27.09. Found (for fraction with 95% of the more slowly eluted material): C, 50.68; H, 8.58; S, 27.25.

The nmr spectra of these materials showed that about 1% *cis*-1-methoxy-3-methylthiopropene was present in the *cis*-3-methoxy-1-methylthiopropene and about 1% *trans*-1-methoxy-3-methylthiopropene was present in the *trans*-3-methoxy-1-methylthiopropene.

3-Methylthiopropionaldehyde Dimethyl Acetal.—A nitrogen stream was used to carry 26 ml (0.49 mole) of methyl mercaptan into a solution of 12.0 g (0.52 mole) of sodium metal in 220 ml of absolute ethanol. The resulting solution was heated at reflux while 67.0 g (0.48 mole) of 3-chloropropionaldehyde (prepared by the method of Wohl and Momber[48]) was added slowly with stirring. Most of the alcohol was removed on a steam bath and the precipitated sodium chloride removed by filtration. The salt was washed three times with 15-ml portions of 95% ethanol, which were then added to the solution from which the salt had been filtered. The resulting material was then concentrated and distilled through a Todd column, yielding 51.7 g (72%) of colorless liquid, bp 102–103°, $n^{29}D$ 1.4516. The nmr spectrum

---

(46) *Cf.* A. Sporzynski, *Chem. Zentr.*, **107** (II), 1704 (1936).

(47) *Cf.* R. H. Hall and E. S. Stern, *J. Chem. Soc.*, 2657 (1955).

(48) A. Wohl and F. Momber, *Ber.*, **47**, 3346 (1914).

of this material showed singlets at τ 6.73 and 7.96, a triplet at τ 5.55, and multiplets at τ 7.52 and 8.21, with relative areas of 5.90, 3.02, 1.04, 2.02, and 2.02, respectively. The glpc of this material showed only one peak.

Anal. Calcd for $C_6H_{14}O_2S$: C, 47.97; H, 9.39; S, 21.34. Found: C, 47.77; H, 9.19; S, 21.14.

When 39 g of the 3-methylthiopropionaldehyde dimethyl acetal, prepared as described above, was kept at 170° for 80 min, it decomposed with the formation of methanol, which was removed continuously by fractional distillation. The residue from this process was distilled to give 6.36 g of colorless liquid, bp 57° (13 mm). The nmr spectrum of this liquid showed that 1-methoxy-3-methylthiopropene was probably present, but we were not able to isolate this product in reasonable purity by refractionation.

1-Methoxy-3-methylthiopropene.—A solution of 61.7 g (0.59 mole) of 3-methylthiopropionaldehyde (prepared by the method of Heilbron and co-workers[49]) in 100 ml of *n*-hexane was placed in a three-necked flask fitted with gas-addition tube, stirrer, addition funnel, and ice-cooled condenser. The flask was placed in an ice bath and dry hydrogen chloride gas was passed in while 18.9 g (0.59 mole) of dry methanol was added slowly. After the addition of methanol was complete, the addition of hydrogen chloride was continued for 20 min so as to saturate the reaction mixture. The upper layer was then decanted, 80 g (0.66 mole) of N,N-dimethylaniline was added to it, and the mixture was heated to reflux for 1 hr. The dark lower layer that had formed was separated from the hexane layer, combined with a small amount of water, and extracted with ether. The ether extract and hexane layer were combined, concentrated, and distilled through a spinning-band column to give 20.2 g (29% yield) of colorless liquid, bp 59–67° (17 mm). Refractionation of this liquid through the same column at the same pressure yielded seven fractions. Analysis by glpc showed the same two peaks for each fraction. The more rapidly eluted peak comprised 73% of the first fraction and only 9% of the last fraction ($n^{25}\text{D}$ 1.4898), with the intermediate fractions being of intermediate composition. Preparative glpc was used to obtain a sample containing about 90% of the more rapidly eluted compound. The nmr spectra of these two materials were deduced from the nmr spectra of the various fractions obtained. From the results, summarized in Table I, the structures *cis*- and *trans*-1-methoxy-3-methylthiopropene were assigned to the more rapidly and more slowly eluted materials, respectively. It was analogously deduced that the *cis* compound has infrared maxima at 1660, 1110, 1670, 1140, 1270, 1230, 2920, 2930, 1380, 770, and 1050 cm^{-1} and the *trans* compound at 1220, 1660, 1140, 940, 2920, 1670, 1240, 2940, 1440, 2950, 2830, 1420, 1450, 980, and 1470 cm^{-1} (both in the order of decreasing intensity).

Anal. Calcd for $C_5H_{10}OS$: C, 50.81; H, 8.53; S, 27.13. Found (for fraction with 90% of the more rapidly eluted material): C, 50.70; H, 8.41; S, 26.95. Found (for fraction with 91% of the more slowly eluted material): C, 50.78; H, 8.42; S, 26.98.

Equilibration of the Methoxymethylthiopropenes.—A mixture containing about 30% *cis*- and 70% *trans*-3-methoxy-1-methylthiopropene was used to prepare (under nitrogen) a solution in dimethyl sulfoxide that was 0.74 *M* in total olefin and 0.18 *M* in potassium *t*-butoxide. This solution was placed in a thin-walled nmr tube and kept in a 50° constant-temperature bath. Nmr analysis for the four compounds of interest was carried out by measurements on the methoxy singlets of the 1-methoxy-3-methylthiopropenes and the methylthio singlets of the 3-methoxy-1-methylthiopropenes. In dimethyl sulfoxide solution, all four of these peaks are separated from each other. A single analysis after 240 min gave results within the range of a quadruplicate analysis after 530 min, which showed 32 ± 1% *cis*- and 65 ± 1% *trans*-1-methoxy-3-methylthiopropene and about 1% *cis*- and 2% *trans*-3-methoxy-1-methylthiopropene.

In a similar run, a mixture of 60% *cis*- and 40% *trans*-1-methoxy-3-methylthiopropene was used as the starting material. After 45 min, the mixture contained about 37% *cis* and 63% *trans* isomer and, after 300, 480, and 1200 min, it contained 33 ± 2% *cis*- and 64 ± 2% *trans*-1-methoxy-3-methylthiopropene and about 1% *cis*- and 2% *trans*-3-methoxy-1-methylthiopropene. An analogous run starting with 16% *cis*- and 84% *trans*-1-methoxy-3-methylthiopropene gave, after 300, 480, and 1200 min, the same equilibrium mixture that had been obtained starting with the 3-methoxy-1-methylthiopropenes.

***trans*-1-Methoxy-4-methylthio-2-butene.**—Over a period of 30 min, 333 ml of 3.0 *M* methanolic sodium methoxide was added with stirring to 126 g (1.00 mole) of freshly distilled *trans*-1,4-dichloro-2-butene and 100 ml of dry methanol in a three-necked flask fitted with a reflux condenser. The heat of reaction brought the solution to a boil. After standing for 1 hr, the solution was found to be 0.01 *M* in base. A solution of 40 g (1.00 mole) of sodium hydroxide in 200 ml of methanol was then saturated with methyl mercaptan and added to the reaction mixture, which was stirred overnight and filtered. The salt that had been removed by filtration was washed twice with 100-ml portions of methanol which were added to the filtrate. The resulting solution was concentrated and water and hexane were added. The organic layer was washed with water, dried over Drierite, and found to give three peaks in addition to the hexane on glpc analysis. The first peak, with a retention time equal to that of *trans*-1,4-dimethoxy-2-butene, accounted for 38% of the total area; 56% of the area was due to the second peak, attributed to *trans*-1-methoxy-4-methylthio-2-butene; and the third peak, containing 6% of the total area, is presumably due to *trans*-1,4-bis(methylthio)-2-butene. The hexane solution was concentrated and distilled through a Todd column to give a forerun of 20 g, bp 68–75° (48 mm), that was probably largely *trans*-1,4-dimethoxy-2-butene.[50,51] The main fraction consisted of 33 g (25% yield), bp 101.5–103° (48 mm). This material was refractionated on a spinning-band column to give material, bp 91° (30 mm), $n^{25}\text{D}$ 1.4839, which gave only one peak on glpc through a 300-ft capillary column containing Apiezon L. The nmr spectrum of this material consisted of singlets of about equal area at τ 6.70 (methoxy protons) and 8.00 (methylthio protons) and three rather complex multiplets, each about two-thirds as large, at τ 4.33 (vinyl protons), 6.07 (methylene group adjacent to oxygen), and 6.91 (methylene group adjacent to sulfur). The infrared spectrum showed peaks at 1120, 2920, 970, 2820, 1080, 1070, 1190, 2980, 1420, 1430, 1370, and 1440 cm^{-1} (in the order of decreasing intensity).

Anal. Calcd for $C_6H_{12}OS$: C, 54.50; H, 9.15; S, 24.25. Found: C, 54.63; H, 9.07; S, 24.46.

Reaction of *trans*-1-Methoxy-4-methylthio-2-butene with Sodium Methoxide.—A dimethyl sulfoxide solution 0.20 *M* in sodium methoxide and 0.10 *M* in *trans*-1-methoxy-4-methylthio-2-butene was prepared, allowed to stand overnight at about 25°, and then kept at 100° for 1 hr. Samples were withdrawn at various times, diluted with water, and extracted with pentane. The glpc analysis of the pentane extracts using a 2-m diisodecyl phthalate column at 150° showed that the original peak at 14.3 min decreased in intensity, a peak at 13.0 min first increased and then decreased, and peaks at 4.6 and 4.7 min appeared and increased in intensity. The percentage that each of these peaks comprised of the total area at different times is shown in Table II. Distillation of the remainder of the reaction mixture yielded largely a fraction boiling at 61–65° (48 mm). In carbon tetrachloride solution, the nmr spectrum of this material showed two singlets of unequal size, at τ 7.90 and 7.92, and two complex multiplets, around τ 5.4 and 6.4. The infrared spectrum showed a strong peak at 1600 cm^{-1}.

Table II

Glpc Analysis of the Products from NaOMe and *trans*-$MeOCH_2CH{=}CHCH_2SMe$ in Me_2SO

Temp, °C	Time	% of total area 4.6 min	4.7 min	13.0 min	14.3 min
25	0	0	0	0	100
25	1 day	8	7	25	60
100	5 min	19	15	25	42
100	15 min	41	36	8	15
100	60 min	43	48	3	6

***cis*- and *trans*-Methyl 4-Methylthio-3-butenoate.**—A 15-ml sample of methyl 4-methylthiocrotonate[38] was heated with 2.0 ml of triethylamine overnight at 100° and then distilled through a spinning-band column. Several fractions with a total volume

---

[49] J. R. Catch, A. H. Cook, A. R. Graham, and I. Heilbron, *J. Chem. Soc.*, 1609 (1947).

[50] Petrow reported that 1,4-dimethoxy-2-butene boils at 50° (20 mm).[51]

[51] A. A. Petrow, *Zh. Obshch. Khim.*, **19**, 1050 (1949).

of 14 ml were collected between 88 and 99° (12 mm). These fractions were found to contain varying amounts of three compounds, which had retention times of 10.9, 12.7, and 13.8 min on a 10-ft phenyldiethanolamine succinate column at 190°. The 13.8-min peak was shown to be due to the starting material. The materials responsible for the 10.9- and 12.7-min peaks were obtained in purities of 95 and 90%, respectively, by preparative glpc, the impurities being the other isomers. The material responsible for the 10.9-min peak had an nmr spectrum consisting of singlets at τ 7.73 and 6.38, a doublet ($J = 6.7$ cps) of doublets ($J = 1.3$ cps) at 6.90, a doublet ($J = 9.5$ cps) of triplets ($J = 6.7$ cps) at 4.36, and a doublet ($J = 9.5$ cps) of triplets ($J = 1.3$ cps) at 3.89, with relative areas of 2.98:3.01:2.00:0.92:0.94. This compound was taken to be methyl *cis*-4-methylthio-3-butenoate. The material responsible for the 12.7-min peak had an nmr spectrum consisting of singlets at τ 7.84 and 6.48, a doublet ($J = 6.7$ cps) at 7.06, a doublet ($J = 14.6$ cps) of triplets ($J = 6.7$ cps) at 4.80, and a doublet ($J = 14.6$ cps) at 4.06, with relative areas of 3.15:2.96:1.88:0.96:0.97. This compound is assumed to be methyl *trans*-4-methylthio-3-butenoate.

Anal. Calcd for $C_6H_{10}O_2S$: C, 49.28; H, 6.89; S, 21.93. Found (for 95% *cis*): C, 49.10; H, 7.00; S, 21.91. Found (for 90% *trans*): C, 49.16; H, 6.95; S, 21.95.

The Reaction of Methyl 4-Methoxycrotonate with Methanolic Sodium Methoxide.—A mixture of 5 ml of 0.08 *M* sodium methoxide in methanol, 5 ml of methyl 4-methoxycrotonate,[37] and 1 ml of mesitylene was kept at 35° and 0.25-ml samples were withdrawn at intervals. These samples were added to a volume (0.0355 ml) of methanolic hydrogen chloride found, by titration of the first sample to the *p*-nitrophenol end point, to be required to neutralize the base present. Glpc analysis on a phenyldiethanolamine succinate column at 170°, using the mesitylene as an internal standard, showed that the concentration of starting material, with a retention time of 6.0 min, decreased and that new peaks were formed with retention times of 4.9, 5.6, and 7.0 min. By the time the reaction was stopped, the last peak had the largest area and the first peak the second largest area. The materials responsible for these two peaks were separated by preparative glpc. The fraction eluted first was thought to be methyl *cis*-4-methoxy-3-butenoate, on the basis of evidence to be described in the next section. The fraction with the longest retention time had an nmr spectrum with strong singlets of about equal intensity at τ 6.60, 6.89, and 6.93 (neat, with reference to external TMS). There were also apparent doublets ($J \sim 1$ cps) at τ 6.81 and 7.83 and a singlet at 7.72, each with almost one-third the intensity of any one of the strong singlets. Weaker, more complex peaks stretched from about τ 6.3–7.0. The compound was assigned the structure of methyl 3,4-dimethoxybutanoate. Measurements in methanol solution showed that the value of

$$K = \frac{[\mathrm{MeOCH_2CHOMeCH_2CO_2Me}]}{[\mathrm{MeOH}][\mathrm{MeOCH_2CH{=}CHCO_2Me}]}$$

becomes about 0.13 M^{-1} after 5 hr and has not changed after 24 hr. With 1 *M* methanol in *t*-butyl alcohol, *K* was found to be 0.19 M^{-1}.

Methyl *cis*-4-Methoxy-3-butenoate.—A solution of 1.80 g (0.0138 mole) of methyl 4-methoxycrotonate[37] and 0.5 ml of 2 *M* methanolic sodium methoxide in 11 ml of dry *t*-butyl alcohol was kept at 45° for 15 min. After being cooled, it was quenched with aqueous pH 7 buffer to which enough acetic acid had been added to neutralize the sodium methoxide. A chloroform extract of the resulting mixture was washed with water and dried over magnesium sulfate; the chloroform was removed at 30-mm pressure to give 1.3 g of crude product. Glpc analysis of this material showed the same four peaks that had been observed when the reaction was carried out in methanol (preceding section), but the fourth peak, believed to be due to methyl 3,4-dimethoxybutanoate, had only about 0.1 the area of the first peak. The second and third (starting material) peaks were even smaller than the fourth. Distillation of the crude product gave material boiling at 74–76° (15 mm) from which the material responsible for the first glpc peak was obtained pure by preparative glpc ($n^{25}\mathrm{D}$ 1.4348). The nmr spectrum of this material showed singlets at τ 6.40 and 6.42, a doublet ($J = 6.9$ cps) of doublets ($J = 1.6$ cps) at 6.95, a quartet ($J \sim 6.7$ cps) at 5.50, and a doublet ($J = 6.5$ cps) of triplets ($J = 1.6$ cps) at 3.98, with relative areas of 2.98:3.08:1.97:1.03:0.94.

Anal. Calcd for $C_6H_{10}O_3$: C, 55.37; H, 7.75. Found: C, 55.28; H, 7.72.

The second glpc peak was relatively small and it overlapped the much larger first peak. For these reasons we did not obtain a pure sample of it. However, by preparative glpc a small sample containing about 60% of this material, about 40% of the material responsible for the first peak, and a small amount of methyl 4-methoxycrotonate was obtained. From this mixture it was learned that the nmr spectrum of the material responsible for the second peak had singlets at τ 6.48 and 6.36, a doublet ($J = 7.2$ cps) of doublets ($J = 1.2$ cps) at 7.13, and doublets ($J = 13$ cps) of triplets (with *J* values of 7.2 and 1.2 cps) at 5.28 and 3.67, with relative areas of about 2.7:3.4:1.8:1.1:0.9.

Equilibration of the Methyl 4-Methylthiobutenoates.—Glpc methods were considered for the analysis of mixtures of methyl 4-methylthiobutenoates, but on most of the columns tried there was serious overlap of peaks and on a phenyldiethanolamine succinate column the constituents of the mixture appeared to isomerize somewhat as they passed through the column. Nmr spectra of mixtures of the three isomers in carbon tetrachloride or carbon disulfide solution showed that the singlets due to the methylthio groups are separated enough to permit reliable determination of the area under each peak. Areas were measured using a planimeter and by using the integrator on the nmr spectrometer. The latter method gave somewhat more nearly constant values for the composition of the equilibrium mixture. The singlet due to the methoxy group of the 4-methylthiocrotonate is separated sufficiently from those of the *cis*- and *trans*-4-methylthio-3-butenoates (which overlap strongly) so that its area can also be determined reliably.

A typical equilibration solution was prepared by adding 1.00 ml of ester, 5.00 ml of *t*-butyl alcohol, and 0.25 ml of triethylamine to a flask fitted with a rubber serum cap. The flask was placed in a constant-temperature bath at 35.0° and 0.625-ml samples were withdrawn by syringe at various times. Each sample was added to a centrifuge tube (through its serum cap) containing 0.40 ml of carbon disulfide and 6.00 ml of pH 7 buffer to which enough hydrochloric acid had been added to neutralize the triethylamine in the sample. The material was shaken and centrifuged; the lower (organic) layer was transferred to a thin-walled nmr tube. The spectrum was recorded using a sweep rate of 0.4 cps/sec, a sweep width of 100 cps, a filter band-width setting of 4, and a radio frequency field setting of 0.04 mgauss. The efficiency of extraction was determined by reextracting aqueous solutions that had already been extracted once. It was found in this way that the extract was 92.4, 92.6, and 92.7% efficient for the *cis*-4-methylthio-3-butenoate, *trans*-4-methylthio-3-butenoate, and 4-methylthiocrotonate, respectively. Since these three values are within the experimental uncertainty of each other, no correction for relative extraction efficiencies was made. Inasmuch as the equilibrium constants being determined are dimensionless (they depend not on absolute concentrations but on ratios of concentrations), no correction for incomplete extraction need be made.

The results obtained in three different runs, starting with mixtures rich in each of the three different isomers, are shown in Table III. Integrations using the planimeter were done 3 ± 1 times (except for certain points early in the reaction), electrical integrations 15 ± 5 times, and the results averaged. No nmr peaks were observed in the extracts of the reaction mixtures other than those due to the three isomers and *t*-butyl alcohol. No clear trend in concentrations seems to be observable after about 20 hr. From the average of the results of the electrical integrations (believed to be the more reliable method of analysis) of the areas of the methylthio peaks, all of which had been performed on solutions that had been equilibrating for more than 115 hr, the following composition is obtained for the equilibrium mixture: 23.9 ± 0.2% methyl *cis*-4-methylthio-3-butenoate, 33.8 ± 0.2% methyl *trans*-4-methylthio-3-butenoate, 42.3 ± 0.2% methyl *trans*-4-methylthiocrotonate. From the fact that measurements on the methoxy peaks give a value of 41.4 ± 0.2% for the equilibrium content of methyl 4-methylthiocrotonate, it seems clear that the actual experimental uncertainty is considerably larger than might be indicated by the average deviations listed with the equilibrium concentrations in the previous sentence.

Equilibration of the Methyl 4-Methoxybutenoates.—When methyl 4-methoxycrotonate was added to a solution of sodium methoxide in dimethyl sulfoxide, a dark red color was formed almost immediately and later it appeared that there was solid material suspended in the solution. Addition of methyl 4-methoxycrotonate to a solution of potassium *t*-butoxide in *t*-butyl

TABLE III
EQUILIBRATION OF THE METHYL 4-METHYLTHIOBUTENOATES IN *t*-BUTYL ALCOHOL AT 35°

	Mole %				
	3-Butenoate[a]		*trans*-Crotonate[d]		
Time, hr	*cis*	*trans*	Method A[a]	Method B[b]	Method of analysis[c]
		Run 1			
0	3.0	12.7	84.4	87.5	P
2.0	11.3	7.7	81.0		P
20.3	25.4	30.8	43.7	43.2	P
65.4	23.8	30.9	45.3	40.4	P
115.3	27.0	33.3	39.6	38.7	P
	23.7	33.6	42.7		E
137.3	29.0	33.1	37.8	41.7	P
	24.1	33.8	42.0	41.4	E
		Run 2			
0.0	59.3	7.2	33.5		P
16.3	28.9	25.0	46.2	44.7	P
61.0	24.8	33.8	41.3	41.0	P
119.0	23.4	34.6	42.0	39.2	P
	24.0	33.7	42.3		E
133.0	24.3	33.3	42.2	43.4	P
	23.8	34.0	42.1	41.1	E
		Run 3			
0.0	15.0	73.6	11.4	13.3	P
119.3	24.0	33.6	42.4		E
133.0	23.8	33.9	42.2	41.6	E

[a] By nmr measurements of the methylthio peaks. [b] By nmr measurements of the methoxy peaks. [c] P refers to integration by planimeter and E to the electrical integrator on the spectrometer. [d] Registry no., 13168-98-4.

alcohol gave a similar result somewhat more slowly. Several other sets of conditions either yielded similar results or failed to bring about isomerization of the ester. Solutions of potassium methoxide in *t*-butyl alcohol, prepared by adding a small excess of methanol to standard solutions of potassium *t*-butoxide in *t*-butyl alcohol, were found to bring about isomerization with the formation of no precipitate and only a light yellow color.

A *t*-butyl alcohol solution 0.209 *M* in potassium methoxide and 1.02 *M* in methyl 4-methoxycrotonate was kept at 35.0°. At various intervals, 0.625-ml samples were withdrawn and added to a centrifuge tube fitted with a rubber septum and containing 0.40 ml of carbon disulfide, 0.60 ml of pH 7 buffer, and enough hydrochloric acid to neutralize the potassium methoxide. The contents of the tube were shaken and centrifuged and some of the lower layer was added to an nmr tube. The relative areas under the various peaks in the nmr spectra were measured and from these the relative concentrations of the methyl *trans*-4-methoxycrotonate and methyl *cis*-4-methoxy-3-butenoate in the extract were calculated. From blank experiments it had been determined that this ratio of crotonate to 3-butenoate must be multiplied by 1.15 to obtain the ratio present in the equilibration mixture. After 40 sec, the ester was 58% *trans*-4-methoxycrotonate. This figure dropped to 29, 5.2, 2.1, 1.9, and 2.0% after 100, 400, 1000, 3000, and 3020 sec, respectively. In all cases the rest of the material was almost entirely methyl *cis*-4-methoxy-3-butenoate, but near the end of the reaction a little of the *trans*-4-methoxy-3-butenoate seemed to be present. There was no evidence that this was the equilibrium amount, however, and the fact that considerably more *trans*-3-methoxy-3-butenoate had been obtained in isomerization in methanol shows that equilibrium with respect to this compound had almost certainly not been obtained.

Registry No.—*trans*-3-Methoxy-1-methylthiopropene, 13168-91-7; *cis*-3-methoxy-1-methylthiopropene, 13168-92-8; *trans*-1-methoxy-3-methylthiopropene, 13168-93-9; *cis*-1-methoxy-3-methylthiopropene, 13168-94-0; methyl *trans*-4-methylthio-3-butenoate, 13168-95-1; methyl *cis*-4-methylthio-3-butenoate, 13168-96-2; methyl *trans*-4-methoxy-3-butenoate, 13168-97-3; methyl *cis*-4-methoxy-3-butenoate, 13214-13-6; methyl 4-methoxycrotonate, 13168-99-5; methyl propadienyl ether, 13169-00-1; methyl 1-propenyl ether, 13169-01-2; 3-methoxypropionaldehyde dimethyl mercaptal, 13169-02-3; 1,3-bis(methylthio)propene, 13169-03-4; 1-methoxy-3-methylthio-2-propanol, 13296-19-0; 1-methoxy-3-methylthio-2-propyl acetate, 13169-04-5; 3-methylthiopropionaldehyde dimethyl acetal, 13214-29-4; *trans*-1-methoxy-4-methylthio-2-butene, 13169-05-6; methyl 3,4-dimethoxybutanoate, 13169-06-7.

Acknowledgment.—We wish to acknowledge our indebtedness to the National Science Foundation for Grant GP-2002 in support of this investigation and for a grant that permitted the purchase of the nmr spectrometer used.