Infrared[11] and mass[12] spectra were consistent with assigned structures, and with greater than 97% isotopic purity for all compounds.

Proton n.m.r. spectra were determined on a Varian A-60 high-resolution spectrometer on 10 ± 0.5% w./w. solutions in carbon tetrachloride or deuterium oxide (99.77%), except for samples of 1,1,1,3,3,3-hexadeuteriopropanol-2, which were 20% by weight. Chemical shifts were measured from internal tetramethylsilane (carbon tetrachloride solutions) or internal 3-(trimethylsilyl)-1-propanesulfonic acid, sodium salt monohydrate.[13] Probe temperature was 27 ± 1° during determinations (measured by ethylene glycol peak separation). All spectra were recorded under high resolution conditions: low radiofrequency field, broadest filter band width, and slow scan rate. Coupling constants were measured from the peak separations of at least three different spectra recorded at 100 c.p.s. chart width, and are accurate to ±0.1 c.p.s.

Acknowledgment.—We are grateful to the donors of the American Chemical Society Petroleum Research Foundation funds, to the Research Foundation of the State University of New York, and to the Harpur Foundation for making support available for those projects from which these compounds were obtained.

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[11] Determined on a Perkin-Elmer 521 spectrophotometer, in the gas phase, in a 10-cm. cell at room temperature.

[12] Determined on a Consolidated Electrodynamics Corporation 21-130 mass spectrometer by Mr. Stanley Raider, through the courtesy of the Department of Chemistry, State University of New York at Stony Brook. We are grateful to Mr. Raider for these spectra.

[13] Eastman Kodak, White Label.

Isomerization of the Butenyl Methyl Sulfides with Methanethiol

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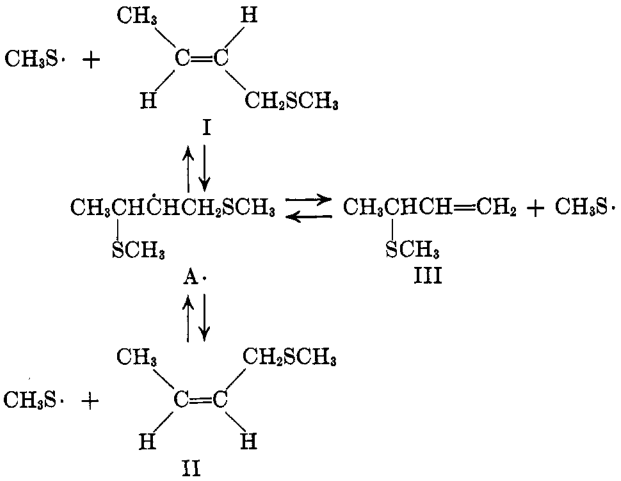
The rapid isomerization of either 1-bromo-2-butene or 3-bromo-1-butene to an equilibrium mixture of the two by hydrogen bromide in the presence of peroxides[2] has been suggested to be caused by the reversible addition of bromine atoms to unsaturated linkages.[3] The reversible addition of thiyl radicals to alkenes[4] suggests that similar isomerizations might occur in the free-radical reactions of the isomeric butenyl methyl sulfides with methanethiol. Addition of a methanethiyl radical ($CH_3S\cdot$) to *trans*-crotyl methyl sulfide (I), *cis*-crotyl methyl sulfide (II), and α-methallyl methyl sulfide (III) yields conformers of a common adduct radical A· from which, on elimination of a methanethiyl radical, a mixture of I, II, and III can result. Gas chromatographic analysis of the unreacted butenyl methyl sulfides resulting from the photoinduced reaction of I and III as well as a mixture of I, II, and III with methanethiol show that such isomerizations do indeed occur (Table I).

TABLE I

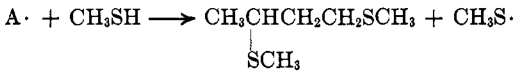
ISOMERIZATION OF BUTENYL METHYL SULFIDES IN PHOTOCHEMICAL REACTIONS WITH METHANETHIOL (23.5 hr. at 35°)

	Amounts, mmole				
	I	II	III	CH_3SH	Ratio of I:II:III
Before	0.01	0.01	0.75[a]	1.55	0.0:0.0:1.0
After	0.25	0.04	0.024	...	1.0:0.16:0.096
Before	0.01	0.01	0.77	1.54	0.0:0.0:1.0
After	0.33	0.047	0.024	...	1.0:0.14:0.088
Before	0.73	0.00	0.00	1.51	1.0:0.0:0.0
After	0.16	0.022	0.013	...	1.0:0.13:0.080
Before	0.79	0.00	0.00	1.51	1.0:0.0:0.0
After	0.13	0.022	0.008	...	1.0:0.17:0.061
Before	0.57	0.070	0.085	1.49	1.0:0.12:0.15
After	0.33	0.059	0.024	...	1.0:0.18:0.073
Before	0.58	0.072	0.089	1.58	1.0:0.12:0.15
After	0.44	0.071	0.031	...	1.0:0.16:0.070

[a] Purity of III was 98.4% with 1.4% contamination of the other isomers.



If the rates of elimination of $CH_3S\cdot$ from A· to yield I, II, and III are considerable faster than the reaction of A· with methanethiol to yield the addition product 1,3-di(methanethio)butane (IV), it is possible that



$$A\cdot + CH_3SH \longrightarrow \underset{\displaystyle SCH_3}{CH_3CH}CH_2CH_2SCH_3 + CH_3S\cdot$$

IV

an equilibrium mixture of the three isomers might be formed before all of the butenyl methyl sulfides have been consumed. The ratio of the three isomers found after 30–70% consumption of the butenyl methyl sulfides in the addition reaction is essentially the same starting with either I or III or with mixtures of the three isomers, suggesting that equilibration is very nearly attained well before the addition reaction is complete. The observed composition of the mixture is consistent with that which would be expected for an equilibrium mixture, namely, the internally unsaturated compounds I and II are more stable than the terminally unsaturated one (III) and the *trans* isomer I is more stable than the *cis* isomer II.[5]

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[1] National Science Foundation Cooperative Fellow, 1963–1965. The work described was taken from the thesis submitted by R. M. K. in partial fulfillment of the requirements for the Ph.D. degree from the University of Kansas.

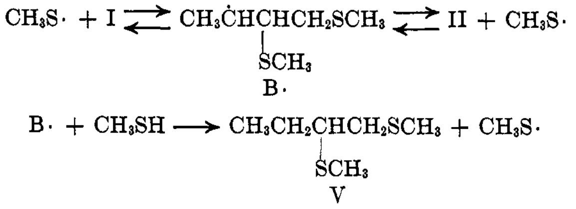
[2] M. S. Kharasch, E. T. Margolis, and F. R. Mayo, *J. Org. Chem.*, **1**, 393 (1936); W. G. Young and K. Nuzak, *J. Am. Chem. Soc.*, **62**, 311 (1940).

[3] C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, p. 305.

[4] C. Walling and W. Helmreich, *J. Am. Chem. Soc.*, **81**, 1144 (1959); R. H. Pallen and C. Sivertz, *Can. J. Chem.*, **35**, 723 (1957).

[5] J. Hine, "Physical Organic Chemistry," 2nd Ed., McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p. 19.

The methanethiyl radical can add to I and II in such a manner that the adduct radical B· is formed. Although the reversible addition to yield B· could result in equilibration of I and II, there could be no positional isomerization of the double bond yielding III involving this radical. Reaction of B· with methanethiol would yield 1,2-di(methanethio)butane (V) as an addition product. Investigation of the addition products produced in the reaction of a mixture of I, II, and III showed that both IV and V were formed



$$CH_3S\cdot + I \rightleftarrows \underset{\mathrm{B}\cdot}{CH_3\dot{C}H\underset{|\atop SCH_3}{C}HCH_2SCH_3} \rightleftarrows II + CH_3S\cdot$$

$$B\cdot + CH_3SH \longrightarrow \underset{\mathrm{V}}{CH_3CH_2\underset{|\atop SCH_3}{C}HCH_2SCH_3} + CH_3S\cdot$$

indicating that both A· and B· were present to react with methanethiol.

Illumination of a mixture consisting predominately of III and a smaller amount of I in the absence of methanethiol resulted in partial isomerization to I and II (Table II). The mechanism of this isomerization is very likely the same as that proposed for the reactions with methanethiol. The isomerization is not as extensive as it is in the reactions with methanethiol possibly because fewer chains are induced by photolysis of the butenyl methyl sulfides in the absence of the thiol.

TABLE II

PHOTOINDUCED ISOMERIZATION OF α-METHALLYL METHYL SULFIDE (III)

	Amounts, mmole			
	I	II	III	Ratio of I:II:III
Before	0.085	0.00	0.674	0.113:0.00:1.00
After	0.328	0.044	0.209	1.00:0.13:0.64

Experimental

α-Methallyl Methyl Sulfide (III).—A mixture consisting of 90% α-methallyl chloride and about 10% of the crotyl chlorides (b.p. 64–65°) was prepared by reaction of crotyl alcohol with thionyl chloride in the manner described previously.[6] Reaction of 14.1 g. (0.156 mole) of this mixture in refluxing methanol with 0.175 mole of sodium methyl sulfide, obtained by reaction of methanethiol with sodium methoxide in methanol, yielded 14.1 g. (0.138 mole, 88.5% of theory) of a mixture of the butenyl methyl sulfides. Fractional distillation of the mixture through a 24-in. spinning-band column yielded 9.80 g. of α-methallyl methyl sulfide (b.p. 103.5–106.5°).

Anal. Calcd. for $C_5H_{10}S$: C, 58.75; H, 9.88; S, 31.37. Found: C, 58.75; H, 9.89; S, 31.60.

The n.m.r. spectra of this material showed a doublet (1.30 p.p.m.) due to the α-methyl protons, a singlet (1.99 p.p.m.) due to the protons of the sulfur-bonded methyl group, a quintet (3.25 p.p.m.) due to the allylic proton, and an absorption in the vinyl-proton region (4.8–5.2 p.p.m.). The infrared spectra showed a strong absorption at 11.0 μ due to the terminal methylene group. Gas chromatographic analysis on a 12 ft. × 0.125 in. column packed with β,β′-oxydipropionitrile on Chromosorb W, a column capable of resolving the isomeric butenyl methyl sulfides, indicated the material to be 98.6% pure. A second fraction collected during the distillation (b.p. 113–124°) amounting to 1.90 g. was a mixture of the *cis-* and *trans-*crotyl methyl sulfides.

***trans*-Crotyl Methyl Sulfide (I).**—A mixture of α-methallyl and crotyl chlorides was prepared by reaction of a mixture of the alcohols with concentrated hydrochloric acid. Successive redistillations of the mixture through a 12-in. helices-packed column gave 90% pure *trans*-crotyl chloride (b.p. 75–80°). Reaction of a portion of this material (27.1 g., 0.29 mole) with sodium methyl sulfide (0.30 mole) in methanol in the manner described above yielded a mixture of the butenyl methyl sulfides. Repeated distillation through a 24-in. spinning-band column yielded a fraction (3.4 g.) which was *trans*-crotyl methyl sulfide (b.p. 118–120°) and showed no trace of the isomeric butenyl methyl sulfides on gas chromatographic analysis.

Anal. Calcd. for $C_5H_{10}S$: C, 58.75; H, 9.88; S, 31.37. Found: C, 58.67; H, 9.91; S, 31.15.

The infrared spectra had an absorption at 10.41 μ due to the *trans*-vinyl hydrogens. The n.m.r. spectra showed the singlet of the CH_3S group (1.95 p.p.m.), the doublet of the CH_2 group (1.70 p.p.m.), the doublet of the CH_3 (2.95 p.p.m.), and a complex absorption centered at 5.42 p.p.m. due to the vinyl protons.

Isomerization of Butenyl Methyl Sulfides with Methanethiol.—Samples of the butenyl methyl sulfides (70–80 mg.) were accurately weighed into glass tubes. The tubes were cooled in a Dry Ice bath and about 75 mg. of methanethiol (Matheson Co.) was introduced, the tubes were tightly stoppered and warmed to room temperature, and the amounts of the methanethiol were determined by reweighing the tubes. After sealing the tubes, they were placed in a constant temperature bath (35°) and illuminated with a 275-w. General Electric sunlamp for 23.5 hr. The tubes were cooled, opened, tightly stoppered, warmed to room temperature, reweighed, and chilled again, and chlorobenzene (17–18 mg.) was added. The exact amount of chlorobenzene added was determined by reweighing the stoppered tubes at room temperature.

Gas chromatographic analyses of the reaction mixtures were performed on a 13.5 ft. × 0.25 in. column packed with β,β′-oxydipropionitrile on Chromosorb W. The peaks appeared in the order: methanethiol, α-methallyl methyl sulfide, *trans*-crotyl methyl sulfide, *cis*-crotyl methyl sulfide, and chlorobenzene. The amounts of the butenyl methyl sulfides were determined from their peak areas (two or three chromatograms made in each case) using the chlorobenzene peak area as an internal standard.

Addition Products of the Butenyl Methyl Sulfides and Methane thiol.—A 2:1 mixture of *trans*-crotyl methyl sulfide and α-methallyl methyl sulfide (2.08 g., 0.020 mole) was sealed in a glass tube with a fourfold excess of methanethiol. The tube was illuminated at 35° for 48 hr. The contents of the tube were poured into aqueous sodium hydroxide and the organic layer, which amounted to about 3 g., was separated and dried over anhydrous magnesium sulfate. The 1:1 addition product mixture was isolated by preparative gas chromatography on a 5 ft. × 0.25 in. column packed with 10% phenyldiethanolamine succinate on Chromosorb W.

Anal. Calcd. for $C_6H_{14}S_2$: C, 47.93; H, 9.41; S, 42.66. Found: C, 47.94; H, 9.36; S, 42.54.

The n.m.r. spectra of the mixture showed a doublet centered at 1.25 p.p.m. which was assigned to the protons on the 4-carbon of IV and a triplet centered at 1.00 p.p.m. which was assigned to the protons on the 4-carbon of V. There were also four singlets (2.00–2.19 p.p.m.) which can be assigned to the methyl protons of the four different methanethiol groups present in a mixture of the two addition products. Gas chromatographic analysis of the mixture on a 5 ft. × 0.125 in. column packed with Carbowax 1540 on Chromosorb W separated it into two peaks with an area ratio of 2:1. The integrated n.m.r. resonance of the doublet at 1.25 p.p.m. was twice that of the triplet at 1.00 p.p.m. indicating that IV was the predominant isomer formed in the reaction.

Photoinduced Isomerization of α-Methallyl Methyl Sulfide (III).—Gas chromatographic analysis of a sample of III that had been refrigerated for several months showed that the content of I had increased from about 1 to 10.5%. Distillation of the mixture showed that a small amount of higher boiling materials had also been formed as evidenced by a residue remaining after removal of the butenyl methyl sulfides. Illumination of 75 mg. (0.75 mmole) of the redistilled mixture of I and III at 38° for 24 hr. with a 275-w. sunlamp yielded a mixture, determined by the gas chromatographic method described above, that consisted of 0.209 mmole of III, 0.328 mmole of I, and 0.044 mmole of II. The remainder was most likely converted to higher boiling products which did not pass through the gas chromatographic column.

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[6] F. F. Caserio, G. E. Dennis, R. H. De Wolfe, and W. G. Young, *J. Am. Chem. Soc.*, **77**, 4182 (1955).