comparison, the *tert*-butyltropenyl radical has hfs of $a_2 = 4.39, a_3 = 2.71$, and $a_4 = 3.88$ at 173°.[4]

The observed mixing could, in theory, be either vibronic or thermal, or both in origin. Although it appears that vibronic coupling is relatively unimportant in the dianion radicals at low temperature, it does not necessarily follow that it is equally ineffectual in the neutral radical cases. If one does assume that mixing is purely a thermal equilibration between A and S states, the electrical perturbation, 2δ,[8] between the states is calculated to be 406 and 551 cal for the cyclopropyl and methyl cases, respectively. These figures would only be lower limits if vibronic coupling is important.

It is interesting that cyclopropyl engenders a smaller perturbation than methyl. It is possible to offer two plausible electronic explanations. First, it is expected that the nearly sp^2 hybridized cyclopropyl group will be less electron donating, inductively, than methyl. That part of the perturbation which is of inductive genesis will thus be smaller for cyclopropyl. Further, cyclopropyl is, to a greater extent than methyl, a conjugating group and, as has been seen, conjugation preferentially stabilizes the S orbital. The net destabilization of the S orbital by cyclopropyl is thus expected to be less than that by methyl.

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Vinyl Radicals. VII. Stereochemistry of the Free Radical Addition of Ethyl Mercaptan to Ethoxyacetylene. A 1-Alkoxyvinyl Radical

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Abstract: Preparative scale free radical additions of ethyl mercaptan to ethoxyacetylene give mixtures of *cis*- and *trans*-1-ethoxy-2-(ethylthio)ethenes (**1**). The stereochemistry of this addition was studied over an initial mercaptan concentration range of 1 *M* to 8×10^{-4} *M*. The lowest conversion sample in each case shows *cis*-**1**/*trans*-**1** > 100. The kinetically controlled addition, therefore, is stereospecific and trans. These results are discussed in terms of an intermediate *cis*-1-ethoxyvinyl radical which is formed stereospecifically and which has appreciable configurational stability.

We previously described the results of extended Hückel molecular orbital calculations of the energies of some plausible geometries of the 1-vinyl vinyl radical.[1] These results, in part, prompted us to propose a linear structure with the half-filled p orbital conjugated with the substituent π system as the preferred structure for the 1-vinyl and the related 1-phenyl vinyl radicals. This geometry provided a convenient rationalization[1] of the unusually stereoselective reactions of the 1,2-diphenyl vinyl radical.[2] Similar calculations[1] predict bent geometries for the vinyl and 1-methyl vinyl radicals; the former result is in agreement with many other calculations.[3] Our calculations also predict planar and pyramidal geometries for methyl[4] and trifluoromethyl[5] radicals, in accord with experiment. As part of the calculations, we compared the energies of bent and linear 1-substituted vinyl radicals as an estimate of the barriers to interconversion of isomeric, bent radicals. The vinyl and 1-methyl vinyl radicals both show[1] a small preference for bent geometries. This result is in accord with esr studies and chemical experiments which indicate that vinyl and 1-alkyl vinyl radicals are bent and that stereoisomeric radicals interconvert rapidly.[6] A more stimulating finding was that bent (120°) 1-hydroxy and 1-fluoro vinyl radicals calculate to be very much more stable than the linear forms (180°). The calculations, therefore, suggested[7] candidates for bent, configurationally stable vinyl radicals. This paper reports a study of the stereochemical capabilities of a 1-alkoxy vinyl radical obtained as an intermediate in the free radical addition of ethyl mercaptan to ethoxyacetylene.

Results

The free radical addition of ethyl mercaptan to 1 equiv of ethoxyacetylene in pentane gives a mixture of *cis*- and *trans*-1-ethoxy-2-(ethylthio)ethene (*cis*- and *trans*-**1**).[8] Each isomer was obtained in a high state of

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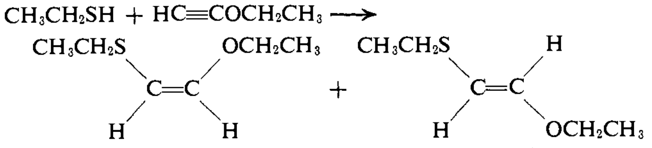
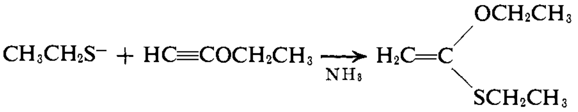

cis-**1** *trans*-**1**

purity (>99%) by preparative gas chromatography (gc) and was shown by reinjection to be configurationally stable to gc conditions for analyzing mixtures of these isomers. The infrared spectrum of each isomer is nearly identical with that previously reported.[8] Alkema and Arens demonstrated the gross 1-ethoxy-2-(ethylthio)ethene (**1**) structure by the hydrolysis of a mixture of cis and trans isomers to (ethylthio)acetaldehyde. The nmr spectra of the isomers are in full accord with the 1-ethoxy-2-(ethylthio)ethene (**1**) structures and the vinylic coupling constants of 5 and 13 Hz establish the stereochemistry as *cis*-**1** and *trans*-**1**, respectively.[9] Samples of 1-ethoxy-2-(ethylthio)ethene (**1**) decompose in air. The crude product mixture also slowly isomerizes toward the equilibrium value if stored at room temperature. However, refrigerated pentane solutions of mixtures of pure *cis*- and *trans*-**1**, obtained by preparative gc, are relatively stable with respect to both decomposition and isomerization. Samples of varying compositions of *cis*- and *trans*-**1** were deliberately equilibrated by small amounts of *o*-methylbenzenethiol in refluxing pentane. The equilibrium constant, *cis*-**1**/*trans*-**1**, is 0.37 at 35°.

Additional comment is in order regarding the infrared spectra of *cis*- and *trans*-**1**. Alkema and Arens[8] observed a doublet for each isomer near 1600 cm^{-1} (C=C). In the spectrum of the cis isomer, the higher frequency band was more intense and in the spectrum of the trans isomer the reverse was true. The less intense member of the doublet in each spectrum was attributed to contamination by the other isomer. We obtained samples of each of these isomers in greater than 99% isomeric purity by preparative gc. The spectra of these isomers correspond quite closely to those reported by Alkema and Arens, including the relative intensity of the doublets near 1600 cm^{-1}. It is, therefore, clear that each isomer has a doublet near 1600 cm^{-1} and that the spectral samples used by Alkema and Arens were actually of rather high isomeric purity. Examination of bands in the fingerprint region of each spectrum supports this conclusion. The spectrum of the trans isomer shows bands at 945 and 855 cm^{-1} which are absent in the spectrum of the cis isomer. The spectrum of *cis*-**1** has a fairly intense band at 1240 cm^{-1} which is negligible in the spectrum of *trans*-**1**.

1-Ethoxy-1-(ethylthio)ethene (**2**) was prepared by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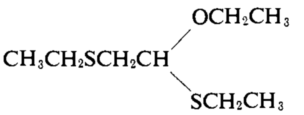
the nucleophilic reaction of excess ethyl mercaptide with ethoxyacetylene in liquid ammonia.[8] Some 1-ethoxy-2-(ethylthio)ethene (**1**) and unreacted mercaptan and ethoxyacetylene were also found in the crude reaction mixture. The relative amount of **1** increased during work-up. The *cis*-**1**/*trans*-**1** isomer ratio initially favored cis but shifted toward the trans rich equilibrium value with time. The formation of the isomeric 1-ethoxy-2-(ethylthio)ethenes (**1**) occurred largely, if not entirely, during work-up and is attributed to the free radical reaction of excess ethyl mercaptan with unreacted ethoxyacetylene. Isomerization of the 1-ethoxy-2-(ethylthio)ethene (**1**) toward the equilibrium value supports this view. In addition, a carbon tetrachloride solution of a pure sample of **2**, after standing for 3 days, showed no nmr resonances attributable to **1**, indicating that **2** does not rearrange to **1**. A pure sample of **2** was obtained by preparative gc. The ir spectrum is also consistent with this structure. Of particular note is the resonance of the two vinyl protons at relatively high field (δ 4.16), characteristic of β protons of vinyl ethers.[10] The hydrolysis of **2** to acetic acid further establishes the structure;[8] **2** is also observed to be unstable in air.

Diadduct, 1-ethoxy-1,2-bis(ethylthio)ethene (**3**), is obtained by treating excess ethyl mercaptan with ethoxyacetylene in pentane and purified by preparative gc. The nmr spectrum shows one methine proton (δ 4.36) as a doublet of doublets due to spin–spin coupling with the nonequivalent protons of the adjacent methylene.[11] The two methylene protons adjacent to oxygen in the ethoxy group are also discernibly nonequivalent and give rise to a broad, complex multiplet centered at δ 3.48, characteristic of the methylene of an ethoxy group attached to an asymmetric carbon.[12] Six methylene protons adjacent to sulfur appear as an undifferentiated grouping centered at δ 2.58 and the three methyls show as a nine-proton multiplet centered at δ 1.21. The product of two successive acid-catalyzed additions, **4**, is easily ruled out by the observed proton counts. The alternative radical diadduct, **5**, is also readily excluded. The methine proton of **5** is expected to be a triplet since the adjacent methylene protons are equivalent. Also, the ratio of methylene protons adjacent to sulfur–methylene protons adjacent to oxygen would be expected to be 4/4 instead of the ratio of 6/2 observed for **3**. The expected free radical adducts,[8] *cis*- and *trans*-**1** and diadduct **3**, are thus established as the products of the "uncatalyzed" addition of ethyl mercaptan to ethoxyacetylene in pentane. The base-catalyzed addition of mercaptan to ethoxyacetylene gives mainly **2** as reported;[8] we also observe a maximum of 20% yield of **1** which we attribute to a free radical reaction during work-up. Even if **1** is really formed in the nucleophilic reaction, this cannot be the source of **1** in the uncatalyzed reaction in pentane since only 0.6% of the total product in pentane is **2**.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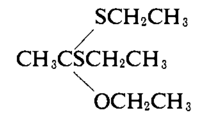
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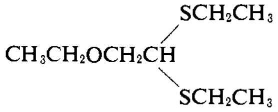
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Table I. Free Radical Addition of Ethyl Mercaptan to Ethoxyacetylene at 0°

Run	Ethyl mercaptan, *M*	Ethoxyacetylene, *M*	% reaction[a]	% *trans*-**1**	% *cis*-**1**	*cis*-**1**/*trans*-**1**
A	1.01	10.77	7.28	0.76	99.24	130.6
			9.66	0.78	99.22	127.2
			13.68	1.03	98.97	95.4
			23.55	1.31	98.69	75.3
			31.97	1.51	98.49	65.2
			36.95	1.57	98.43	62.7
			44.58	1.77	98.23	55.5
			78.01	2.30	97.70	42.5
B	0.2724	0.8628	1.18	0.67	99.33	148.3
			6.29	1.84	98.16	55.3
			46.34	6.22	93.78	15.1
			96.99	12.14	87.86	7.2
C	8.981×10^{-2}	0.9278	0.69	≤0.3[b]	≥99.7	≥332.3
			2.02	0.3	99.7	332.3
			5.11	0.8	99.2	124.0
			10.26	1.1	98.9	89.9
			37.33	2.3	97.7	42.5
			46.77	3.2	96.8	30.3
D	8.37×10^{-3}	0.7118	24.52	0.3	99.7	332.3
			32.91	0.4	99.6	249.0
E[c,d]	8.096×10^{-4}	1.052	3.84	≤0.52	≥99.48	≥191.3
			3.97	≤0.87	≥99.13	≥113.9

[a] Based on ethyl mercaptan. [b] The inequalities indicate that the gc peak due to *trans*-**1** was not observable. The number recorded is based on a conservative estimate of the minimum observable peak areas under the specific gc conditions of the run. [c] At 35°. [d] Unpurified ethyl mercaptan was used.

An acid-catalyzed reaction involving protonation of ethoxyacetylene, followed by nucleophilic attack of ethyl mercaptan, also should give **2**.[8] The 1-ethoxy-2-(ethylthio)ethenes, *cis*- and *trans*-**1**, therefore, are clearly the products of free radical reactions.

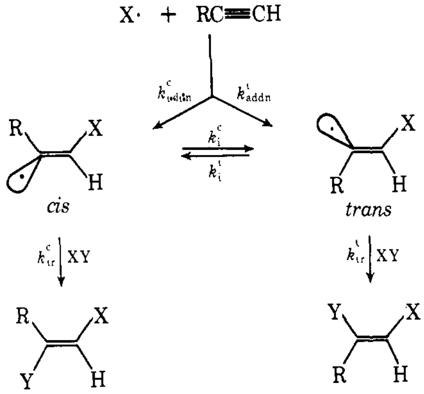
The uncatalyzed free radical addition of ethyl mercaptan to ethoxyacetylene in pentane was examined at various initial mercaptan concentrations. Solutions of the mercaptan and ethoxyacetylene were mixed under nitrogen with efficient stirring. Samples were withdrawn periodically and stored under liquid nitrogen until they were analyzed. The *cis*-**1**/*trans*-**1** ratio was determined by gc. An internal standard was used so that absolute yields could be calculated. Ethoxyacetylene was used in excess in order to depress product isomerization. Reactions were studied in which the initial concentration of ethyl mercaptan was varied from 1.01 *M* to 8.096×10^{-4} *M*. The results of these five experiments are given in Table I. The lowest conversion sample in each run shows *cis*-**1**/*trans*-**1** > 100. This must represent the kinetically controlled ratio since the thermodynamic mixture is established as *cis*-**1**/*trans*-**1** ≅ 0.37. The free radical addition of ethyl mercaptan to ethoxyacetylene, therefore, is stereospecifically trans. The *cis*-**1**/*trans*-**1** ratio decreases gradually with increasing per cent reaction within a run. Since the limiting reagent is the mercaptan, this might be due to changes in mercaptan concentration as the reaction proceeds. That this is not the case is shown by a comparison between runs in which the initial mercaptan concentration varies by about 10^3, without effect on the initial *cis*-**1**/*trans*-**1** ratio. Rather, the effect is assigned to isomerization of the products **1** by thiyl radicals, a process employed independently to establish the equilibrium mixture. As expected, the effect is most pronounced when the relative concentration of product is large, *i.e.*, high conversion and a small acetylene/mercaptan ratio (run B). In the most concentrated reaction solution the ethyl mercaptan concentration was initially 1.01 *M* (run A). This mixture was examined for 1-ethoxy-1,2-(ethylthio)ethene (**3**) after >78% reaction. Compound **3** was found to be present in 1.7% of the amount of *cis*- and *trans*-**1**. The small amount of diadduct formation is consistent with the slow interconversion of *cis*- and *trans*-**1** under the reaction conditions, since both processes require an initial addition of thiyl radical to **1**.

For the reaction described in run D, samples were examined at lower per cent reaction than those shown. No *trans*-**1** was observed, but the area of the peak due to *cis*-**1** was too small to permit a meaningful conclusion. The gc sample injection size could not be significantly increased since tailing of the pentane solvent peak became more severe at the high sensitivities employed and interfered with the analysis of *cis*- and *trans*-**1**. The analysis of the lowest concentration mixture (run E) was accomplished only by using a longer gc column. Further, the free radical addition is very slow at this extreme dilution. In order to increase the reaction rate, unpurified mercaptan was used and the solution refluxed (35°). Run E was further complicated by the appearance of a peak in the gc that was not observed in the experiments employing higher concentrations of reactants (runs A–D). The "new" peak grew in size with increasing reaction time and was much larger than the peak due to *cis*-**1**, but did not interfere with analysis of *cis*- and *trans*-**1**. This new peak is formed by refluxing ethoxyacetylene in pentane without mercaptan and, therefore, appears to be due to a side reaction of ethoxyacetylene that becomes significant only when the formation of *cis*- and *trans*-**1** becomes very slow.

Discussion

The stereochemistry of free radical chain additions to alkynes involving bent vinyl radicals intermediates was analyzed by Chen[13] (Scheme I). Three distinct

Scheme I



A, $k_i^c, k_i^t \gg k_{tr}^c[XY], k_{tr}^t[XY]$
B, $k_i^c, k_i^t \ll k_{tr}^c[XY], k_{tr}^t[XY]$
C, $k_i^c, k_i^t \approx k_{tr}^c[XY], k_{tr}^t[XY]$

situations were recognized, depending on the relative rates of isomerization and capture of the vinyl radicals. The two limiting ends of the competitive scale, cases A and B, are readily recognized because the cis/trans product composition is independent of the concentration of the chain transfer agent, XY.

As shown in Table I, the kinetically controlled *cis*-**1**/*trans*-**1** ratio does not depend on the initial concentration of mercaptan. A competition between isomerization and chain transfer is, therefore, ruled out and either case A or B must be the proper description of the free radical addition of ethyl mercaptan to ethoxyacetylene under the conditions studied. Case A, involving rapidly equilibrating isomeric radicals and slow product-forming steps, is the situation described by the Curtin–Hammett analysis.[14] The product composition, under these restrictions, is determined by the difference in the free energies of the two transition states leading to the isomeric products. This analysis also obtains to an addition involving a single, linear vinyl radical intermediate. Since *cis*-**1**/*trans*-**1** is >100, a relatively large difference (>2.8 kcal/mol) in the free energies of the transition states of the chain transfer steps would be required to accommodate the data.[1] Such stereoselectivity is not observed in any of the cases thought to involve rapidly equilibrating or linear vinyl radicals.[6] In any event, case A is rigorously ruled out by the results of studies[15] of the thermal decompositions of *tert*-butyl *cis*- and *trans*-1-methoxypercrotonates in cumene. Isomeric 1-methoxy-1-propenyl radicals, of known configurations, are generated by this route and found to capture hydrogen from cumene prior to isomerization. Linear and rapidly equilibrating 1-alkoxy vinyl radicals must, therefore, be dismissed. Further, since mercaptan is a better H donor than cumene[16] equilibrating radicals cannot be involved in the mercaptan additions. Case B, therefore, must obtain.

When chain transfer is much more rapid than isomerization of the vinyl radical (case B), then the product composition is given by the ratio of the rate constants of the initial addition steps *cis*-**1**/*trans*-**1** = $k_{\text{addn}}^c/k_{\text{addn}}^t$. The addition of ethyl thiyl radical to ethoxyacetylene is, therefore, a stereospecific process, $k_{\text{addn}}^c/k_{\text{addn}}^t > 100$. The radical which has added and the new half-filled "sp^2" orbital are trans in the initial vinyl radical. Skell and Allen drew the same conclusion from the observation[17] that hydrogen bromide adds stereospecifically to propyne to give *cis*-1-bromo-1-propene.

The initial concentration of the chain transfer agent, ethyl mercaptan, was varied in an attempt to observe competitive isomerization and capture of the intermediate vinyl radical. The kinetically controlled *cis*-**1**/*trans*-**1** ratio, however, failed to respond to a >1000-fold change in mercaptan concentration. The results at the lowest mercaptan concentration (Table I, run E) permit an estimate of a minimum barrier to isomerization of the intermediate 1-ethoxy vinyl radical. The rate constant for the reaction of alkyl radicals with mercaptan is about $10^5\ M^{-1}\ \text{sec}^{-1}$.[18] Using this value for k_{tr}^c and specifying $k_{tr}^c[C_2H_5SH]/k_i^c > 100$, then k_i^c is calculated as $\lesssim 0.8\ \text{sec}^{-1}$ and $\Delta G^\ddagger \gtrsim 18$ kcal/mole. Since a vinyl radical is probably more reactive than an alkyl radical, the model for k_{tr}^c is a poor one. If k_{tr}^c is $\sim 10^9\ M^{-1}\ \text{sec}^{-1}$, *i.e.*, approximately diffusion controlled, then $k_i^c \lesssim 10^4\ \text{sec}^{-1}$ and $\Delta G_i^\ddagger \gtrsim 12$ kcal/mole.

The stereochemical capabilities of 1-alkyl vinyl radicals have been studied in detail. The general conclusion is that such radicals are bent and interconvert so rapidly that they can be trapped with retention of stereochemistry only by the most aggressive radical scavengers (*e.g.*, hydrogen bromide,[17] electron transfer[19]). In contrast to the results described in this paper, the nonstereospecific addition of thiolacetic acid to 1-hexyne, involving a 1-alkyl-substituted vinyl radical, is best described by stereochemical equilibration prior to chain transfer (case A).[13] 1-Alkyl and 1-alkoxy radicals, therefore, represent extremes of the spectrum of competition between isomerization and chain transfer. Singer has properly cautioned that these studies reveal only ratios of rates and that variations in the ratios cannot be rigorously attributed to only one of the rate constants.[20] Nevertheless, it seems likely that there is considerable variation in k_i as a function of the nature of the 1 substituent and that the order of configurational stabilities is 1-methyl vinyl $\ll$ 1-alkoxy vinyl. This conclusion is in harmony with the results of the EHMO calculations which stimulated these experiments. More recent CNDO calculations are not in quantitative agreement with either the EHMO calculations or these experiments. While predicting the most stable form of the 1-methoxy vinyl radical to be bent, the energy difference between that most stable structure and the linear structure is calculated to be only 2.4 kcal/mole.

Experimental Section

General. The nmr spectra were determined on Varian A-60 and Joelco C-60HL spectrometers. Infrared spectra were recorded on a Perkin-Elmer Model 137B spectrophotometer, and ultra-

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violet spectra were obtained using a Cary Model 11 spectrophotometer. Mass spectra were determined with a Hitachi Perkin-Elmer RMU-6E mass spectrometer. An F and M Model 720 gas chromatograph was used for analysis of preparative scale reactions and for gas chromatographic (gc) purifications. Although several types of columns were examined and gave reasonable separations of *cis*- and *trans*-1-ethoxy-2-(ethylthio)ethene (*cis*- and *trans*-**1**), all analyses and preparative gc collections were carried out using a 10 ft × 0.25 in. stainless steel column packed with 10% di-*n*-decyl phthalate on 45–60 mesh acid-washed Chromosorb W treated with dimethyldichlorosilane. Unless otherwise specified, a column temperature of 100° and a helium flow of 100 ml/min were used. In the experiments where the *cis*-**1**/*trans*-**1** composition was determined as a function of per cent reaction, an F and M Model 700 dual flame detector gas chromatograph was used. Unless otherwise specified, either 10 ft or 20 ft × 0.125 in. aluminum columns packed with 10% di-*n*-decyl phthalate on acid-washed Chromosorb W (60–80 mesh) treated with hexamethyldisilazane were employed at 80 and 100°, respectively. Fischer Infrared Spectranalyzed *n*-pentane was used in the preparative experiments. For experiments where the *cis*-**1**/*trans*-**1** ratio was determined as a function of per cent reaction, the pentane had been stirred with 20% fuming sulfuric acid for 4 days, washed with water, washed with 10% potassium hydroxide, stirred for 1 day with basic potassium permanganate, washed with water, dried ($MgSO_4$), and distilled (bp 36–37°) from calcium hydride. Ethoxyacetylene was either prepared by the reaction of diethyl chloro acetal with sodamide,[21] or purchased from Farchan Research Laboratories, Willoughby, Ohio 44094, and was distilled (bp 51–52°) under nitrogen prior to use. Ethyl mercaptan (Eastman Organic Chemicals) was used without further purification in the preparative experiments and in run E, Table I. In all other experiments where the *cis*-**1**/*trans*-**1** ratio was determined as a function of per cent reaction, the ethyl mercaptan was purified by passing it through a column of neutral activity grade I alumina (Woelm) followed by distillation (bp 35°) through a short column under nitrogen. Purified mercaptan reacts with ethoxyacetylene in pentane at a significantly slower rate than the unpurified material. Temperatures are uncorrected.

***cis*- and *trans*-1-Ethoxy-2-(ethylthio)ethane (*cis*- and *trans*-1).**[8] In a typical preparation, a solution of 1.406 g (0.0201 mole) of ethoxyacetylene in 15 ml of pentane under nitrogen was treated with 1.18 g (0.019 mole) of ethyl mercaptan and heated to reflux for 4 hr. Evaporation at reduced pressure gave 2.16 g (86.3%) of a faintly yellow liquid. The gc showed the isomer composition to be 40% *trans*-**1** (retention time, 19 min) and 60% *cis*-**1** (retention time, 24 min). *cis*- and *trans*-**1** accounted for 97.9% of the total peak area. In addition to a minute peak for pentane, overlapping peaks having the same retention times as ethyl disulfide (11 min, 1.5%) and 1-ethoxy-1-(ethylthio)ethene (**2**) (12 min, 0.6%) were observed. The nmr of the crude product was essentially that expected from a mixture of *cis*- and *trans*-**1**. The uv spectrum of a gc-collected sample containing approximately equal amounts of *cis*- and *trans*-**1** showed $\lambda_{\max}^{\text{cyclohexane}}$ 251 nm (ϵ 2.95 × 10^3), shoulder 300 nm (ϵ 55.4). Each isomer was obtained by preparative gc and was shown to be stable to the analytical conditions by reinjection of the purified samples. Samples of *trans*-**1** were easily collected from the gc and could be shown to be at least 99% isomerically pure by reinjection. The cis isomer proved somewhat more difficult to obtain in high isomeric purity. Successive gc passes gave *cis*-**1** that was 99.7% isomerically pure by reinjection.

Gas chromatographically purified *trans*-**1** gives an ir spectrum in good agreement with that reported:[8] nmr (CCl_4) δ 6.58 (d, 1, J = 13 Hz, =C*H*O) 5.15 (d, 1, J = 13 Hz, =CHS), 3.76 (q, 2, J = 7 Hz, OCH_2), 2.42 (q, 2, J = 7 Hz, SCH_2), 1.25 (m consisting of two overlapping triplets, 6, J = 7 Hz, 2-CH_3's); mass spectrum (75 eV) *m/e* (rel intensity) 134(6), 133(8), 132(100, parent), 105(5), 104(68), 103(14), 89(17), 77(21), 76(71), 75(39), 64(6), 61(14), 60(6), 59(12), 58(10), 51(6), 48(15), 47(61), 46(13), 45(33), 43(10), 41(17).

Gas chromatographically purified *cis*-**1** (99.3% isomerically pure) gives an ir spectrum in good agreement with that reported:[8] nmr (CCl_4) δ 6.03 (d, 1, J = 5 Hz, =C*H*O), 4.63 (d, 1, J = 5 Hz, =CHS), 3.79 (q, 2, J = 7 Hz, OCH_2), 2.54 (q, 2, J = 7 Hz, SCH_2), 1.25 (m consisting of two overlapping triplets, 6, J = 7 Hz, 2-CH_3's); mass spectrum (75 eV) *m/e* (rel intensity) 134(6), 133(8), 132(100, parent), 120(6), 106(5), 105(6), 104(80), 103(17), 89(20), 76(70), 75(40), 74(5), 63(5), 61(15), 60(5), 59(14), 58(10), 48(16), 47(36), 46(15), 45(30), 44(9), 43(6), 41(24).

Equilibration of *cis*- and *trans*-1. A 38.4-mg sample of *trans*-**1** was collected by preparative gc and dissolved in 1.0 ml of pentane. Gc analysis of this solution showed a composition of 99% *trans*-**1** and 1% *cis*-**1**. *o*-Methylbenzenethiol (4 μl) was added, and the solution was refluxed under nitrogen for 15 hr. Gc analysis showed a composition of 73.5% *trans*-**1** and 26.5% *cis*-**1** (cis-**1**/trans-**1** = 0.36).

A 67.2-mg sample of *cis*-**1** was collected by preparative gc and dissolved in 2.0 ml of pentane. Gc analysis of this solution showed a composition of 8% *trans*-**1** and 92% *cis*-**1**. *o*-Methylbenzenethiol (6 μl) was added, and the solution was refluxed under nitrogen for 15 hr. Gc analysis showed a composition of 72.7% *trans*-**1** and 27.3% *cis*-**1** (*cis*-**1**/*trans*-**1** = 0.37).

1-Ethoxy-1,2-bis(ethylthio)ethane (3). A solution of 1.0 g (14.3 mmoles) of ethoxyacetylene in 20 ml of pentane under nitrogen was treated with 3.3 ml (2.8 g, 45 mmoles) of ethyl mercaptan and refluxed for 46 hr. Evaporation under reduced pressure gave 1.97 g of crude material. Gas chromatography of this material gave the major peak at 180 min. Substantial amounts of *trans*- and *cis*-**1** (19 and 24 min, respectively), as well as seven other peaks between 10 and 118 min were observed. Distillation and water pump vacuum up to 64° gave a small forerun. The main fraction was collected at 58° (0.15 mm). Gc still showed contaminating materials in addition to the major peak at 180 min. The major peak was collected by preparative gc using a column temperature of 125° to give pure **3**. The nmr spectrum showed δ 4.36 (dd, 1, J = 5 and 7 Hz, methine *H*), 3.48 (broad m, 2, OCH_2) 2.58 (m, 6, 3-SCH_2's), and 1.21 (m, 9, 3-CH_3's). In a spin decoupling experiment in which the δ 2.58 multiplet was irradiated, the doublet of doublets at 4.36 collapsed to a singlet and the CH_3 area (δ 1.21) simplified. Irradiation of the multiplet at δ 1.21 led to simplification of the multiplet at 3.48 and 2.58, but no change in the doublet of doublets at 4.36; mass spectrum (20 eV) *m/e* (rel intensity) 194(2, parent) 150(10), 149(9), 148(100), 120(9), 119(19), 85(9), 75(24), 59(9), 45(12).

1-Ethoxy-1-(ethylthio)ethene (2).[8] **2** was synthesized by the nucleophilic addition of sodium ethylmercaptide to ethoxyacetylene. Ethyl mercaptan (1.86 g, 0.030 mole) in 40 ml of liquid ammonia under nitrogen was treated with 0.69 g (0.030 g-atom) of sodium; the blue color was just removed by adding a few drops of ethyl mercaptan. Ethoxyacetylene (1.05 g, 0.015 mole) was added, and the mixture was stirred for 1 hr; the ammonia was then allowed to evaporate overnight (17 hr) in a slow stream of nitrogen. Ether (10 ml) was added, and the flask was fitted with a reflux condenser. Water (4 ml) was then added slowly under nitrogen at 0°. An additional 10 ml of ether and 24 ml of water were added to dissolve all of the solid. The ether layer was separated and washed with water (2 × 5 ml). The combined aqueous phases were extracted with 10 ml of ether. The ether was washed with water (2 × 5 ml). This process was repeated twice and the combined ether solutions were dried ($MgSO_4$) under nitrogen. This solution was immediately analyzed by gc and showed peaks in order of increasing retention times corresponding to: ethyl thioacetate (trace); **2** (79.6%); *trans*-**1** (1.8%); *cis*-**1** (18.6%). The solution was stored overnight under nitrogen at room temperature. The same peaks were evident in the gas chromatogram of this solution but their relative areas had changed: ethyl thioacetate (trace); **2** (54.2%); *trans*-**1** (21.0%); *cis*-**1** (24.8%). Using an ambient gc column temperature, peaks for ethyl mercaptan and ethoxyacetylene were also observed. Evaporation under reduced pressure gave 0.68 g of crude material which was stored under nitrogen. The gas chromatogram of this liquid, in addition to the peaks previously mentioned, exhibited a peak which corresponded in retention time to that for **3**. The peak attributed to **2** was collected by preparative gc and gave an ir spectrum that was essentially identical with that reported:[8] nmr (CCl_4) δ 4.16 (s, 2, =CH_2), 3.79 (q, 2, J = 7 Hz, OCH_2), 2.65 (q, 2, J = 7 Hz, SCH_2), 1.27 (m consisting of two overlapping triplets, 6, J = 7 Hz, 2-CH_3's). This nmr solution was allowed to stand at room temperature for 3 days. It then showed some additional nmr peaks due to a small amount of decomposition. However, no absorption corresponding to the vinyl protons of *cis*- or *trans*-**1** was observed. In fact, no absorption at a chemical shift greater than δ 4.16 was seen.

Determination of the Cis-Trans Composition of 1 as a Function of Per Cent Reaction in the Free Radical Addition of Ethyl Mercaptan to Excess Ethoxyacetylene. Spectro grade dodecane (Eastman Organic Chemicals) was used as an internal standard without further purification. The relative gas chromatographic response of

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[21] E. R. H. Jones, G. Eglinton, M. C. Whiting, and B. L. Shaw, "Organic Syntheses," Collect. Vol. IV, Wiley, New York, N. Y., 1963, p 404.

the **1** and dodecane was determined from a pentane solution (25.0 ml) containing weighed amounts of dodecane (19.6 mg) and a gc-collected mixture of *cis*- and *trans*-**1** (7.1 mg). In one case, bromobenzene was employed as an internal standard. The relative gc-response was determined in the same manner. *cis*- and *trans*-**1** were assumed to give the same relative response. The results of runs A–E, described below, are presented in Table I. Reactions were carried out at either 0 or 35° (refluxing pentane).

Solutions of ethoxyacetylene and ethyl mercaptan were mixed with efficient stirring under nitrogen. Samples were withdrawn periodically with a syringe and were stored at liquid nitrogen temperature for subsequent gc determinations of the cis–trans composition of **1** as a function of per cent reaction.

Run A. A 10.0-ml solution of dodecane (0.0189 g) and ethoxyacetylene (8.1487 g) was treated with ethyl mercaptan (0.68 g) at 0°. The initial concentrations of reactants in the resulting solution were 10.77 *M* ethoxyacetylene and 1.01 *M* ethyl mercaptan.

The molar ratio of ethoxyacetylene/ethyl mercaptan was 10.6. After analyzing the last reaction sample (78.01% reaction) the gc column temperature was increased so that diadduct **3** could be determined. The presence of a small amount of **3** was verified by coinjection with authentic material. Assuming that **1** and **3** have the same gc response, **3** corresponded to only 1.7% of the amount of **1**.

Run B. A 25.0-ml pentane solution of bromobenzene (0.0079 g) and ethoxyacetylene (3.0236 g) was treated with a 25.0-ml pentane solution of ethyl mercaptan (0.8464 g) at 0°. The initial concentrations of reactants in the resulting solution were 0.8628 *M* ethoxyacetylene and 0.2724 *M* ethyl mercaptan. The molar ratio of ethoxyacetylene/ethyl mercaptan was 3.17.

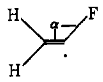
Run C. A 25.0-ml pentane solution of dodecane (0.0210 g) and ethoxyacetylene (2.2513 g) was treated with a 25.0-ml pentane solution of ethyl mercaptan (0.2790 g) at 0°. The initial concentrations of reactants in the resulting solution were 0.9278 *M* ethoxyacetylene and 0.08981 *M* ethyl mercaptan. The molar ratio of ethoxyacetylene/ethyl mercaptan was 10.32.

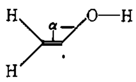
Run D. A 25.0-ml pentane solution of dodecane (0.0071 g) and ethoxyacetylene (2.4946 g) was treated with a 25.0-ml pentane solution of ethyl mercaptan (0.0260 g) at 0°. The initial concentrations of reactants in the resulting solution were 0.7118 *M* ethoxyacetylene and 0.00837 *M* ethyl mercaptan. The molar ratio of ethoxyacetylene/ethyl mercaptan was 85.0.

Run E. A 100.0-ml pentane solution of ethoxyacetylene (14.7471 g) at reflux was treated with a 100.0-ml pentane solution of dodecane (0.0070 g) and unpurified ethyl mercaptan (0.01006 g). The initial concentrations of reactants in the resulting solution were 1.052 *M* ethoxyacetylene and 8.096×10^{-4} *M* ethyl mercaptan. The molar ratio of ethoxyacetylene/ethyl mercaptan was 12.99. It was necessary to run this reaction for 4 days at 35° in order to obtain sufficient **1** for a meaningful gc analysis. During this time, the solution turned pale yellow and a very small amount of brown solid formed on the wall of the flask at the liquid level. A new, previously unobserved peak appeared in the gc and appeared to continuously grow as a function of reaction time. This peak occurred at a retention time between those for *trans*- and *cis*-**1**, but did not interfere with the determination of either of them although it was considerably larger than the peak due to the cis isomer. A 10.0-ml solution of ethoxyacetylene (0.7979 g) in pentane, without any added ethyl mercaptan, was refluxed under nitrogen as a control experiment. The solution became pale yellow and a small amount of brown solid formed. A gc peak grew with reaction time that coinjected with the "new" peak in the reaction mixture described previously. Run E was analyzed on a 20 ft × 0.125 in. di-*n*-decyl phthalate column which permitted larger injection volumes than the 10 ft × 0.125 in. di-*n*-decyl phthalate used for analysis of runs A–D.

Calculations. Extended Hückel[22] and CNDO[23] programs were obtained from the Quantum Chemistry Program Exchange, Indiana University. The EHMO calculations were performed[7] on an IBM 7074 computer using the following parameters: *K* in the Wolfsberg–Helmholtz approximation, 1.5; Slater exponents: H, 1.000; C, 1.625; O, 2.275; F, 2.600; H_{ii}2s and H_{ii}2p (eV): C, −21.40, −11.40; O, −35.30, −17.91; F, −35.00, −20.88; bond lengths (Å): C–H, 1.10; C–C, 1.54; C=C, 1.34; C–O, 1.43; O–H, 1.00; C–F, 1,32; bond angles: <HHC, <CCH, 120°; <COH, 109°; all atoms in the molecular plane. The results are given in Table II. CNDO calculations were performed with an IBM 360 computer using the following fixed parameters: bond lengths (Å):[24] C_3–H_4 and C_3–H_5, 1.07; C_2–C_3, 1.34; C_1–O, 1.427; C_1–H_1, C_1–H_2, and C_1–H_3, 1.101; bond angles: at C_3, 120°; at C_1, 109°28′; $<C_1OC_2$, 111°; H_4H_5, C_3, C_2, O, coplanar. The total energy of the linear radical was minimized with respect to the C_2–O bond length and the angle θ, the dihedral angle defined by the planes $H_1C_1OC_2$ and $C_2C_3H_4H_5$, *i.e.*, θ describes the conformation of the methoxy group with respect to rotation about the C_2–O bond. The energy of the bent radical was minimized with respect to the C_2–O bond length, θ, and α, the angle defined as $<C_3C_2O$. The results are given in Table III. Similar calculations for vinyl, 1-methyl vinyl, and 1-fluoro vinyl radicals were in excellent agreement with previous results.[6]

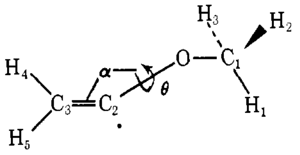
Table II. Total Electronic Energy, eV





	α 120°	α 180°
F	−343.2561	−342.0873
OH	−302.5653	−301.5786

Table III



α	θ	C_2–O distance, Å	Total energy, au	Relative energy, kcal/mole
180	0	1.40	−43.23259	12.95
	45	1.40	−43.23304	12.67
	90	1.40	−43.23359	12.33
	90	1.37	−43.24290	6.48
	90	1.34	−43.24833	3.08
	90	1.32	−43.24954	2.37
	90	1.31	−43.24918	2.54
	90	1.28	−43.24468	5.37
160	90	1.40	−43.23732	9.98
155	90	1.40	−43.23847	9.26
150	90	1.40	−43.23915	8.84
150	60	1.40	−43.23816	9.46
150	0	1.40	−43.23612	10.73
148	90	1.40	−43.23922	8.79
148	90	1.35	−43.25147	1.11
148	90	1.33	−43.25317	0.04
148	90	1.32	−43.25323	0.00
148	90	1.30	−43.25164	1.00
145	90	1.40	−43.23907	8.89
120	0	1.40	−43.20472	30.44

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[22] R. Hoffmann, *J. Chem. Phys.*, **45**, 628 (1966).

[23] J. A. Pople and G. A. Segal, *ibid.*, **44**, 3289 (1966).

[24] L. Sutton, Ed., *Chem. Soc., Spec. Publ.*, No. 11 (1958); No. 18 (1965); see tables of interatomic distances.