Tetrahedron Letters No.27, pp. 2607-2611, 1967. Pergamon Press Ltd. Printed in Great Britain.

ORIENTATION IN THE NUCLEOPHILIC ADDITION OF MERCAPTANS TO 2-METHYL-1-BUTENE-3-YNE

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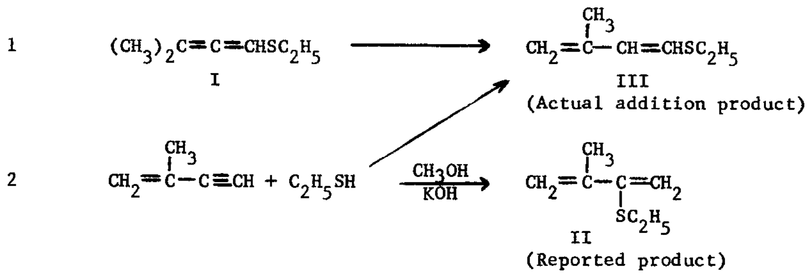
(Received 24 April 1967)

In the course of studying the chemical properties of 1-thioethoxy-3-methyl-1,2-butadiene (I) we observed the rearrangement of this compound on gas liquid chromatography columns to a 1,3-diene (reaction 1) whose properties were identical to those of the addition product from 2-methyl-1-buten-3-yne and ethyl mercaptide ion. This adduct was reported(1) to be 3-methyl-2-thioethoxy-1,3-butadiene (II). The reaction of mercaptide ions with acetylenes has been reported to give trans addition. With terminal acetylenes the alkylthio group is sometimes found on the terminal carbon, sometimes on the unprotonated carbon; orientation is believed to depend on the stability of the incipient carbanion.(2a,b,c)

It seemed unlikely that I would rearrange to II and the structure of the addition product from reaction 2 was therefore reinvestigated.



It was found that the addition reaction actually yields cis III (the product of trans addition).(3)

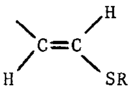
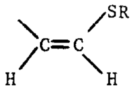
The addition was carried out as reported(1) (2-methyl-1-buten-3-yne, ethanethiol, potassium hydroxide and anh. methanol: 1.5, 1.5, 0.75, and 3 moles; 120°C; 3 hrs.) except that a stainless steel autoclave was used instead of a sealed glass tube. The yield of III was 56%, b.p. 67.5-70.0°/15 torr, n_D^{25} 1.5262; reported(1) b.p. 71-72°/20 torr, n_D^{20} 1.5285. Anal. Calcd.

for $C_7H_{12}S$: C, 65.56; H, 9.43; S, 25.01. Found: C, 65.60; H, 9.15; S, 25.61. IR (crude product): 3080(m) (olefinic C-H), 1620(s) and 1575(s) (conjugate $>C=C<$), 880(s) (broad band, $>C=CH_2$), and 690 cm^{-1} (m) (cis -CH=CH-); no absorption corresponding to allenic or terminal acetylenic compounds was seen. Distillation of the product gave material with the same spectrum but g.l.c. at ~ 100° [on a 10' X 3/8" O.D. column of Dow-Corning Silicone Oil 550 (20% w/w) supported on 60-80 mesh acid-washed Chromosorb W] produced material with essentially the same spectrum plus a new strong band at 940 cm^{-1} (trans -CH=CH-).

The p.m.r. spectrum of neat, crude reaction product was consistent with either II or III: (values are in p.p.m. downfield from tetramethylsilane present as an internal standard; s = singlet, d = doublet, t = triplet, q = quartet), 1.24 (t, 3 protons, J = 7 c.p.s., CH_3 of thioethoxy), 2.62 (q, 2 protons, J = 7 c.p.s., CH_2 of thioethoxy), 1.93 (distorted t, 3 protons, J ~ 1 c.p.s., CH_3), 4.93 (distorted q, 2 protons, J ~ 1 c.p.s., terminal $CH_2=$), 5.93 (s, 2 protons). The basis for the original assignment(1) of II as the structure of the addition product was the singlet at 5.93. This singlet, although somewhat broad, could not be split into the expected AB quartet at lower sweep width. Such splitting was realized by examination of the compound in various solvents; results are given in Table 1. This evidence establishes the structure of the main addition product as III rather than II. There is no evidence in the p.m.r. spectrum of any allenic product which might have arisen by conjugate addition, but the spectrum showed enough extraneous signal in the olefinic proton region so that the presence of up to 10% of II could not be excluded.

TABLE I

Olefinic Proton Chemical Shifts of (III)[a,b]

	Trans isomer		Cis isomer	
				
Neat	6.17(s)		5.93(s)	
Dilute CCl_4 Solution	6.14(s)		5.90(s)	
16% Acetone[c]	6.30(s)		5.97(d)	6.15(d)
21% Benzene[c]	6.12(d)	6.24(d)	5.81(d)	5.92(d)
25% DMSO[c]	6.21(d)	6.29(d)	5.93(d)	6.16(d)

a. In p.p.m. downfield from internal tetramethylsilane standard.
b. Chemical shifts of AB systems are corrected, L.M. Jackmann, Application of NMR in Org. Chem., p. 89, Pergamon Press, New York, N.Y. (1959).
c. Weight/weight percent of solute consisting of 46% trans and 54% cis isomer.

Chemical evidence for III was obtained by treatment with acidic 2,4-dinitrophenylhydrazine to yield the 2,4-dinitrophenylhydrazone of 3-methyl-2-butenal, m.p. 178-178.5° (from ethanol/ethyl acetate); reported(4) m.p. 178-178.5°. Hydrolysis of III in 1N sulfuric acid gave a complex mixture of products, mainly sulfides, from which 3-methyl-2-butenal could be isolated as the principal sulfur-free compound, b.p. 58-60°/56 torr, reported(5), 62-64°/60 torr; semicarbazone, m.p. 211.5-212.5° (water/ethanol), reported(6) 213°. The IR spectrum of the aldehyde showed a medium band at 2760 $cm.^{-1}$ and a strong carbonyl band at 1680 $cm.^{-1}$ The p.m.r. spectrum was that expected: 1.58 (d, 3 protons, $J \sim 1$ c.p.s., CH_3), 1.80 (d, 3 protons, $J \sim 1$ c.p.s., CH_3), 5.43 (2 multiplets separated by 8 c.p.s., 1 proton, coupling within each multiplet ~ 1 c.p.s., =CH-), 9.56 (d, 1 proton, J = 8 c.p.s., aldehydic proton).

Rearrangement of cis III or trans III has not been investigated in detail, but with a freshly-prepared g.l.c. column at 100° it appeared to go to completion; at slightly lower temperatures after the column had been in use for some time as much as 55% of the cis III remained unrearranged. The p.m.r. spectrum of trans III was that expected: 1.26 (t. 3 protons, J = 7 c.p.s., CH_3 of thioethoxy), 2.68 (q, 2 protons, J = 7 c.p.s., CH_2 of thioethoxy), 1.80 (complex t, 3 protons, CH_3), 4.80 (complex q, 2 protons, $=CH_2$), 6.17 (s, 2 protons, -CH=CH-). The singlet behaved in solvents as shown in Table I. From spectra in dimethylsulfoxide the coupling constant of the doublet for cis III is 10.9 c.p.s. and for trans III, 15.6 c.p.s.; this serves as further evidence (in addition to that from IR) for assignment of cis and trans configurations to the isomers of III, and for the conclusion that trans addition occurs.

A mixture of 55% cis III and 45% trans III in cyclohexane had the expected ultraviolet spectrum: λ_{max} 276 mμ (ε 1.65×10^4), λ_{max} 207 mμ (ε 7.10×10^3), inflection point between 217 and 227 mμ. Varying cis to trans ratios gave spectra differing somewhat in the intensity of absorption without observable shifts in wavelengths.

Rearrangement of I to III occurred on the g.l.c. column under the conditions mentioned and also on several other columns. In a typical run the product contained 6% cis III and 94% trans III, but rearrangement of the cis isomer to the trans doubtless occurred during the experiment so that the steric course of rearrangement of I to III remains uncertain. The rearrangement of allenes to conjugated dienes is under study.

Addition of propyl mercaptide to 2-methyl-1-buten-3-yne was also reported(1) to yield the 2-alkylthio-3-methyl-1,3-butadiene because the p.m.r. signals for the olefinic hydrogens were singlets. We did not repeat this addition because it seemed so probable that the adduct actually obtained was 3-methyl-1-thiopropoxy-1,3-butadiene. However addition of thiophenoxide was of interest in connection with studies of the rearrangement of thioallenyl ethers to conjugated dienes and also to see if the anisotropic effects of the phenyl group would produce the expected AB quartet (pair of doublets) even when measured neat.

3-Methyl-1-thiophenoxy-1,3-butadiene prepared from 2-methyl-1-buten-3-yne and thiophenol under the conditions described for III was obtained in 29% yield. The adduct is a liquid, b.p. 113-116°/4 torr. Anal. Calcd. for $C_{11}H_{12}S$: C, 74.94; H, 6.86; S, 18.19. Found: C, 75.08; H, 7.00; S, 18.05. IR (crude product): 3070(m), 1640(m) and 1590(s) (conjugated double bonds), 950(m) (trans -CH=CH-), 888(s and broad)($=CH_2$), and 690 $cm.^{-1}$ (s)(cis -CH=CH-). P.m.r. confirmed the presence of 52% cis and 48% trans isomer in the crude product mixture; cis isomer: 1.98 (t, 3 protons, $J \sim 1$ c.p.s., CH_3), 5.05 (distorted q, 2 protons, $J \sim 1$ c.p.s., $=CH_2$), 6.01 (d, 1 proton), 6.17 (d, 1 proton), 7.0-7.4 (m, 5 protons, aromatic). The two doublets correspond to an AB system from -CH=CH-, J_{AB} 10.8 c.p.s. Trans isomer: 1.73 (t, 3 protons, J ~ 1 c.p.s., CH_3), 4.83 (distorted q, 2 protons, J ~ 1 c.p.s., $=CH_2$), 6.25 (d, 1 proton), 6.40 (d, 1 proton), 7.0-7.4 (m, 5 protons, aromatic); for the olefinic protons J_{AB} = 15.5 c.p.s. Neither the IR nor the p.m.r. spectrum gave any evidence for an allenic product and the extraneous resonance in the olefinic proton region was low enough to limit the presence of 3-methyl-2-thiophenoxy-1,3-butadiene to no more than 10%. It is interesting that addition to the triple bond in this instance appears to give both cis and trans products, but no attempt was made to establish that rearrangement of cis to trans product did not occur under the reaction conditions. It is likely that such rearrangement does occur because repeated distillation of the product at 4 torr slowly increased the trans/cis ratio.

The ultraviolet spectrum of 73% trans/27% cis 3-methyl-1-thiophenoxy-1,3-butadiene in cyclohexane showed λ_{max} 287 mμ (ε 1.50 x 10^4) and λ_{max} 202 mμ (ε 1.67 x 10^4); fine structure between these values could not be specifically assigned.

Figures 1 and 2 show the mass spectra at 70 e.v. for III and the corresponding thiophenoxy compounds, respectively. These unsaturated sulfides tend to give carbon-sulfur cleavage predominantly and to an even higher degree than reported for simple saturated aliphatic sulfides(7a,b)

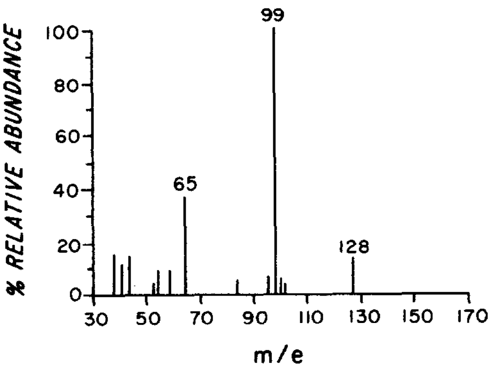


FIG. I
Mass Spectrum of 3-Methyl-1-thioethoxy-1, 3-butadiene

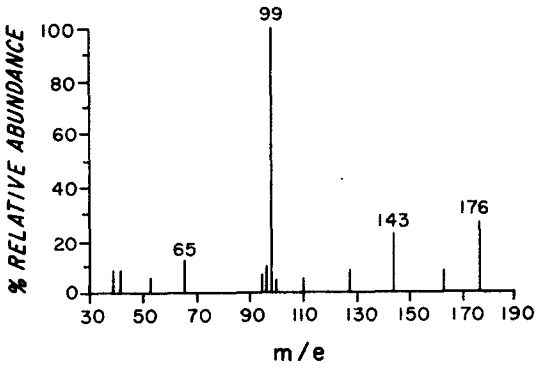


FIG. 2
Mass Spectrum of 3-Methyl-1-thiophenoxy-1, 3-butadiene

Acknowledgements. We wish to thank Professor F. A. L. Anet for helpful suggestions and advice in the interpretation of the p.m.r. spectra and the National Science Foundation for generous financial support of this work under Grant GP-5530.

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