

FORMATION OF UNSATURATED SULFIDES BY PYROLYTICAL ELIMINATION

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Direction of the pyrolytical elimination in $\text{CH}_3\text{—CH(OCOCH}_3\text{)—CH}_2\text{SR}$ was examined with respect to the temperature- and time-dependence. When the pyrolysis is brief and conducted at lower temperatures, the allyl sulfides predominate. On the other hand, (*E*)- and (*Z*)-propenyl sulfides are the principal products at elevated temperatures due to the preferential pyrolysis of allyl sulfides. The most advantageous synthesis of conjugated unsaturated sulfides consists in alkali-catalysed dehydration of 2-hydroxysulfides at an elevated temperature.

The pyrolysis of esters is an important method for the preparation of less accessible unsaturated compounds. Considerable attention has been therefore paid to the effect of various substituents on the rate and direction of the elimination. The pyrolysis of the esters $\text{CH}_3\text{—CH(OCOCH}_3\text{)—CH}_2\text{X}$ was reported to afford (from the total amount of unsaturated compounds) (*E*)- and (*Z*)- $\text{CH}_3\text{—CH=CH—X}$ (X given) in the following yields: CH_3 (43%)^{1,2}, OCH_3 (53%)³, Cl (53%)¹, OCOCH_3 (25%)⁴, CH=CH_2 (65%)⁵, C_6H_5 (75%)⁶, and COOC_2H_5 (85%)⁷; when X was equal to COCH_3 (*cf.*⁵) and NO_2 (*cf.*⁸), the conjugated isomer was claimed as the single product. In the present paper, direction of the pyrolytical elimination in 1-alkylthio-2-propyl acetates was examined with the aim to find a preparative approach to conjugated unsaturated sulfides which are accessible only with difficulty because of isomerisation and hydrolysis.

The starting 1-alkylthio-2-propyl acetates were prepared by the RSNa -catalysed addition of RSH (R = methyl, ethyl, isopropyl, tert-butyl) to 2-methyloxirane and acetylation of resulting 1-alkylthio-2-propanols with acetyl chloride and pyridine. Pyrolyses were performed in a flow reactor and the changes in concentration were checked by gas chromatography. In all cases (Table I), the yields of pyrolyses are relatively low and decrease with increasing temperature due to decomposition of unsaturated sulfides. In the preparative run at 500°C, the pyrolysis yielded mainly 1-(methylthio)propenes (18% of the *E*- and 17% of the *Z*-isomer) along with a small amount (0.6%) of 3-(methylthio)propene. However, in pyrolyses with short retention times, the formation of 3-(methylthio)propene was observed to predominate

at temperatures up to 400°C. With increasing temperature, the decomposition of 3-(methylthio)propene is much more faster than that of the isomeric conjugated sulfide, the yield of which increases with increasing temperature up to 500°C (Fig. 1). The pyrolysis of the analogous 1-methoxy-2-propyl acetate was reported³ to afford 30% of (*E*)- and 23% of (*Z*)-1-methoxypropene while the other authors⁹ claim the exclusive formation of 3-methoxypropene.

In this connection, the thermal stability of 1- and 3-(alkylthio)propenes was examined in the temperature range of 280–460°C: 3-(alkylthio)propenes were observed to undergo the thermal decomposition from 340°C while 1-(alkylthio)propenes (Fig. 2) were much more stable.

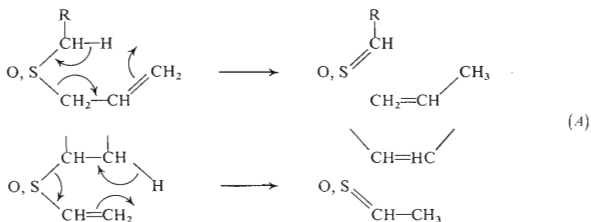
TABLE I

Pyrolysis of 1-Alkylthio-2-propyl Acetates (Procedure A)

| °C | % <i>E</i> | % (<i>Z</i>)-CH ₃ CH=CH-SR | % CH ₂ =CHCH ₂ SR | Acetate recovery % |
|---|------------|---|---|-----------------------|
| 1-Methylthio-2-propyl acetate ^a | | | | |
| 381 | 7.3 | 5.4 | 3.8 | 62 |
| 423 | 14.9 | 13.0 | 4.5 | 30.4 |
| 464 | 18.7 | 17.2 | 2.4 | 11 |
| 505 | 18.0 | 16.7 | 0.6 | 2.7 |
| 1-Ethylthio-2-propyl acetate ^a | | | | |
| 381 | 7.5 | 5.8 | 2.6 | 63 |
| 423 | 15.3 | 13.8 | 2.9 | 27.1 |
| 464 | 17.9 | 17.0 | 1.6 | 8.4 |
| 505 | 14.4 | 14.2 | 0.2 | 1.5 |
| 1-Isopropylthio-2-propyl acetate ^b | | | | |
| 381 | 8.0 | 6.3 | 2.2 | 59 |
| 423 | 14.7 | 13.5 | 2.0 | 24 |
| 464 | 16.4 | 15.8 | 0.8 | 8.7 |
| 505 | 12.0 | 12.1 | 0 | 1.3 |

^a Dosage 0.16–0.18 mol/h, analysed in a 240 cm column, XE-60 on Chromaton at 40°C, and a 120 cm column, 4% PEGA at 90°C. ^b A 240 cm column, packed with 120 cm of 9% SE-52 on Chromaton and 120 cm 9% QF-1 at 40°C. Determination of acetates: 4% PEGA on Porovina (0.2 to 0.25 mm), 120 cm column, 105°C.

The pyrolysis of 3-(alkylthio)propenes was examined by Giles, Marty, and de Mayo¹⁰. Under conditions of a flash pyrolysis at 600°C, a mixture of compounds was obtained containing thiocarbonyl compounds and their polymers in addition to propene. The elimination is most probably governed by a cyclic mechanism analogous to the reaction of allyl alkyl ethers¹¹; see equation (A).



The monomolecular cyclic mechanism of the thermal decomposition was also established in pyrolyses of alkoxyvinyl ethers^{12,13}. A simultaneous radical decomposition was observed with both ether types¹¹. Concerning the relative thermal stability of 1-(alkylthio)propenes, the differences between decomposition rates

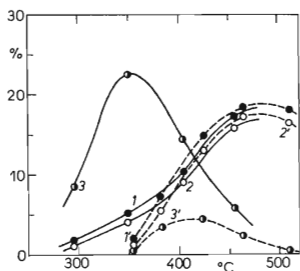


FIG. 1

Pyrolysis of 1-Methylthio-2-propyl Acetate, Temperature-Dependence

Procedure A (see Experimental), dashed line; Procedure B, full line. 1, 1' (*E*)-1-(methylthio)propene; 2, 2' (*Z*)-1-(methylthio)propene; 3, 3' 3-(methylthio)propene.

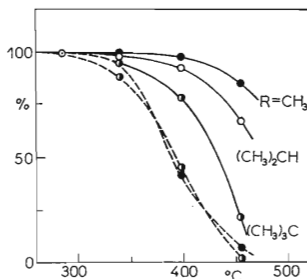


FIG. 2

Pyrolysis of (Alkylthio)propenes (Procedure B)

R-S-CH=CH-CH₃ (*E* + *Z*) full line;
R-S-CH₂-CH=CH₂ dotted line.

considerably increase with increasing temperature in the alkyl series $\text{CH}_3 < \text{C}_2\text{H}_5 < < (\text{CH}_3)_2\text{CH} < (\text{CH}_3)_3\text{C}$ (Fig. 2), while the differences are low in the case of 3-(alkylthio)propenes. This observation indicates a great proportion of the radical cleavage with the formation of $\text{CH}_2=\text{CH}-\text{CH}_2^*$ and RS^* radicals. For this reason, the proportion of products in the cleavage of 1-(alkylthio)propenes and 3-(alkylthio)propenes was also checked by gas chromatography and mass spectrometry.

In the pyrolysis of 3-(ethylthio)propene at 430°C , the following products (the quantity is expressed in % of the relative content and verified by standards) were found: hydrogen sulfide (the quantity was not determined), ethene (2.4%), propene (34%), ethanethiol (7.5%), 1,3-pentadiene (6.3%), 1,5-hexadiene, 2-propenethiol (2%), diethyl sulfide, thiophene (1.4%), compound $\text{C}_5\text{H}_6\text{S}$ (probably methylthiophene), and $\text{C}_4\text{H}_8\text{S}_2$ (about 5%); recovery, 30.2% of 3-(ethylthio)propene. From compounds with higher retention times, seven additional substances were present in amounts up to 1% such as various disulfides $\text{C}_4\text{H}_8\text{S}_2$ (corresponding to the ethanethial dimer; $\text{C}_5\text{H}_{10}\text{S}_2$ (probably allyl ethyl disulfide), and $\text{C}_6\text{H}_{12}\text{S}_2$. Pyrolysis of 3-(methylthio)propene at 430°C yielded hydrogen sulfide, propene, 1,3-butadiene, methanethiol, 2-propenethiol, thiophene, and 6 additional compounds. In view of the high content of propene, both mechanism types are probably involved simultaneously: the cyclic mechanism is typical of the formation of propene while the majority of the other products corresponds to the radical decomposition. In the pyrolysis of a mixture of the (*E*)- and (*Z*)-isomers of 1-(ethylthio)propene, the following products were found under analogous conditions: hydrogen sulfide (the quantity was not determined), ethene (1.8%), propene (1.2%), ethanethiol (1.6%), thiophene (0.3%), 1,3-pentadiene and heptadiene (1%), 2-propenethiol (0.4%), compound $\text{C}_3\text{H}_6\text{S}$ (corresponding to propanethial; 0.4%), and 3-(ethylthio)propene (0.4%); recovery, 89.7% of 1-(ethylthio)propenes. Moreover, ten additional compounds with longer retention time resulted in amounts up to 0.5%, e.g., the disulfides $\text{C}_6\text{H}_{12}\text{S}_2$ (this formula corresponds to the dimer of propanethial), $\text{C}_6\text{H}_{14}\text{S}_2$ (probably $\text{C}_2\text{H}_5\text{S}(\text{CH}_2)_2\text{SC}_2\text{H}_5$ according to the fragmentation), $\text{C}_7\text{H}_{16}\text{S}_2$, $\text{C}_4\text{H}_8\text{S}_4$, $\text{C}_8\text{H}_{16}\text{S}_2$, and $\text{C}_8\text{H}_{14}\text{S}$. In the pyrolysis, an incomplete *E-Z* isomerisation takes place since a mixture of 90% (*Z*)- and 10% (*E*)-1-(ethylthio)propenes gave a mixture of 63% (*Z*)- and 34% (*E*)-isomers while a mixture of 38% (*Z*) and 62% (*E*) recovered sulfides was obtained from a mixture of 89% (*E*)- and 11% (*Z*)-isomer. Since the formation of propanethial and ethene would be typical of a pyrolysis governed by a cyclic mechanism, the above products indicate a predominant thermal radical cleavage in the case of 1-(alkylthio)propenes. In view of the subsequent pyrolyses of the above primary sulfides, the pyrolyses of esters are not advantageous for preparative purposes. The unsaturated conjugated sulfides can be preferably prepared from 2-hydroxysulfides by heating with solid alkali metal hydroxide under removal of the unsaturated sulfide and water by distillation¹⁴. The alkali-catalysed dehydration at $160-200^\circ\text{C}$

is not accompanied by isomerisations of the carbon skeleton and mainly affords conjugated unsaturated sulfides.

EXPERIMENTAL

Gas-chromatographic analyses were carried out on a Chrom 3 apparatus (Laboratory Apparatus, Prague). Preparative gas chromatography was performed on the 3003 Chromatograph (Developmental Workshops, Czechoslovak Academy of Sciences, Prague). Mass spectra were taken on a Jeol D 100 spectrometer (1.6 kV, 75 eV) attached to a gas chromatograph with a 180 cm long column packed with 10% SE-30 on Chromaton (20–120°C, 0.19 MPa He). The IR spectra were measured on a UR-20 apparatus (Carl Zeiss, Jena). Pyrolyses were performed *a*) in a flow reactor (a quartz tube), heated space of 11 mm in diameter and 450 mm of length with a 50 mm layer of quartz wool, gasification in a stream of argon, 5 ml per min, the temperature measured by a thermocouple, the acetates introduced by the rate of 5 ml per min and the products collected in a receiver cooled by liquid nitrogen; and *b*) in a quartz pyrolyser (50 × 10 mm quartz wool) directly attached to a gas chromatograph, nitrogen as carrier gas, 55–60 ml per min, dosage with the Hamilton microsyringe. The ¹H-NMR spectra were measured on a Jeol FX-60 spectrometer, tetramethylsilane as internal standard, chemical shifts in ppm, δ scale.

1-Alkylthio-2-propanols

2-Methyloxirane (58.1 g; 1 mol) was added to a solution of the appropriate RNa in RSH (obtained by addition of 1.1 mol of RSH to a cooled solution of 3 g of sodium in 100 ml of methanol). The mixture was stirred at 20°C for 30 min, neutralised (Methyl Orange) with hydrochloric acid, the sodium chloride filtered off, and the methanol evaporated. The residue was washed with 20% aqueous potassium carbonate, dried over anhydrous sodium sulfate, and distilled under diminished pressure.

1-Methylthio-2-propanol (71%), b.p. 57°C/1.33 kPa, n_D^{20} 1.4836. Reported¹⁵, b.p. 67°C/2.66 kPa, n_D^{20} 1.4869. ¹H-NMR spectrum (CDCl₃): CH₃ 1.28 (d), CH₃S (2.12 (s), 2.60 (d), 2.38 (d), CH 3.93 m).

1-Ethylthio-2-propanol (82%), b.p. 66.5°C/1.33 kPa, n_D^{20} 1.4771. Reported¹⁶, b.p. 76.5°C/1.99 kPa.

1-Isopropylthio-2-propanol (83%), b.p. 73°C/1.33 kPa, n_D^{20} 1.4706. For C₆H₁₄OS (134.2) calculated: 53.68% C, 10.51% H, 23.90% S; found: 53.71% C, 10.65% H, 23.74% S.

1-tert-Butylthio-2-propanol (76%), b.p. 77°C/1.33 kPa, n_D^{20} 1.4687. For C₇H₁₆OS (148.3) calculated: 56.70% C, 10.9% H, 21.6% S; found: 56.52% C, 10.65% H, 21.87% S.

1-Alkylthio-2-propyl Acetates

Acetyl chloride (43.2 g; 0.55 mol) was added dropwise at 0°C to a mixture of the appropriate 1-alkylthio-2-propanol (0.5 mol), pyridine (0.55 mol), and chloroform (200 ml). The mixture was stirred at room temperature for 20 min, washed with 2.5M-HCl (three 100 ml portions) and 15% aqueous potassium carbonate, dried over anhydrous calcium chloride, and distilled under diminished pressure.

1-Methylthio-2-propyl acetate (84%), b.p. 65°C/1.33 kPa, n_D^{20} 1.4532 (in accordance with the lit.¹⁷).

1-Ethylthio-2-propyl acetate (87%), b.p. 75°C/1.33 kPa, n_D^{20} 1.4536. For C₇H₁₄O₂S (162.3) calculated: 51.82% C, 8.80% H, 19.76% S; found: 52.03% C, 8.72% H, 19.65% S.

1-Isopropylthio-2-propyl acetate (91%), b.p. 85.5°C/1.33 kPa, n_D^{20} 1.4528. For $C_8H_{16}O_2S$ (176.3) calculated: 54.51% C, 9.15% H, 18.19% S; found: 54.38% C, 9.18% H, 18.24% S.

1-(tert-Butylthio)-2-propyl acetate (88%), b.p. 87°C/1.33 kPa, n_D^{20} 1.4537. For $C_9H_{18}O_2S$ (190.3) calculated: 56.80% C, 9.53% H, 16.85% S; found: 56.48% C, 9.60% H, 16.9% S.

The purity of 1-alkylthio-2-propanols and 1-alkylthio-2-propyl acetates was checked by gas chromatography (120 cm column, 4% PEGS on Chromaton NAWDMCS; 240 cm column, 10% XE-60) at 90–110°C, nitrogen flow rate 90 ml per min.

3-(Alkylthio)propenes

3-(Methylthio)propene and 3-(ethylthio)propene were prepared according to the literature¹⁸ and purified by preparative gas chromatography on a 300 cm column (8 mm in diameter), 12% dinonyl phthalate on Porovina (0.2–0.25 mm), 50°C, 0.176 MPa N_2 . 3-(Isopropylthio)propene (70%), b.p. 129°C/99 kPa. For $C_6H_{12}S$ (116.2) calculated: 62.04% C, 10.41% H; found: 61.82% C, 11.0% H. 3-(tert-Butylthio)propene (45%), 80–82°C/12 kPa. For $C_7H_{14}S$ (130.2) calculated: 64.58% C, 10.84% H; found: 64.40% C, 10.73% H. Gas-chromatographic analysis: 240 cm column with 6% SE-52 on Porovina (0.2–0.3 mm) at 40°C and 120 cm column with 9% QF-1 on Chromaton at 40°C.

1-(Alkylthio)propenes

A. By pyrolysis of 1-alkylthio-2-propyl acetates followed by the preparative gas chromatography.

B. The appropriate 1-alkylthio-2-propanol (0.25 mol) was added dropwise over 1 h to potassium hydroxide (28 g; 0.5 mol) at 220–250°C and the vapours were passed through a 20 cm Vigreux column. The unsaturated sulfides were separated from water, dried, and rectified on a 20 TP column. The isomers were separated by preparative gas chromatography.

1-(Methylthio)-2-propanol yielded 16 g (73%) of a mixture of 48.4% (*Z*)- and 47.3% (*E*)-1-(methylthio)propene along with 4.3% of 3-(methylthio)propene (b.p. 98–101°C/100 kPa). As reported¹⁹, a mixture of isomers boiling at 105–106°C was prepared by cleavage of 1-(2-butylthio)propene with sodium and the subsequent alkylation with methyl iodide. For the mixture of C_4H_8S (88.2) isomers calculated: 54.49% C, 9.15% H; found: 54.54% C, 9.39% H. From this mixture, the *Z*-isomer (b.p. 96°C) and the *E*-isomer (b.p. 100°C) were separated by preparative gas chromatography under conditions analogous to those in the preparation of 3-(methylthio)propene.

1-(Ethylthio)-2-propanol yielded by dehydration and rectification 69% of a mixture of ethylthiopropenes (4.7% of 3-(ethylthio)propene, 50.8% of the (*Z*)- and 44.5% of the (*E*)-1-(ethylthio)propene), b.p. 118.5–120°C/100 kPa. For $C_5H_{10}S$ (102.2) calculated: 58.80% C, 9.87% H; found: 58.48% C, 9.92% H. Separation by preparative gas chromatography (300 cm column with 12% dinonyl phthalate on Porovina (0.2–0.25 mm), 60°C, 0.19 MPa N_2 ; analytical run on a 240 cm column with 10% of XE-60 on Chromaton, 40°C) yielded the *Z*-isomer (b.p. 118°C) and the *E*-isomer (b.p. 121°C).

1-Isopropylthio-2-propanol afforded by dehydration and rectification a mixture of 2.6% of 3-(isopropylthio)propene, 52.7% (*Z*)- and 44.7% (*E*)-1-(isopropylthio)propene in 66% yield. For $C_6H_{12}S$ (116.2) calculated: 62.04% C, 10.41% H; found: 61.54% C, 10.78% H. The isomers can be separated analytically by gas chromatography in a column packed according to Sváta²⁰ with 120 cm of 9% SE-52 and 120 cm of 9% QF-1 on Chromaton NAWDMCS (40°C). The attempted preparative gas chromatography failed; enriched fractions were obtained only.

1-(tert-Butylthio)-2-propanol furnished by dehydration a 60% yield of a mixture, b.p. 142.5°C/98.4 kPa. For $C_7H_{14}S$ (130.2) calculated: 64.58% C, 10.84% H; found: 64.0% C, 11.22% H. Gas chromatography resulted in an incomplete separation of isomers. The quantity was calculated from areas.

Spectra. The IR spectra of *Z*-isomers²⁰ exhibit a strong absorption at $\nu(C=C)$ 1614–1617 cm^{-1} and δ 660–664 cm^{-1} (the *E*-isomers, 1620–1625 and 936–940 cm^{-1}). The mass spectra were interpreted with the use of Tables²¹; the peaks *m/e* 28, 32, and 40 were not taken into account because of the potential presence of air in the sample. In addition to the fragmentation, the pyrolytical products were identified on the basis of retention data by comparison with standard specimens. The presence of ethene and propene was confirmed by conversion to dibromo derivatives, that of hydrogen sulfide by precipitation with Cd^{2+} and Fe^{2+} ions.

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