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Abstract

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Interaction of Diacetylene with Ethyl Mercaptan and Some Properties of the Compounds Obtained

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Syntheses based on diacetylene made it possible to obtain a series of ethynylvinyl ethers ([1,3]), which are of interest from the standpoint of their reactivity and the preparation from them of 1-alkoxybutadienes-1,3 ([4]). In these studies it was shown that alcohols of the aliphatic and hydroaromatic series react smoothly with diacetylene, forming the corresponding ethynylvinyl ethers and acetals of butynal of the type $CH \equiv C—CH = CH—OR$ and $CH_3—C \equiv C—CH(OR)_2$. It was also of interest to study the interaction of diacetylene with mercaptans. In the literature on this question there is only a patent ([5]) describing the reaction of diacetylene with butyl mercaptan and benzyl mercaptan. The only products isolated by the authors were the corresponding ethynylvinyl ethers. We studied the interaction of diacetylene with mercaptans using the most readily available ethyl mercaptan, whose reaction with diacetylene has not been described. It turned out that the interaction of ethyl mercaptan with diacetylene takes place even upon slight heating of the mixture, while under the influence of alkali it begins at room temperature and is accompanied by self-heating. The presence of azoisobutyric acid nitrile caused almost no additional initiation of the reaction, which indicates that the first stage of the interaction of diacetylene with mercaptans proceeds mainly by an ionic mechanism. The reaction follows scheme (I) and, depending on the ratio of the starting substances and the temperature, is accompanied by the formation of ethynylvinyl thioethyl ether and the product of addition of two molecules of mercaptan (II), having a butadiene structure:

$$\begin{aligned} CH \equiv C—C \equiv CH \xrightarrow{RSH} CH \equiv C—CH = CH—SR \xrightarrow{RSH} \\ \rightarrow RS—CH = CH—CH = CH—SR \end{aligned} \quad (1)$$

The interaction proceeds stepwise, as is demonstrated by the possibility of the second stage proceeding independently and with another mercaptan. However, the addition of mercaptan to ethynylvinyl thioethyl ether can proceed under the influence of various reagents and factors: alkali, HCl, radical initiators, and heating. In the last two cases the reaction gives higher yields of the final product, which indicates that the process of addition of mercaptan to ethynylvinyl

thioethyl ether by a radical mechanism proceeds more readily than by an ionic one. In this case the main reaction products are dithioalkylbutadienes-1,3:

$$\mathrm{CH\equiv C—CH=CH—SR + R'SH \rightarrow R'S—CH=CH—CH=CH—SR}$$

$$\text{or} \quad \mathrm{CH_2=C(SR')—CH=CH—SR}$$

$$\mathrm{R \text{ and } R' = C_2H_5 \text{ (III)};\ R = C_2H_5,\ R' = C_6H_5 \text{ (IV)} \qquad (2)}$$

This is evidenced by the fact that the products obtained by the ionic and radical mechanisms reacted with maleic anhydride to form adducts of diene synthesis, which in the reaction split off two molecules of mercaptan with formation of phthalic anhydride:

$$\mathrm{CH=CH-CH=CH\underset{SR}{|}\quad \underset{SR}{|} + \begin{matrix} CH-C=O \\ \| \quad \backslash O \\ CH-C=O \end{matrix} \rightarrow \left[\begin{matrix} SR \\ \text{cyclohexadiene anhydride adduct} \\ SR \end{matrix}\right] \rightarrow \text{phthalic anhydride} + 2RSH} \qquad (3)$$

Some difference in the physical constants and the large exaltation of the molecular refraction in the product of addition of two molecules of mercaptan to diacetylene are apparently explained by the presence of isomeric compounds, among which, besides compounds with a butadiene structure, other isomeric products are also possible. To prove the structure of the isolated products, the method of sulema titration, proposed by one of us and Prilezhaeva [6,7] for determining vinyl thioalkyl ethers, was applied. Ethynylvinyl thioethyl ether reacts with an alcoholic solution of sulema with quantitative formation of ethylmercaptomercury chloride, an equivalent amount of HCl and, apparently, ethynylvinyl ethyl ether according to equation (4)

$$\mathrm{CH\equiv C-CH=CH-S-C_2H_5 + HgCl_2 + C_2H_5OH \rightarrow}$$

$$\mathrm{\rightarrow C_2H_5SHgCl + HCl + [CH\equiv C-CH=CH-OC_2H_5]} \qquad (4)$$

and, consequently, this method can be used for the quantitative determination of ethynylvinyl thioalkyl ethers. The action of an aqueous solution of sulema on ethynylvinyl thioethyl ether and on the product with two mercapto groups leads to incomplete decomposition of the starting substances. Ethylmercaptomercury chloride and HCl were thereby isolated on average in 40 and 60%, respectively.

$$\mathrm{CH\equiv C-CH=CH-SC_2H_5 + H_2O + HgCl_2 \rightarrow}$$

$$\mathrm{\rightarrow C_2H_5SHgCl + HCl + (CH_3-C\equiv C-CHO).} \qquad (5)$$

Interaction of diacetylene with ethyl mercaptan. Into a reaction apparatus equipped with a stirrer and a reflux condenser connected to a coil trap, there was placed a 2% solution of caustic potash in 26.1 g of ethyl mercaptan (b.p. 36–36.5°) and 20 ml of dioxane. At 65–70° 7 g of diacetylene was absorbed, after which the mass was stirred at the same temperature for another 1 hour. After completion of the reaction the mixture was washed several times with water, dried over potash, and distilled in vacuo:

I fraction 47–50°/8 mm, 9.1 g;
II fraction 112–120°/5 mm, 4.6 g;
Residue 1.9 g.

Fraction I was ethynylvinyl thioethyl ether with b.p. 65–65.5°/17 mm; $n_D^{20} = 1.5468$; $d_4^{20} = 0.9516$. Found $MR_D = 37.38$; calculated for $C_6H_8S|{=}\equiv MR_D = 35.35$. Yield 58.1% of theory.

Found %: C 64.02; 64.32; H 7.29; 7.18; S 27.96
C_6H_8S. Calculated %: C 64.23; H 7.19; S 28.58

Fraction II after double distillation had the following constants: b.p. 116.0°/5 mm; $n_D^{20} = 1.5853$; $d_4^{20} = 1.0193$. Found $MR_D = 57.34$; calculated for $C_8H_{14}S_2$ $2|{=}MR_D = 54.15$, and it was the product of addition of two molecules of mercaptan to diacetylene (II). Yield 18.8% of theory.

Found %: C 54.86; 54.86; H 7.78; 7.94
$C_8H_{14}S_2$. Calculated %: C 55.12; H 8.09

The product did not give a reaction for an acetylenic bond with ammoniacal $AgNO_3$ solution, and, upon addition of an excess of sulema solution, both isolated products gave an acid reaction with methyl orange. Table 1 summarizes experiments carried out under various conditions.

Decomposition of ethynylvinyl thioethyl ether (I) and of the product with two mercapto groups (II) by alcoholic sulema solution. A weighed portion of the substance and 6–7 ml of a 20% solution of sulema in ethyl alcohol (with a sulema content 2.2 times greater than theoretically required according to equation (4)) were placed in a conical flask. A light-colored precipitate immediately formed, which, on standing for a day, settled to the bottom. The contents of the flask were diluted with 25 ml of distilled water and titrated with 0.1 N NaOH in the presence of methyl orange. After the titration, the precipitate of ethylmercaptomercury chloride was filtered through a glass tared filter, washed with hot xylene, and dried in a vacuum desiccator. The isolated ethylmercaptomercury chloride did not melt on heating to 200° and decomposed at about 320° ([5]). The titration results and the yield of ethylmercaptomercury chloride are shown in Table 2.

Table 1

Interaction of diacetylene with ethyl mercaptan

No.	Reagent	Molar ratio diacetylene: mercaptan	Time, h	T., °C	Yield of thioether, % of theory	Yield of diadduct, % of theory
1	KOH	1 : 1	1	18–60	48.2	Traces
2	KOH	1 : 2	1	50–55	46.7	5.4
3	KOH	1 : 3	1	50–55	68.0	6.8
4	KOH	1 : 3	1	65–70	58.1	18.8
5	KOH	1 : 3	2	65–70	50.0	33.0
6	–	1 : 1	2	50–55	~10.0	–
7	Nitrile	1 : 1	2	50–55	~10.0	–

Table 2

Quantitative determination of ethynylvinyl thioethyl ether

No.	Weighed portion of ether, g	0.1 N NaOH consumed, ml	Thioether found, % of theory	Yield of ethylmercaptomercury chloride, g	Yield of ethylmercaptomercury chloride, % of theory
1	0.2042	18.20	99.91	0.52	96.1
2	0.2076	18.56	100.2	0.53	96.5

Hydrolysis of ethynylvinyl thioethyl ether and of the product with two mercapto groups in the presence of sulema. A weighed portion of the substance was mixed with an excess of a 5.5% aqueous solution of sulema. A light-colored precipitate of ethylmercaptomercury chloride and the formation of a dark resinous mass settling on the walls of the flask were observed immediately. After prolonged standing, the solution was titrated with 0.1 N NaOH, after which the precipitate was filtered off and thoroughly washed with acetone to remove resin, then dried and weighed. The isolated ethylmercaptomercury chloride did not melt on heating to 230°. The results of the experiments are presented in Table 3.

Interaction of ethynylvinyl thioethyl ether with ethyl mercaptan and thiophenol. The reaction was carried out in sealed ampoules or in a flask, at different temperatures and under the influence of various reagents (Table 4).

The product with two mercapto groups (II), obtained under the influence of azoisobutyric acid nitrile, had the following constants: b.p. 120.0°/5 mm; $n_D^{20} = 1.6062$, $d_4^{20} = 1.0134$; $MR_D = 59.29$. Calculated for $C_8H_{14}S_2$, 2|= = 54.15.

Found, %: C 55.26; 55.12; H 8.28; 8.16; S 36.59; 36.65
$C_8H_{14}S_2$. Calculated, %: C 55.12; H 8.09; S 36.78.

Table 3

Hydrolysis of ethynyl vinyl thioethyl ether and diethylthiobutadiene-1,3 in the presence of sulema

No.	Sample weight, g	0.1 N NaOH consumed, ml	Found, % of theory: ether	Found, % of theory: butadiene	Yield of ethylmercaptomercuric chloride, g	Yield of ethylmercaptomercuric chloride, % of theory
1	0.2114	7.81	41.4	–	0.26	46.4
2	0.1942	7.31	42.2	–	0.25	48.1
3	0.1832	6.90	–	32.38	0.40	64.0
4	0.1856	7.01	–	32.46	0.41	64.8

Constants of the isolated dithio(ethylthienyl)butadiene-1,3 (III). B.p. 165.0-165.2°/2.5 mm; $n_D^{20} = 1.6697$; $d_4^{20} = 1.0990$; $MR_D = 76.56$. Calculated for $C_{12}H_{14}S_2$ $-MR_D = 69.02$.

Found, %: C 64.79; 64.64; H 6.36; 6.32; S 29.20; 29.30
$C_{12}H_{14}S_2$. Calculated, %: C 64.81; H 6.34; S 29.51

Table 4

Reaction of ethynyl vinyl thioethyl ether with ethyl mercaptan and thiophenol

No.	Reagent	Experimental temperature, °C	Duration of experiment	Yield of product II, % of theory
1	1 drop HCl	20	5 h	52.2
2	2 drops HCl	20	month	54.5
3	1 drop HCl; hydroquinone	70	5 h	45.1
4	2% KOH	80	6 »	58.8

No.	Reagent	Experimental temperature, °C	Duration of experiment	Yield of product II, % of theory
5	0.5% nitrile	80	6 »	99.2
6	0.5% »	20	month	94.0
7	None	80	6 h	90.9
8	0.5% nitrile with thiophenol	20–70	1 »	95.0*

* Product III.

Condensation with maleic anhydride. From 12.6 g of the product of addition of ethyl mercaptan to ethynyl vinyl thioethyl ether (II) and 7.8 g of maleic anhydride in a solution of 35 ml of benzene, on heating to 130° for 10 h, 4.6 g (69.4% of theory) of phthalic anhydride was obtained; it melted at 130.5° (from petroleum ether) and gave no depression on melting with an authentic sample. Literature m.p. 131.6° (8).

Found, %: C 65.14; 64.94; H 2.93; 2.82
$C_8H_4O_3$. Calculated, %: C 64.87; H 2.72

Ethyl mercaptan was isolated from the benzene fraction in the form of 2,4-dinitrophenylethyl sulfide with m.p. 114°; no depression was observed on melting a mixed sample. Literature m.p. 115° (9). Phthalic anhydride was also obtained from product III.

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Note: Figure translations are in progress. See original paper for figures.