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CHEMISTRY

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Abstract

Full Text

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ON THE INTERACTION OF 3-AMINOPROPENE-1,2-THIOCARBONATE WITH AMMONIA AND WITH AMINES

In a previous paper (1) we reported on the possibility of obtaining various amino derivatives of alkenethiocarbonates by the interaction of the corresponding chloroalkenethiocarbonates with ammonia and with amines. Continuing the study of the properties of the amino derivatives obtained, it seemed of interest to us to investigate their interaction with ammonia at elevated temperature (150°). In this case we expected to obtain an aminothioglycol by analogy with the reaction that occurs in the interaction of ethylenetrithiocarbonate with ammonia (2)

$$H_2N{-}CH_2{-}CH{-}CH_2SCO + 2NH_3 \rightarrow H_2N{-}CH_2{-}C(OH)H{-}CH_2SH + CO(NH_3)_2.$$

However, the experiments showed that, instead of the expected 3-amino-1-mercaptoisopropanol, a product not containing nitrogen was obtained. Along with it, urea was obtained in quantitative yield. The reaction product contained sulfur, did not show a qualitative sulfhydryl group, and contained a hydroxyl group. By its properties and composition (C_3H_6OS) it corresponded to 1-hydroxypropene-2,3-thiirane:

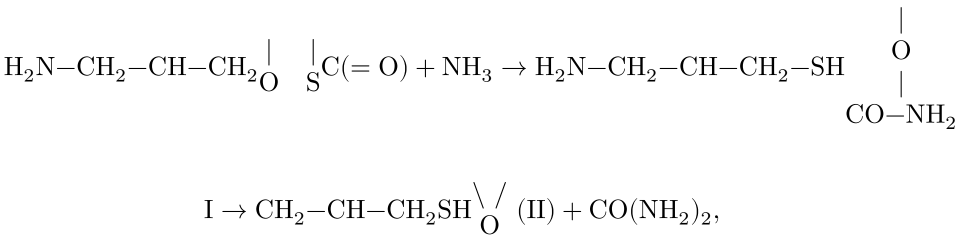
$$HO{-}CH_2{-}CH{-}CH_2S.$$

To prove the structure of the compound obtained, we prepared it by saponification of the thioglycidyl ester of acetic acid:

$$CH_3C(=O){-}O{-}CH_2{-}CH{-}CH_2S + KOH \xrightarrow{EtOH} HOCH_2{-}CH{-}CH_2S + CH_3COOK.$$

The thiirane obtained had the same constants, and a mixed sample of the α-naphthylurethanes melted without depression.

The formation of 1-hydroxypropene-2,3-thiirane by the interaction of 3-aminopropenethiocarbonate may be represented as proceeding by the following mechanism:



$$H_2N{-}CH_2{-}CH{-}CH_2\begin{matrix}|\\O\end{matrix}\ \ \begin{matrix}|\\S\end{matrix}C(=O)+NH_3 \rightarrow H_2N{-}CH_2{-}CH{-}CH_2{-}SH\ \ \begin{matrix}|\\O\\|\\CO{-}NH_2\end{matrix} \qquad (I)$$

$$I \rightarrow CH_2{-}CH{-}CH_2SH\underset{O}{\backslash/}\ (II)+CO(NH_2)_2,$$

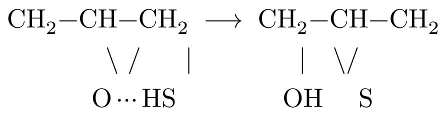
$$II \rightarrow HO{-}CH_2{-}CH^*{-}CH_2S.$$

The validity of the proposed scheme for the formation of urea from the reacting ammonia and the amino group of the thiocarbonate was proved by the fact that, when ammonia was replaced by dimethylamine, N,N-dimethylurea was obtained in high yield.

In the scheme given above we also indicate the rearrangement of 2,3-epoxypropanethiol to 1-hydroxypropene thiirane, which occurs. The presence of such a rearrangement was proved by us by obtaining thiirane when we started from epichlorohydrin and sodium hydrosulfide. Instead of the expected 2,3-epoxypropanethiol, 1-hydroxypropene-2,3-thiirane was obtained:

$$OCH_2{-}CH{-}CH_2Cl+NaSH \longrightarrow OCH_2{-}CH{-}CH_2SH \longrightarrow HOCH_2{-}CH{-}CH_2S.$$

There are no data in the literature on the interaction of epichlorohydrin with sodium hydrosulfide. Only a very old paper is known (^{3}), in which it is stated that 2,3-epoxypropanethiol is obtained in the reaction of epichlorohydrin with an alcoholic solution of KHS. However, the constants of the compound obtained are not given in that work. In our opinion, the author of the cited work obtained 1-hydroxypropene-2,3-thiirane. The rearrangement can be explained by intramolecular interaction of the sulfhydryl hydrogen atom with the oxirane ring:



$$\begin{array}{c}CH_2{-}CH{-}CH_2\\ \backslash\,/\quad\ \ |\\ O\cdots HS\end{array} \longrightarrow \begin{array}{c}CH_2{-}CH{-}CH_2\\ |\quad \backslash/\\ OH\quad S\end{array}$$

In the interaction of 3-(N-methylamino)-propenethiocarbonate with ammonia under the same conditions, the occurrence of a reaction was also observed, but, apparently, of a more complicated one, owing to the instability of the methylurea formed on heating above its melting point. 3-(N,N-Dimethylamino)-propenethiocarbonate does not react with ammonia under the indicated experimental conditions.

Experimental Part

Reaction of 3-aminopropenethiocarbonate with ammonia and with amines. 12 g of aminothiocarbonate in ampoules, 2 g in each, was heated with a threefold molar excess of ammonia in alcoholic solution at 120–130° for 8–10 h. After heating, 5 g of urea (m.p. 132° from alcohol) was filtered off, and 6.5 g of a liquid product was obtained, from which, on distillation, 1-hydroxypropene-2,3-thiirane was obtained in an amount of 5 g (yield 61%), b.p. 75–76°/6 mm, n_D^{20} 1.5415; d_4^{20} 1.2170.

Found, %:	C 40.16; H 6.72; S 35.56; OH 18.60
C_3H_6OS. Calculated, %:	C 40.00; H 6.66; S 35.60; OH 18.90

Molecular weight found 91, calculated 90; MR found 23.33, calculated 23.31. α-Naphthylurethane, m.p. 165–166°.

10 g of aminothiocarbonate (in 10 ampoules, 1 g each) was treated with an alcoholic solution of dimethylamine in threefold molar excess. The ampoules were sealed and heated at 140–150° for 8–10 h. After the reaction, 3.5 g of N,N-dimethylurea was filtered off (m.p. 180° from alcohol). A mixed sample with N,N-dimethylurea obtained by saponification of N,N-dimethylcyanamide (from dimethylamine and BrCN in ether) ([4]) melted without depression. From the liquid part of the reaction product a fraction with b.p. 75–76°/6 mm was isolated in an amount of 2.11 g, with n_D^{20} 1.5408, d_4^{20} 1.2170, OH 18.3%. According to the analysis, the compound corresponds to 1-hydroxypropene-2,3-thiirane. α-Naphthylurethane, m.p. 165–166°.

Synthesis of thioglycidyl acetate. 155 g of thioepichlorohydrin was heated with 140.3 g of anhydrous CH_3COOK in 300 ml of glacial CH_3COOH for one hour at 110°. The mixture was poured into water, neutralized with soda, and extracted with ether. After removal of the ether, the residue was distilled in vacuum, giving 105 g of thioglycidyl acetate (yield 55%), b.p. 72–73°/9 mm, n_D^{20} 1.4880, d_4^{20} 1.1784.

Found, %:	C 45.32; H 6.08; S 24.33
$C_5H_8O_2S$. Calculated, %:	C 45.40; H 6.05; S 24.30

Molecular weight found 133.5, calculated 132; MR found 32.40, calculated 32.91; saponification equivalent found 128.2, calculated 132.0.

Saponification of thioglycidyl acetate. 90 g of thioglycidyl acetate was treated with 38.2 g of KOH in 200 ml of alcohol under reflux for one hour.

The alcohol was then distilled off, and the residue was washed three times with ether. After removal of the ether, 1-oxypropene-2,3-thiirane was fractionated under vacuum, b.p. 70–71°/5 mm. 49.4 g was obtained (yield 81%), n_D^{20} 1.5415, d_4^{20} 1.2155, OH 19.10%. β-Naphthylurethane, m.p. 165–166°. Mixed samples with the urethanes of thiiranes obtained by all the methods described above melted without depression.

Reaction of epichlorohydrin with sodium hydrosulfide. 11.5 g of Na was dissolved in 100 ml of dry methanol. The sodium methylate solution was saturated with hydrogen sulfide. To the hydrosulfide obtained, 46.25 g of epichlorohydrin was slowly added from a dropping funnel; a vigorous reaction with evolution of heat was observed. The reaction mixture was cooled, the precipitated sodium chloride was filtered off, and the methanol was distilled off. The remaining viscous liquid was fractionated under vacuum. 7 g of 1-oxypropene-2,3-thiirane was obtained with b.p. 78–80°/8 mm, n_D^{20} 1.54126, d_4^{20} 1.2165, OH 18.60%, α-naphthylurethane, m.p. 165–166°.

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

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