REACTION OF 2-CHLOROETHYL ISOTHIOCYANATE WITH N-PHENYLETHYLENEIMINE AND ETHYLENE SULFIDE

A. P. Sineokov and V. S. Kutyreva

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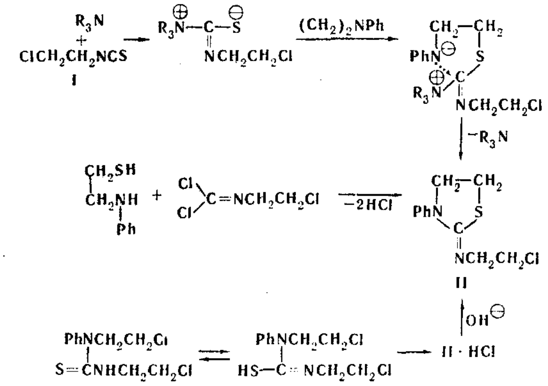
The reaction of 2-chloroethyl isothiocyante with N-phenylethyleneimine in the presence of triethylamine gives 2-(2-chloroethyl)imino-3-phenyl-1,3-thiazolidine. A mixture (1 : 2) of 2-(2-chloroethyl)imino-3-phenyl-1,3-thiazolidine and 7-phenyl-2,3,5,6-tetrahydroimidazo-[2,1-b]thiazolinium chloride is obtained in the absence of a catalyst. The reaction of 2-chloroethyl isothiocyanate with ethylene sulfide in the presence of triethylamine gives 2,3,5,6-tetrahydrothiazolo[2,3-b]thiazolinium chloride, while the reaction with tetraethylammonium bromide gives 2-ethyleneiminium-1,3-dithiolane chloride.

Isothiocyanates react with N-phenylethyleneimine [1] and ethylene sulfide [2-4] with opening of the C = S bond. In the process, expansion of the three-membered ring occurs for ethyleneimine, while ethylene sulfide forms copolymerization products.

The reaction of three-membered heterocycles with 2-chloroethyl isothiocyanate (I) proceeds unusually. In the presence of triethylamine, N-phenylethyleneimine reacts with I at room temperature at the C = S bond to give 2-(2-chloroethyl)imino-3-phenyl-1,3-thiazolidine (II).



Its structure was confirmed by the presence of a $\nu_{C=N}$ band at 1650 cm^{-1} in the IR spectrum and by alternative synthesis from 2-mercaptoethylaniline and 2-chloroethylcarbylamine chloride in the presence of triethylamine and also from I and 2-chloroethylaniline, in analogy with methods in [5, 6].

In the absence of a catalyst, the reaction of N-phenylethyleneimine and I gives a mixture of II and water-soluble crystals that contain ionic halogen. Treatment of the crystals with alkali, followed by acidification, gave 3-(2-mercaptoethyl)-1-phenylimidazolidin-2-one [5, 6]. The reaction apparently proceeds at the C = N bond of the isothiocyanate to form 3-(2-chloroethyl)-1-phenyl-1,3-imidazolidine-2-thione, which spontaneously rearranges to III.

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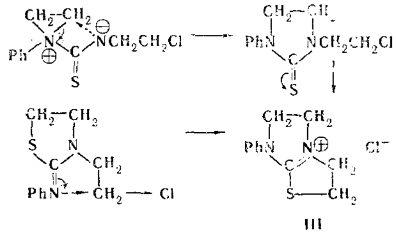
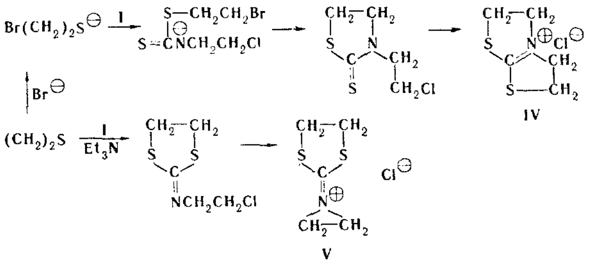


The results of IR spectroscopy and elementary analysis confirm the correctness of the proposed scheme. In addition, the indicated compound was also obtained by an alternative route from di(2-chloroethyl)amine and phenyl isothiocyanate [5, 6] through 2-phenylimino-3-(2-chloroethyl)-1,3-thiazolidine, which is also capable of intramolecular conversion to form III.

Ethylene sulfide reacts with I in the presence of tetraethylammonium bromide to give a water-soluble crystalline compound that is identical to the known 2,3,5,6-tetrahydrothiazolo[2,3-b]thiazolinium chloride (IV) previously synthesized from di(2-chloroethyl)amine and CS_2 [7, 8]. It can be assumed that the reaction proceeds at the C=N bond of the isothiocyanate with subsequent intramolecular alkylation.

With triethylamine as the catalyst, ethylene sulfide and I form a water-soluble compound that corresponds to the 1 : 1 addition of the components but differs in chemical properties from IV. It can be assumed that the reaction proceeds in this case at the C=S bond of the isothiocyanate, and the resulting 2-(2-chloroethyl)imino-1,3-dithiolane probably gives an iminium salt (V).



EXPERIMENTAL

2-(2-Chloroethyl)imino-3-phenyl-1,3-thiazolidine (II). A) A mixture of 3 g (24.7 mmole) of 2-chloroethyl isothiocyanate (I), 3 g (25.1 mmole) of N-phenylethyleneimine, and 0.02 g (0.19 mmole) of triethylamine was held at room temperature in an ampul for 20 days, during which the contents crystallized to give 5 g (83%) of II with mp 45° (from petroleum ether). IR spectrum, cm^{-1}: 2880 weak (w), 1650 very strong (vs), 1600 strong (s), 1510 s, 1390 s, 1315 vs, and 760 s. Found: C 54.9; H 5.6; N 11.7%; M 241.5.* $C_{11}H_{13}ClN_2S$. Calculated: C 54.9; H 5.40; N 11.6%; M 240.5.

B) A solution of 9.1 g (56 mmole) of 2-chloroethylcarbylamine chloride [9] in 25 ml of absolute ether was added to a mixture of 8.67 g (56 mmole) of 2-mercaptoethylaniline and 11.2 g (11.2 mmole) of triethylamine in 50 ml of ether at room temperature. The mixture was allowed to stand for 1 h, and the triethylamine hydrochloride was removed by filtration. Workup of the filtrate gave 12 g (90%) of II.

C) A solution of 3 g (24.7 mmole) of I in 25 ml of ether was added to 3.8 g (24.6 mmole) of 2-chloroethylaniline in 25 ml of ether, and the mixture was allowed to stand for 3-3.5 h. A viscous mass that gradually crystallized was formed. Treatment of it with aqueous alkali gave 4.2 g (71.5%) of II.

7-Phenyl-2,3,5,6-tetrahydroimidazo[2,1-b]thiazolium Chloride (III). A mixture of 2.8 g (23 mmole) of I and 2.8 g (23 mmole) of N-phenylethylamine was held at room temperature for 14 days, during which the contents crystallized. Treatment with hexane gave 1.7 g (30.3%) of II and 3.6 g (60%) of III with mp 80° (from acetone) (mp 75-77° [5, 6]). Found: C 51.0; H 6.0; N 11.1; S 12.4%. $C_{10}H_{13}ClN_2S \cdot H_2O$. Calculated: C 51.1; H 6.0; N 11.0; S 12.4%.

Treatment of the product with alkali, followed by acidification, gave 3-mercaptoethyl-1-phenylimidazolidin-2-one with mp 70° (from methanol) [5, 6].

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*Cryoscopy.

2,3,5,6-Tetrahydrothiazolo[2,3-b]thiazolinium Chloride (IV). A mixture of 4 g (3.3 mmole) of I, 2 g (33 mmole) of ethylene sulfide, and 0.02 g (95 mmole) of tetraethylammonium bromide was held at room temperature for 20 days and worked up to give 5.5 g (83%) of IV with mp 89-90° (from methanol–ether). (The dihydrate was reported to have mp 91-92° [7] and mp 95° [8].) Found: N 7.0; S 32.2%. $C_5H_9ClNS_2 \cdot H_2O$. Calculated: N 7.0; S 32.0%.

2-Ethyleneiminium-1,3-dithiolane Chloride (V). A mixture of 4 g (33 mmole) of I, 2g (33 mmole) of ethylene sulfide, and 0.02 g (0.19 mmole) of triethylamine was held at room temperature for 14 days, during which the contents crystallized. Workup of this mixture gave 5.6 g (77%) of V with mp 90° (from methanol–ether). Found: C 27.5; H 5.5; S 28.9%. $C_5H_8ClNS_2 \cdot 2H_2O$. Calculated: C 27.6; H 5.5; S 29.4%. $\nu_{C=N}$ 1580 cm^{-1}.

The IR spectra of KBr pellets were recorded with a UR-10 spectrophotometer.

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