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

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The reaction of 2-chloroethyl isothiocyanate 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.


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-mercaptopropanol and 2-chloroethylcarbonylamide chloride in the presence of triethylamine and also from I and 2-chloroethylenimine, 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-mercaptopropanyl)-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.

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 CS₂ [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. * C₁₃H₁₂C₂N₂S. 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-chloroethylamine in 50 ml of ether at room temperature. 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%. C₁₃H₁₅C₃N₄S·H₂O. 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].

* Cryoscopy.