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1,1′-(Thiocarbonyl)bisaziridines

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Although 1,1′-(carbonyl)bisaziridine was prepared by Bestian in 1950 (1), synthesis of 1,1′-(thiocarbonyl)bisaziridines has not yet been reported. As part of another investigation (2) it was necessary to prepare several of these sulfur analogs.

Using a slightly modified version of Bestian's method the 1,1′-(thiocarbonyl)bisaziridines (I and II) were prepared in yields of 66% and 71% respectively. It was essential to conduct these reactions at reduced temperature in order to avoid isomerization of the intermediate 1-(aziridinyl)thiocarbonyl chlorides to 2-chloroalkylisothiocyanates (2).

In contrast to the oxygen analogs, compounds I and II were very thermolabile and prone to undergo polymerization and isomerization reactions. Whereas 1,1′-(carbonyl)bisaziridine is a distillable white crystalline material which is relatively stable at temperatures under 100°, I, is a very unstable material which decomposes violently when stored at room temperature. Even in a pure state, I gradually polymerizes into a light yellow amorphous resin when stored at -18°. The life time of I could be increased by storing in a non polar solvent such as benzene or petroleum ether.

A neat sample of I was intentionally pyrolyzed by warming to its melting point (46-48°). Without resolidifying, the colorless melt decomposed exothermally within several minutes to a predominance of dark tarry material, foul smelling gas and a tan mobile liquid. N.m.r. analysis of a chloroform extract of this mixture showed that the tan liquid was mostly 2-(aziridinyl)-2-thiazoline (III). N.m.r. and infrared spectra were consistent with this structure (see Experimental) and identical to the product obtained by the iodide catalyzed isomerization of I. When I was pyrolyzed in refluxing benzene, 2-aziridinyl-2-thiazoline (III) was the major product and was accompanied by only a small amount of polymer formation. In the presence of catalytic amounts of sodium iodide, I isomerized quantitatively to III within 30 minutes at room temperature.

It was interesting to note that 1,1′-(thiocarbonyl)bis-(2-methyl)aziridine (II) was less thermolabile than I. The orange oily product could be kept at room temperature without undergoing exothermic decomposition, however, it slowly polymerized to intractable syrups after several days under these conditions. Attempts to purify this material by distillation at reduced pressure led to polymerization and isomerization products. The identity of II was well established by both n.m.r. and infrared analysis (see Experimental).

Compound II isomerized in the presence of catalytic amounts of tetrabutylammonium iodide to give the corresponding thiazoline in 38% yield. N.m.r. analysis indicated the predominance of one isomer. It is presumed that the isomerization product is 2-(2-methylaziridinyl)-4-methyl-2-thiazoline (IV) by analogy to previous work reported by Heine. (3).

Discussion

The unusual reactivity of the 1,1′-(thiocarbonyl)bisaziridine compared to the oxygen analogs can best be rationalized in terms of a highly polarized thiocarbonyl group in which the positive charge can be delocalized over both the aziridine nitrogen and the thiocarbonyl carbon as shown by V. This resonance structure contains a highly nucleophilic sulfur atom and activated aziridine moieties (4). In the neat state intermolecular nucleophilic attack on a neighboring activated aziridine ring provides a reasonable propagation scheme via VI as an explanation for the tendency of

CHART I

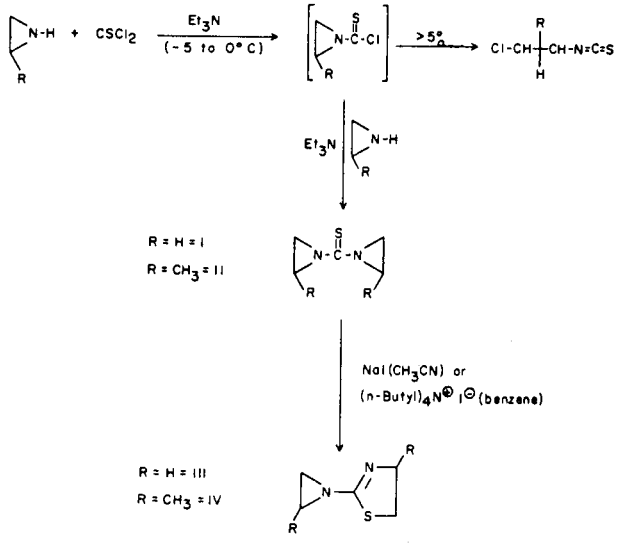
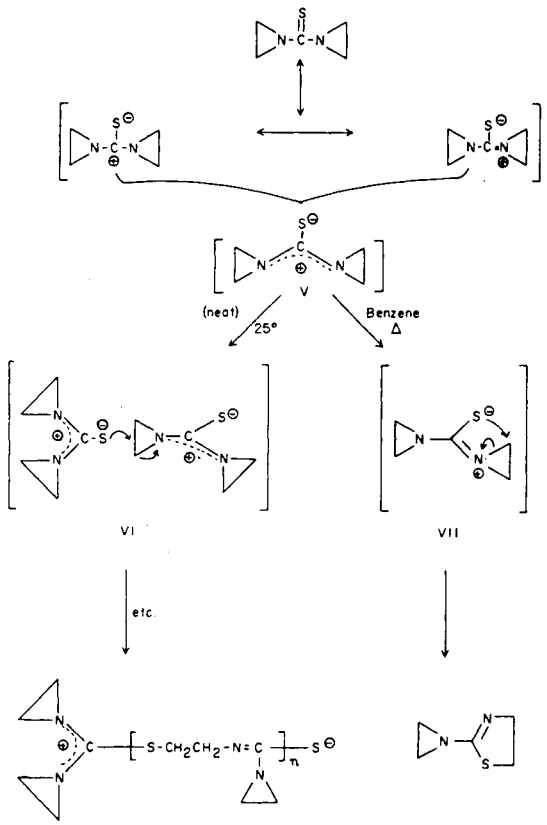
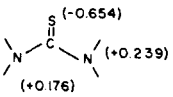


CHART II



these aziridines to undergo facile polymerization reactions. Similarly, the formation of 2-aziridinyl-2-thiazoline as the major product in the solution pyrolysis of I can be rationalized via an intramolecular transition state such as VII.

Recent LCAO MO calculations reported by Janssen (5) indicate that the thiocarbonyl group in thioureas is highly polarized and has an electron density distribution as shown below:



Janssen's work corroborates the above speculation and is consistent with the proposed resonance hybrid V.

Proton chemical shifts for 1,1′-(carbonyl)bisaziridine and 1,1′-(thiocarbonyl)bisaziridine provide further support for the above conjecture. The sulfur derivative gave a sharp singlet at -2.50 p.p.m. (perdeuterioacetonitrile) whereas the oxygen derivative displayed a singlet at -2.19 p.p.m. (perdeuterioacetonitrile). Based on the relative electronegativities of sulfur and oxygen, one would have expected the sulfur derivative to have a proton chemical shift upfield from the oxygen analog. (6) Therefore if one can assume that the thiocarbonyl group does not exhibit a deshielding anisotropic effect then the unexpected deshielding of the aziridine protons in I provides compelling evidence for the importance of the resonance hybrid, V.

EXPERIMENTAL

Nuclear magnetic resonance (n.m.r.) spectra were obtained with a Varian A-60 spectrometer. Chemical shifts are reported as δ (p.p.m.) relative to tetramethylsilane. Infrared spectra were scanned on a Perkin Elmer 337 spectrometer.

1,1′-(Thiocarbonyl)bisaziridine (I).

Aziridine, (4.3 g., 0.10 mole) and triethylamine (10.3 g., 0.10 mole) in 100 ml. of diethyl ether was added dropwise to a stirred solution of thiophosgene (5.7 g., 0.05 mole) in 150 ml. of diethyl ether at -5 to 0°. After the addition the reaction mixture was stirred at 0 to 5° for 4 hours. The triethylamine salt was filtered, followed by removal of the solvent from the filtrate with vacuum at room temperature. A low melting, light yellow solid residue was obtained which weighed 4.2 g. (66%). This product had to be kept cold and recrystallized immediately or it would decompose violently if kept at room temperature for any length of time. The crude product was recrystallized from petroleum ether (30-60°) and was obtained as nice light yellow flakes, m.p. 47-48°. The n.m.r. spectrum consisted of a sharp singlet at -2.50 p.p.m. (perdeuterioacetonitrile) and the infrared spectrum contained high frequency C-H stretching bands at 3010 cm^{-1} and 3090 cm^{-1} which are characteristic of aziridines.

Anal. Calcd. for $C_5H_8N_2S$: C, 46.8; H, 6.29; N, 21.9; S, 25.1. Found: C, 47.0; H, 6.34; N, 22.0; S, 25.2.

1,1′-(Thiocarbonyl)bis-2-methylaziridine (II).

2-Methylaziridine, (28.5 g., 0.5 mole) and triethylamine (50.5 g., 0.5 mole) in 250 ml. of diethyl ether was added dropwise to a stirred solution of thiophosgene (28.75 g., 0.25 mole) at -5 to 0°. The addition was carried out over a period of 4 hours. After the addition was complete the reaction mixture was stirred for 1-2 hours while maintaining the temperature under 0°. The triethylamine salt was filtered off and solvent was removed from the orange colored filtrate by using vacuum at room temperature. An orange colored liquid residue was obtained which weighed 28.3 g. (71%). This material gave an n.m.r. spectrum which consisted of a doublet at -1.40 p.p.m., a doublet at -2.31 p.p.m. and a multiplet at -2.31 to -3.03 p.p.m. (deuteriochloroform). Proton integration was consistent with the proposed structure and the ratio in the order given above was 3:1:2. A C-H stretching band characteristic of aziridine rings occurred at 3075 cm^{-1}. Attempts to distill this product under reduced pressure caused the oil to transform into a polymeric syrup in the distillation flask.

2-Aziridinyl-2-Thiazoline (III).

(A) Isomerization of (I) with Sodium Iodide (Acetonitrile).

To a solution of (I), (10 g. in 75 ml. of anhydrous acetonitrile), was added 100 mg. of anhydrous sodium iodide. This solution was allowed to stand at room temperature (*c.a.* 25°) for 12 hours. Solvent was removed at room temperature under reduced pressure leaving a light amber liquid residue. Fractionation of this product gave 7.5 g. of a colorless liquid, b.p. 47.5-48°/1 mm. The n.m.r. spectrum was consistent with the proposed thiazoline structure and consisted of a singlet at -2.14 p.p.m. and an A_2X_2 pattern with multiplets centered at -3.29 p.p.m. and -3.96 p.p.m. (carbon tetrachloride). A (-C=N-) absorption band characteristic of the 2-thiazoline ring (7) was noted at 1620 cm^{-1} (neat).

Anal. Calcd. for $C_5H_8N_2S$: C, 46.8; H, 6.29; N, 21.9. Found: C, 46.6; H, 6.15; N, 21.6.

The above isomerization was followed by n.m.r. spectroscopy. A sample was prepared by dissolving 300 mg. of I and 10 mg. of sodium iodide (anhydrous) in 1 ml. of perdeuterioacetonitrile. A slight increase in temperature was noted upon combining these reagents. Periodic scanning (25°) showed that the singlet at -2.50 p.p.m. for I was disappearing as a new upfield singlet at -2.16 p.p.m. and a downfield A_2X_2 pattern with multiplets centered at -3.35 and -3.98 p.p.m. were developing. Under these conditions the isomerization was complete and quantitative in 20-30 minutes.

(B) Solution Pyrolysis of I.

A solution of I (200 mg.) in 10 ml. of benzene (A.R. grade) was refluxed for 20 hours. The reaction mixture changed from colorless to a light yellow color. The solvent was then removed under vacuum at room temperature to give a light yellow cloudy oil. N.m.r. and infrared spectra of this product showed that I was completely pyrolyzed to 2-aziridinyl-2-thiazoline and a small amount of polymeric material.

(C) Neat Pyrolysis of I.

A sample of I, m.p. 46-48° (300 mg.) was placed in a Carius combustion tube and left unsealed. The sample was warmed until a colorless melt was obtained. Without resolidifying the sample decomposed within 10 minutes to a brown-black tar, some foul smelling gas and a tan colored mobile oil which condensed on the walls of the tube. Chloroform was added to the tube and the solution was analyzed by n.m.r. A spectrum was obtained consisting of a singlet at -2.23 p.p.m. and an A_2X_2 pattern with multiplets centered at -3.36 and -4.05 p.p.m. An infrared spectrum of this material contained an intense band at 1620 cm^{-1} (-N=C-) and high frequency C-H stretching bands at 3010 cm^{-1} and 3080 cm^{-1} characteristic of aziridines.

2-(2-Methylaziridinyl)-4-methyl-2-thiazoline (IV).

Immediately after isolating II, 18 g. of this product was dissolved in 75 ml. of anhydrous benzene (A.R. grade). To this solution was added 200 mg. of *n*-tetrabutylammonium iodide. The stoppered reaction mixture was allowed to stand at room temperature (about 23-25°) for 3 days. Solvent was removed under reduced pressure at room temperature, leaving an orange-yellow oil residue. The crude product was fractionated to give a major cut, b.p. 102-105° /1.5 mm., 6.8 g. (38%). The n.m.r. spectrum for this product was consistent for the proposed product and contained superimposed doublets at -1.17 to -1.42 p.p.m., a doublet centered at -1.89 p.p.m., multiplet at -2.18 to -2.54 p.p.m., a multiplet at -2.70 to -3.56 p.p.m., and a quartet at -4.06 to -4.47 p.p.m. in a ratio of 1:2:2:1:6 (carbon tetrachloride). The infrared spectrum contained an intense band at 1615 cm^{-1} (-N=C-).

Anal. Calcd. for $C_7H_{12}N_2S$: C, 53.8; H, 7.74; N, 17.93. Found: C, 53.5; H, 7.62; N, 17.69.

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