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1-(Aziridine)thiocarbonyl Chlorides.

Isomerization to 2-(Chloroalkyl)isothiocyanates

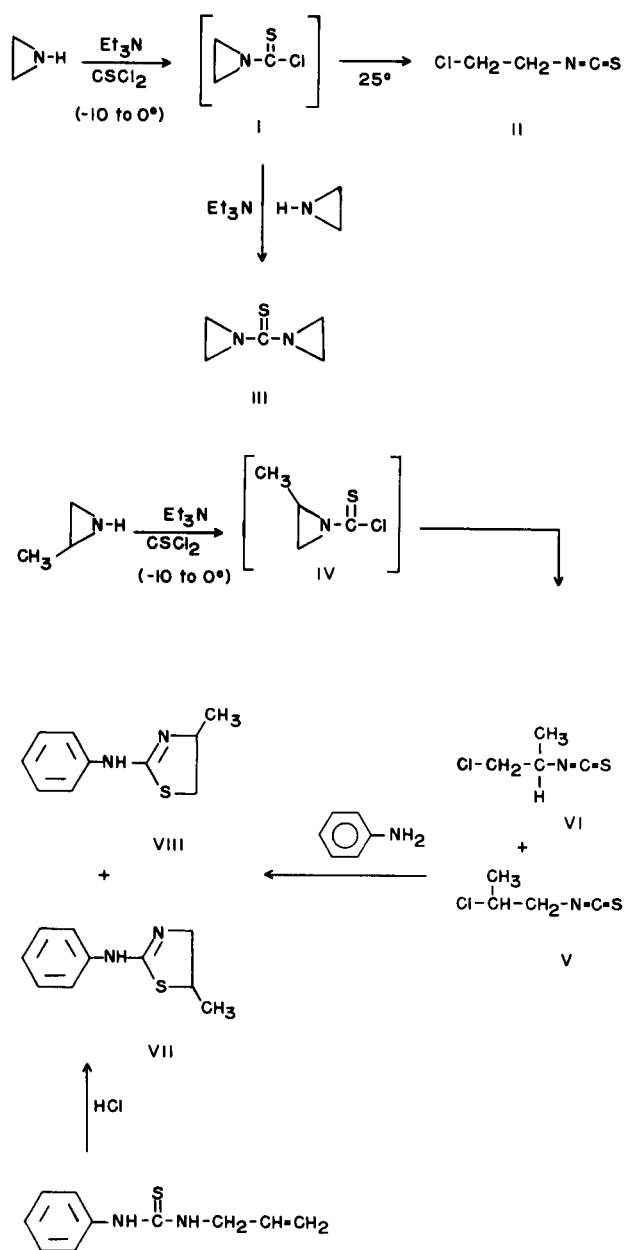
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Sir:

1-(Aziridine)thiocarbonyl chloride (I) was reportedly isolated (1) as a stable compound melting at 125-126°, by allowing equimolar amounts of aziridine and triethylamine to react with thiophosgene (2). This structure assignment was based solely on an elemental analysis. In our hands, attempts to reproduce this work invariably resulted in the formation of 2-chloroethyl isothiocyanate (II) and an unidentified polymer. Further work showed that I was in fact a thermolabile material which, however, could be trapped and characterized in solution at reduced temperatures.

A typical preparation consisted of dropping a solution of aziridine (2.65 g., 0.05 mole) and triethylamine (5.05 g., 0.05 mole) in 100 ml. of carbon tetrachloride or diethyl ether into a rapidly stirred solution of thiophosgene (5.7 g., 0.05 mole) in 125 ml. of the same solvent at temperatures of -10 to 0°. After stirring for 0.5 hour at this temperature, the amine salt was rapidly removed by filtering into a precooled flask (-10 to 0°). A sample of the brilliant canary yellow filtrate was rapidly scanned by infrared between 2500-1250 cm^{-1} , disclosing a medium intensity band at 1690 cm^{-1} (diethyl ether). Allowing this sample to stand at room temperature for several hours resulted in the gradual disappearance of this band, and the appearance of a high intensity band at 2105 cm^{-1} which is characteristic of alkyl isothiocyanates (3).

A carbon tetrachloride solution of I was examined by nmr spectroscopy at a probe temperature of -15° and was found to consist of a major singlet at -2.73 ppm and usually a minor singlet at -2.45 ppm due to the presence of small amounts of III (Fig. I, A). Addition of another equivalent of aziridine and triethylamine caused the complete disappearance of the downfield singlet and an enhancement of the upfield singlet at -2.45 ppm which is presumably consistent with the conversion of I to III (Fig. I, C). By warming the sample up to room temperature (*ca.* 25°), the isomerization of I to II could be followed by observing the disappearance of the singlet at -2.73 ppm accompanied by the appearance of an A_2B_2 pattern centered at -3.75 ppm (Fig. I, B and D). Under these conditions the isomerization was usually complete in 18-20 hours and was invariably accompanied by some polymer formation. Distillation of the reaction mixture gave a 45-50% yield



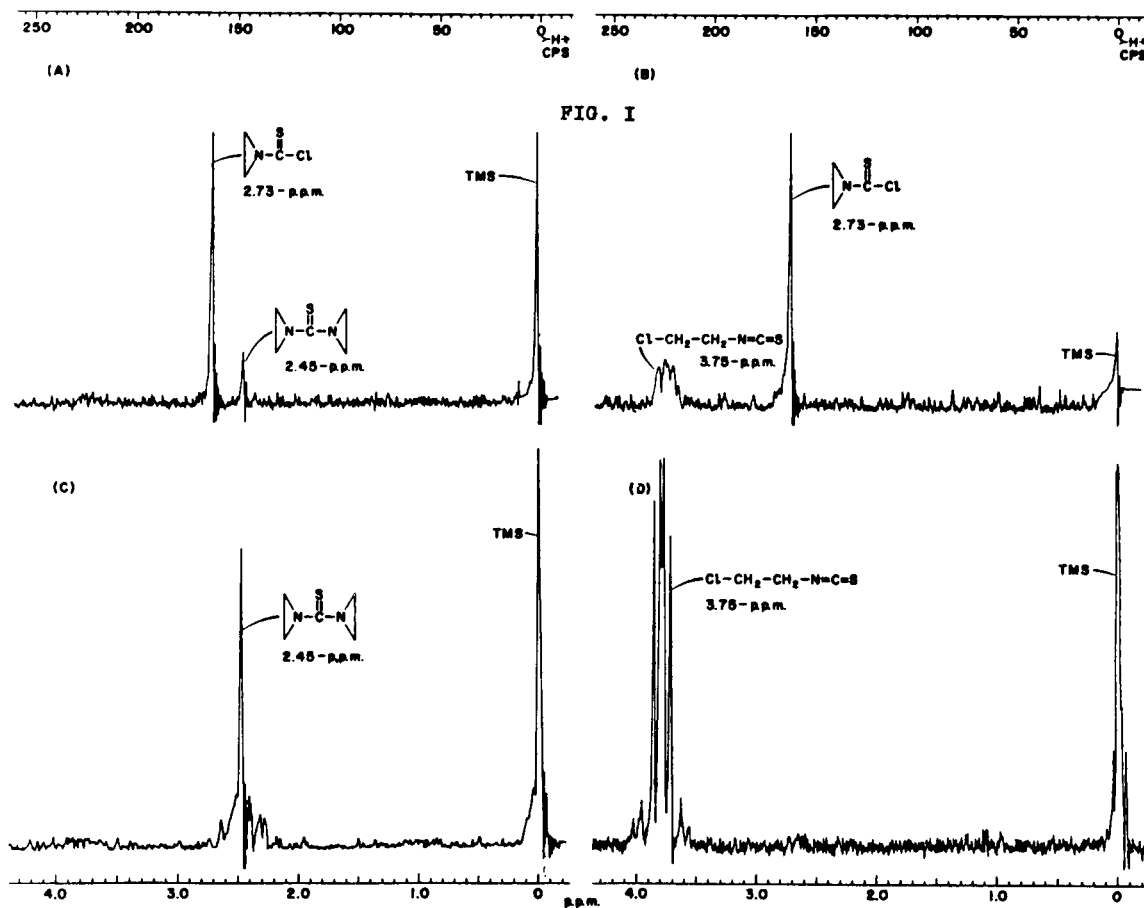


FIG. I

of a colorless oil, b.p. 58-60°/6 mm.

Anal. Calcd. for C_3H_4ClNS : C, 29.63; H, 3.31; N, 12.55. Found: C, 29.40; H, 3.15; N, 12.33. The infrared and nmr spectra were identical to the spectra obtained for an authentic sample of II prepared by an alternate method (4).

In a similar manner 1-(2-methylaziridine)thiocarbonyl chloride (IV) was prepared and characterized at -10° . The nmr spectrum (carbon tetrachloride) consisted of a doublet at -1.50 ppm (CH_3-) as well as a doublet and a multiplet at -2.54 and -2.98 ppm, respectively, for the ring protons. The proton ratio in the order given above was 3:1:2.

Allowing a carbon tetrachloride solution of IV to stand for 20 hours at 25° resulted in complete isomerization, according to nmr analysis. The crude reaction mixture contained a slight predominance of 2-chloropropyl isothiocyanate (V) (55-60%) with a lesser amount of VI (40-45%). An nmr spectrum of the crude isomer mixture in carbon tetrachloride consisted of a complex multiplet at -4.35 to -3.46 ppm (methine and methylene protons) as well as two partially overlapped doublets at -1.62 and -1.49 ppm (methyl protons). The methine, methylene to methyl proton ratio was 1:1. Because of the partially overlapped doublets, integration gave only an approximate value for the ratio of isomeric isothiocyanates, however, it was very evident that the doublet at lower

field predominated. The isomer mixture distilled at $63-65^\circ$ 6 mm. and was obtained as a pale yellow oil in 50% yield. Nmr analysis indicated that this distillate contained ~85% of V and ~15% of VI.

Anal. Calcd. for C_4H_6ClNS : C, 35.41; H, 4.46; N, 10.04. Found: C, 35.33; H, 4.31; N, 9.89. Treatment of the distillate with aniline gave an 86% yield of a tan solid (m.p. $84-95^\circ$) consisting of 1-anilino-5-methyl-2-thiazoline (VIII) (~85%) and 2-anilino-4-methyl-2-thiazoline (VIII) (~15%). An nmr spectrum of this mixture in deuteriochloroform contained complex multiplets at -7.45 to -6.80 ppm (aromatic protons and NH) and at -4.14 to -2.76 ppm (methine and methylene protons) as well as two slightly overlapping doublets centered at -1.40 and -1.24 ppm (methyl protons). The ratio of these protons in the order described was 2:1:1. Integration of the methyl proton resonance bands showed that the lower field doublet (-1.40 ppm) predominates and is present in a ratio of 85:15 with the higher field doublet. The lower field doublet was assigned to 2-anilino-5-methyl-2-thiazoline (VII). This assignment was well established by comparing the nmr spectrum of the mixture with that obtained for an authentic sample of VII which had been prepared by the reaction of *N*-allyl-*N'*-phenylthiourea with concentrated hydrochloric acid (5). Separation of the isomeric 2-thiazolines was accomplished by ex-

tracting the mixture with petroleum ether (30-60°). The more insoluble and major component (VII) was obtained as a white crystalline material melting at 112-114°. This product gave an undepressed admixture melting point with an authentic sample of VII as well as nmr and infrared spectra which were identical to those obtained for authentic VII.

The reaction of equimolar amounts of aziridines and thiophosgene in the absence of an external acid acceptor, such as triethylamine, also led to 2-chloroalkyl isothiocyanates in 45-50% yields. In these cases the aziridine absorbs two equivalents of hydrogen chloride to produce 2-chloroalkylamine salts as the accompanying product. The intermediacy of 1-(aziridine)thiocarbonyl chlorides is suspected in these reactions, but it has not yet been demonstrated.

Acknowledgment.

The author is indebted to Dr. R. M. Stiles and Dr. H. Walborsky for helpful discussions.

REFERENCES

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- (2) Although this product could not be obtained in our hands, it is possible that these workers isolated a trimer of 2-chloroethyl isothiocyanate which would account for their elemental analysis.
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Received July 18, 1966

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