

The By-product Formed in the Ammonolysis of 2-Thenyl Chloride in Liquid Ammonia

Tyo SONE

Department of Applied Chemistry, Faculty of Engineering

(Received September 30, 1978)

Abstract

The by-product which is formed together with the expected amines in the ammonolysis of 2-thenyl chloride in liquid ammonia has been identified as bis[di-(2-thenyl)amino]methane.

Introduction

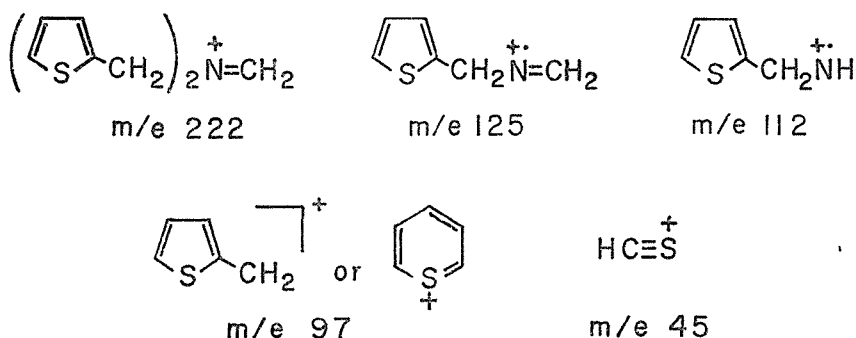
Alkyl and aralkyl halides undergo ammonolysis in liquid ammonia with the formation of primary, secondary, and tertiary amines. The ease of the reaction and the product distribution largely depend upon the structure of the halide and the reaction conditions employed. We previously reported that 2-thenyl chloride (1) reacted readily with liquid ammonia at room temperature to produce 2-thenylamine (2), di(2-thenyl)amine (3), and small amounts of crystalline materials which consisted of tri(2-thenyl)amine (4) and an unknown compound (5).¹⁾ The molecular weight (near 418) determined by Rast method suggested that the unknown product contained four (2-)thenyl units in its molecule, but the structure has remained to be established. This report is a supplement to the previous one and concerned with the identification of 5.

Results

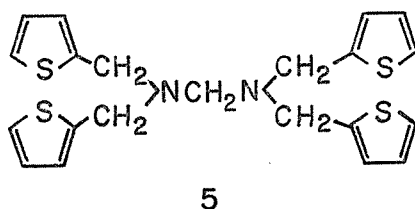
Elemental analysis and the formation of the hydrochloride suggested that 5 was an amine; the lack of the absorption bands in the $3300\text{--}3500\text{ cm}^{-1}$ region in the ir spectrum eliminates primary and secondary amines.

The mass spectrum of 5 exhibited prominent peaks at m/e 222 (relative intensity 20%), 221 (12), 125 (17), 124 (8), 112 (26), 97 (100), 85 (8), 53 (7), and 45 (10). The peak of highest mass number 222 (except for the isotope peaks) should not be that of the molecular ion, but that of a fragment ion. If

the peak at m/e 222 corresponds to the molecular ion, **5** must contain an even number of nitrogen atoms and the nitrogen content must be more than at least 12%, but this is appreciably different from the found value. Furthermore, it does not agree with the molecular weight determined by Rast method. The molecular ion peak is frequently undetectable in highly branched aliphatic amines. Thus, the main peaks must represent the following fragments.



The nmr spectrum (90 MHz; CCl_4 solution) is simple, indicating that the molecule is rather symmetrical; it shows a multiplet (δ 6.7-7.2) arising from the ring protons and two singlets (δ 3.93 and 3.27) with a relative intensity of 6:4:1. The singlet at the low field-side is apparently ascribable to the methylene protons of the 2-thenyl moiety attached to nitrogen atom.²⁾ The high-field singlet can be assigned to two protons of another methylene group attached to two nitrogen atoms, considering its position and relative intensity as well as the mass spectral fragments. These facts are compatible with structure **5**, which was finally established by comparison of the spectral data and the melting point with those of an authentic sample synthesized by the reaction of **3** with aqueous formaldehyde in the presence of sodium hydroxide.



When the reaction was carried out in the presence of ammonium chloride, **5** was not formed; such was also the case with the ammonolysis of **1** in liquid ammonia-methanol or in liquid ammonia-diethylether.¹⁾ These findings may provide a clue to the reaction pathway leading to **5**.

SONE : The By-product Formed in the Ammonolysis of 2-Thenyl Chloride
in Liquid Ammonia

Although it has little preparative value and the mechanism is not clear at this stage, the formation of **5** is of interest in connection with the reactivity of **1** and with the behavior of the thenyl group in 2-thenylamino group in the base-induced reactions.

Experimental

All melting and boiling points are uncorrected. The ir, nmr (90 MHz; TMS as an internal reference) and mass spectra (70 eV) were obtained on Hitachi EPI-S 2, Hitachi R-22, and Hitachi RMU-6 spectrometers, respectively.

*Ammonolysis of 2-Thenyl Chloride (1) in Liquid Ammonia.*¹⁾ The reaction was carried out in the glass pressure tube (capacity, about 80 ml) with a stopcock and metal joints (Fig. 1). The chloride (10 g) was placed in the tube and the

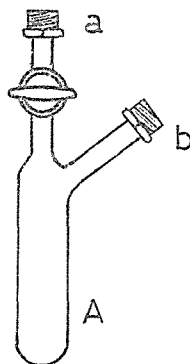


Fig. 1

joint **b** was closed. The tube was evacuated with water pump and cooled with ice-salt bath. Another pressure tube containing liquid ammonia was connected to the joint **a** and the cock was opened to let liquid ammonia (20 ml) introduce into the tube **A** containing **1**. Then the cock was closed and the pressure tubes were disconnected. The chloride was dissolved in a colorless solution with shaking and the mixture was allowed to stand at room temperature. An exothermic reaction occurred within 30 min and a suspension was produced. The solution finally separated in two layers. After 3 hr ammonia gas was evaporated off, and water (15 ml) and sodium hydroxide (4 g) were added to the residue. After extraction with ether and usual work-up the residual oil was distilled under reduced pressure to give 2-thenylamine (**2**; bp 81-83°C/17 mmHg; 3.4g, 40%) and di(2-thenyl)amine (**3**; bp 130-136°C/3 mmHg; 3.1 g, 39%). Fractional recrystallization of the residual mass from alcohol yielded two colorless crystalline materials, tri(2-thenyl)amine (**4**; mp 74.5-75.5°C; 0.15 g, ~2%) and bis-

[di(2-theny)-amino]methane (**5**; mp 116-117°C; 0.6 g, 7.5%).

5: Mol. Wt. 418 (Rast method). Found: C, 58.28; H, 5.23; N, 6.45; S, 29.58%. Calcd for $C_{21}H_{22}N_2S_4$: C, 58.56; H, 5.14; N, 6.50; S, 29.78%. Hydrochloric acid salt: mp 237°C (dec.). Found: N, 5.51%. Calcd for $C_{21}H_{24}Cl_2N_2S_4$: N, 5.56%.

Preparation of 5 by the Reaction of 3 with 40% Aqueous Formaldehyde. The method used here is virtually identical with that described by von Braun and Röver for the preparation of the corresponding benzyl derivative.³⁾ The amine (**3**; 1 g) was added to the ice-cooled 40% aqueous formaldehyde with swirling. Solid mass was formed within 1 hr, which was collected by filtration and recrystallized from alcohol to afford **5** as colorless crystals (mp 117-118°C, 0.5 g). The ir and nmr spectra were identical with those of **5** obtained by the ammonolysis of **1** in liquid ammonia, and the mixture melting point was not depressed.

The author is grateful to Nissei Sangyo Co. Ltd. for the mass spectrum.

References

- 1) Y. Matsuki and T. Sone, *J. Chem. Soc. Jpn., Ind. Chem. Sec.* (Kogyo Kagaku Zasshi), **63**, 834 (1960).
- 2) For example, K. Takahashi, T. Sone, Y. Matsuki, and G. Hazato, *Bull. Chem. Soc. Jpn.*, **36**, 108 (1963).
- 3) J. v. Braun and E. Röver, *Ber.*, **36**, 1196 (1903).

SONE : The By-product Formed in the Ammonolysis of 2-Thenyl Chloride
in Liquid Ammonia

液体アンモニアによる 2-テニルクロリドの 加アンモニア分解の副生成物

曾 根 澄

工学部 応用化学科

著者らは以前に2-テニルクロリドを液体アンモニアと室温で反応させた際に、予期した2-テニルアミン類とともに、窒素を含む構造不明の生成物が少量副生することを認めたがこの副生成物がビス[ジ(2-テニル)アミノ]メタンであることを確かめた。