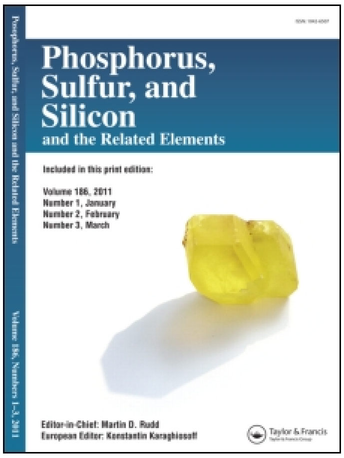

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SYNTHESIS AND MASS SPECTRAL CHARACTERIZATION OF DIISOPROPYLAMINO-ETHANETHIOL, -SULFIDES AND -DISULFIDES AND VINYL SULFIDES

D. K. Rohrbaugh[a]; F. J. Berg[a]; L. J. Szafraniec[a]; D. L. Rossman[a]; H. D. Durst[a]; S. Munavalli[b]
[a] U.S. Army, Edgewood Research Development and Engineering Center, Aberdeen Proving Ground, MD [b] Geo-Centers, Inc., Aberdeen Proving Ground, MD

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SYNTHESIS AND MASS SPECTRAL CHARACTERIZATION OF DIISOPROPYLAMINO-ETHANETHIOL, -SULFIDES AND -DISULFIDES AND VINYL SULFIDES

D. K. ROHRBAUGH[a], F. J. BERG[a], L. J. SZAFRANIEC[a],
D. I. ROSSMAN[a], H. D. DURST[a] and S. MUNAVALLI[b]*

[a]*U.S. Army, Edgewood Research Development and Engineering Center, Aberdeen Proving Ground, MD 21010 and and* [b]*Geo-Centers, Inc., Gunpowder Branch, P.O. Box 68, Aberdeen Proving Ground, MD 21010*

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The sulfur containing chemical agent, O-ethyl-S-2-(diisopropylaminoethyl) methylphosphonothiolate (VX), is an extremely potent inhibitor of the enzyme acetylcholinesterase and exhibits extended neurological effects. It undergoes degradation on standing alone or in the environment. Hence, identification of its primary degradation products assumes considerable importance. The synthesis and mass spectral fragmentation behavior of the title compounds, some of which are present in the VX degradation products, has not received much attention. This communication describes the synthesis and mass spectral characterization of the title compounds.

Keywords: Vinylsulfides; Sulfur Containing Ethylenes; GC-MS-CI and -EI; Free Radical Mechanism; VX Degradation Products

INTRODUCTION

Sulfur containing compounds occur ubiquitously in nature. Since the presence of sulfur in the molecule modifies its biological profile and potency, considerable interest has been evinced in the chemistry and synthesis of sulfur containing compounds[1]. Reactions using elemental sulfur are common and are frequently employed in the synthesis of substituted sulfides,

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* Correspondence Author.

although a complex mixture of products are usually formed[2]. The reaction of Grignard reagents with sulfur generally furnishes thiols and sulfides[1b]. Acetylene also reacts with thiols to yield vinyl sulfides [3].

Several of the organophosphorus compounds are known toxic agents and act as inhibitors of acetylcholinesterase (**AChE**), which is intimately involved with the transmission of nerve impulses. Hence, compounds of this type possess potential military application as Chemical Warfare (**CW**) agents[4]. Though the stockpile of CW agents is being destroyed under the treaty protocol, there is a definite need in the present uncertain global political climate to develop analytical methodology to accurately detect and characterize CW agents and/or their breakdown products. Of the currently available CW agents, the one containing the dialkylaminoethylthiyl moietiy, O-ethyl-S-(2-diisopropylaminoethyl) methylphosphonothiolate, commonly known as **VX,** is the most potent inhibitor of AChE. It often exhibits lethal and extended incapacitating effects. VX appears to be not quite stable, for it has been shown to undergo degradation on standing[5]. It is possible that some of its breakdown products themselves are toxic. The phosphorus-sulfur bond of VX is known to be cleaved under alkaline conditions [6]. A more detailed study of the aqueous hydrolysis of VX over the entire pH range has shown that the phosphorus-sulfur, sulfur-carbon and carbon-oxygen bonds are cleaved simultaneously[7]. Ethyl methylphosphonic acid, diisopropylaminoethyl methylphosphonic acid, diisopropylaminoethyl mercaptan, bis(diisopropylaminoethyl) sulfide and ethyl methylphosphonothioic acid have been identified as the products of hydrolysis[7]. The postulated mechanism endeavors to account for the cleavage of the phosphorus-sulfur, sulfur-carbon and carbon-oxygen bonds. Although the mass spectral analysis of the CW agents has been briefly reported[8], the mass spectral fragmentation behavior of the title compounds, some of which trace their origin to VX, has not been discussed in detail so far. This communication attempts to fill this need.

RESULTS AND DISCUSSION

GC-MS-EI is often used for the characterization of the CW agents, particularly the organophosphorus compounds[8,10]. However, very little information is available about the nature and identity of the degradation products of CW agents[2, 8a]. Not frequently is this information verified via the synthesis of the supposed breakdown products. This observation assumes greater significance when viewed against the background that the degradation products and their parent compounds exhibit similar mass spectral fragmentation behavior and often the molecular ion peaks of the parent organophosphorus compunds are not seen[8a, 8g]. This communication describes the synthesis and the mass spectral characterization of some of the VX degradation products.

The mass spectral fragmentation of alkyl thiovinyl ethers, in particular that of n-heptylvinyl sulfide, has been reported[9]. The ions resulting from the loss of alkyl, radicals, hydrocarbon ions and a strong m/z=60 peak have been cited as the characteristic feature of its fragmentation. Hydrogen transfers are also seen during fragmentation of this type of compounds. In all, **24** compounds were detected in an aged sample of **VX**[8a]. Of these, only two compounds, 1,3-dicyclohexylurea and 1,3-dicyclohexylthiourea can be safely discarded as not arising from the decomposition of **VX.** The structures of two more have not been characterized as yet[8a].

The thermal decomposition of **VX** has been previously examined[11]. It has been claimed that: (a) 2-diisopropylaminoethanethiol (**11**). (b) bis(2-diisopropylaminoethyl) sulfide (**5**), bis[2-(diisopropylaminoethyl)] disulfide (**13**) and O-ethyl-O-[2-diisopropylaminoethyl methylphosphonate are among the products of thermal decompostion[12]. VX per se has been subjected to both GC-MS-EI and -CI analysis [8a and 8g]. In general, the molecular ion peaks were not seen in the GC-MS-EI spectra. A similar observation has been made by others[8a]. The ions corresponding to m/e=167, 127, 114 (100%), 85, 84, 79, 72 and 70 are seen in the GC-MS-EI spectra of VX, although no molecular ion peak was seen. However, with GC-MS-CI, $M^+$was the most intense peak followed by M-1, M-CH_3, 141, 127 and 114 ions[8g]. VX was found to readily lose the -$N(C_3H_7)_2$ moiety. It also yielded a significant peak at m/e=141 [$CH_3P(OH)(SH)(OC_2H_5)$]. The mass spectral breakdown of 2-(diisopropylamino)ethanethiol (**11**), has been described[13]. Two ions m/e=128 and 114 corresponding to [$(C_3H_7)_2(C_2H_4)N$] and [$(C_3H_7)_2NCH_2$], are prominently present in the mass spectra of the compounds examined by us. **Table I** gives GC-MS-EI and -CI mass spectral fragmentation of the compounds cited in the experiemental section. Often observed is the M-CH_3 ion. Also seen are the 102, 100, 86 and 61 peaks corresponding to the ions $H_2N(C_3H_7)_2$, $H_2N(C_3H_7)$ (C_3H_5), 86 (C_4H_8S or $C_3H_7NHC_2H_4$) and 61 (SC_2H_5) respectively. However, the peaks at m/e= 162 and 160 arise from the fragmentation of the 2-diisopropylaminoethanethiol moiety.

TABLE I Mass Spectral Fragmentation of Compounds Cited in the Text

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A: GC-MS-CI

1. 2-Diisopropylaminoethyl bromide (**4**): M^+= 208 (M+H); 192 (M-CH_3); 166 (M-C_3H_5); 128 (M-Br or [$(C_3H_7)_2(C_2H_4)N$], 100%); 114 (128-CH_2) and 86 $C_3H_7NC_2H_5$).

2. 2-Diisopropylaminoethanethiol (**11**): M^+=162 [(M+H), 100%]; 146 (M-CH_3); 128 [M-SH or [$(C_3H_7)_2(C_2H_4)N$]; 120 (M-C_3H_5); 114 (128-CH_2); 102 [$(C_3H_7)_2NH_2$]; 89 (146-NC_3H_7); 73 ($H_2N.CH_2.C_3H_7$); and 61 (C_2H_5S)

3. (2-Diisopropylaminoethyl) vinyl sulfide (**1**): M^+=188 [(M+H), 100%); 172 (M-CH_3); 146 (M-C_3H_5); 128 [$(C_3H_7)_2(C_2H_4)N$]; 114 (128-CH_2) and 87 (NSC_3H_5).

4. Bis(2-Diisopropylaminoethyl) disulfide (**13**): M^+=321 (M+H); 305 (M-CH_3); 289 (305-CH_4); 207 [$(C_3H_7)_2NC_2H_4S_2CH_3$]; 175 [$N(C_3H_7)(C_2H_4)$ SCH_3]; 160 [$(C_3H_7)_2NC_2H_4S$. 100%]; 144 [$(C_3H_7)C_2H_3NC_2H_4S$]; 128 [$(C_3H_7)_2(C_2H_4)N$]; 114 [$(C_3H_7)_2NCH_2$]; 102 [$(C_3H_7)_2NH_2$]; 87 (NSC_3H_5) and 61 (SC_2H_5).

5. (2-Diisopropylaminoethyl) vinyl disulfide (**14**): M^+=220 (M+H); 204 (M-CH_3); 160 (M-SC_2H_3, 100%); 128 [$(C_3H_7)_2(C_2H_4)N$]; 119 (160- C_3H_5); 114 (128-CH_2); 101 [(C_3H_7) (C_3H_6) NH_2] and 61 (C_2H_4SH).

6. (2-Diisopropylaminoethyl) vinyl trisulfide (**15**): M^+=252 (M+H); 236 204 (M-CH_3); 160 (M-$S_2C_2H_3$); 151 (M-$(C_3H_7)_2N$); 128 [$(C_3H_7)_2(C_2H_4)N$]; 114 (128-CH_2); 101 [(C_3H_7) (C_3H_6) NH_2]; 89 (146-NSC_3H_7); 73 (NSC_2H_3) and 61 (C_2H_5S. 100%).

7. Bis(2-Diisopropylaminoethyl) sulfide (**5**): M^+=289 [(M+H), 100%]; 273 (M-CH_3); 188 [M-$(C_3H_7)_2N$]; 175 [$N(C_3H_7)(C_2H_4)SCH_3$]; 160 [$(C_3H_7)_2NC_2H_5S$]; 128 [$(C_3H_7)_2(C_2H_4)N$]; 114 [$(C_3H_7)_2NCH_2$]; and 86 ($C_3H_7NHC_2H_4$).

8. (2-Diisopropylaminoethylthio)(ethylthioethyleno) vinyl sulfide (**6A**or **6B**); M^+=306 (M+H); 246 (M-SC_2H_3); 188 (246-SC_2H_2); 160 (188-C_2H_4); 144 [$(C_3H_7)_2NC_2H_4S$ or $(CH_2CHS)_2C_2H_2$]; 128 [$(C_3H_7)_2(C_2H_4)N$]; 114 [$(C_3H_7)_2NCH_2$]; 100 [$(C_3H_7)(C_3H_5)NH_2$]; 86 ($C_3H_7NHC_2H_4$); 77 ($H_2NC_2H_4SH$); 65 (S_2H) and 61 ((SC_2H_5, 100%). This compound could be either the cis-or the trans isomer. Based on the fragmentation alone, it wasn't possible to decide which one it is.

9. Bis[2-(Diisopropylamino)ethylthio]ethylene (**7A** or **7B**): M^+= 347 (M+H); 220 [$(C_3H_7)SC_2H_4SC_2H_2SH_2$]; 188 [$(C_3H_7)_2SC_2H_2$]; 160 [$(C_3H_7)_2NC_2H_4S$]; 144 [$(C_3H_7)C_2H_3NC_2H_4S$]; 119 ($HSC_2H_2SC_2H_4$); 114 [$(C_3H_7)_2NCH_2$,100%]; 102 [$(C_3H_7)_2NH_2$]; 89 ($C_2HS_2$); 86 ($C_4H_8S$ or $C_3H_7NHC_2H_4$); 72 ($CH_3NHC_3H_6$); 70 ($C_3H_5NHCH_2$); and 60 (C_2H_4S).

10. Bis[2-(Diisopropylamino)ethylthio] ethylene (**7A** or **7B**): M^+= 347 (M+H); 331(M-CH_3); 220 [$(C_3H_7)SC_2H_4SC_2H_2SH_2$]; 188 [$(C_3H_7)_2SC_2H_2$]; 160 [$(C_3H_7)_2NC_2H_4S$]; 144 [$(C_3H_7)C_2H_3NC_2H_4S$]; 119 ($HSC_2H_2SC_2H_4$); 114 [$(C_3H_7)_2NCH_2$,100%]; 102 [$(C_3H_7)_2NH_2$]; 89 ($C_2HS_2$); 86 ($C_4H_8S$ or $C_3H_7NHC_2H_4$); 72 ($CH_3NHC_3H_6$); 70 ($C_3H_5NHCH_2$); and 60 (C_2H_4S). Compounds **7A** or **7B** are cis- and trans-isomers.

11. [2-(Diisopropylaminoethylthio)(ethylthio)][2-(diisopropylamino) ethyl-thio]ethylene (**8A** or **8B**): M^+=407 (M+H); 347 (M-C_2H_3S); 280 [$H_2SC_2H_4SC_2H_2SC_2H_4$-$N(C_3H_7)_2$]; 246 (280-H_2S); 220 ($(C_3H_7)_2N$ $C_2H_4SC_2H_2SH_2$); 128 [$(C_3H_7)_2(C_2H_4)N$]; 114 [$(C_3H_7)_2NCH_2$,100%]; 100 [($(C_3H_7)(C_3H_5)NH_2$]; 86 (C_4H_8S or $C_3H_7NHC_2H_4$); 77 ($H_2NC_2H_4SH$); 70 ($C_3H_5NHCH_2$); and 61 ((SC_2H_5,).

12. [2-(Diisopropylaminoethylthio)ethylthio] [2-(diisopropylaminoethylthio] ethylene (**8A** or **8B**): M^+=407 (M+H); 347 (M- C_2H_3S); 280 [$H_2SC_2H_4SC_2H_2SC_2H_4$-$N(C_3H_7)_2$]; 246 (280-H_2S); 220 ($(C_3H_7)_2N$ $C_2H_4SC_2H_2SH_2$); 128 [$(C_3H_7)_2(C_2H_4)N$]; 114 [$(C_3H_7)_2NCH_2$,100%]; 100 [$(C_3H_7)(C_3H_5)NH_2$]; 86 (C_4H_8S or $C_3H_7NHC_2H_4$); 77 ($H_2NC_2H_4SH$); 70 ($C_3H_5NHCH_2$) and 61 (SC_2H_5). Compounds **8A** or **8B** are cis- and trans-isomers.

13. [2-Diisopropylaminoethylthioethyl][2'-diisopropylaminoethyl]disulfide (**9**): M^+=381 [(M+H), 100%]; 365 (M-CH_3); 321 (M-SC_2H_4); 253 (M-$(C_3H_7)_2NC_2H_4$); 222 [M-$SC_2H_4N(C_3H_7)_2$]; 207 [M-$N(C_3H_7)_2$)]; 188 [$C_2H_4SC_2H_4$ $N(C_3H_7)_2$]; 175 [$CH_3SC_2H_4$-$N(C_3H_7)_2$]; 162 [$HSC_2H_4HN(C_3H_7)_2$]; 160 [$SC_2H_4N(C_3H_7)_2$]; 146 [$HSC_2H_4HN(C_3H_7)(C_2H_3)$]; 128 [$(C_3H_7)_2(C_2H_4)N$]; 114 [$CH_2N(C_3H_7)_2$]; 101 [$(C_3H_7)$ (C_3H_6) NH_2]; 86 (C_4H_8S or $C_3H_7NHC_2H_4$) and 61 ((SC_2H_5).

14. (2-Diisopropylaminoethylethylthio) ethanethiol (**12**): M^+=222 [(M+H), 100%]; 206 (M-CH_3); 188 (M-SH); 160 (M-C_2H_4HS); 128 [$(C_3H_7)_2(C_2H_4)N$]; 114 [$CH_2N(C_3H_7)_2$]; 102 [$H_2N(C_3H_7)_2$]; 89 ($C_3H_7NC_2H_4$); 86 (C_4H_8S or $C_3H_7NHC_2H_4$) and 61 (SC_2H_5).

B: GC-MS-EI

15. 2-Diisopropylaminoethanethiol (**11**): M^+=161; 146 (M-CH_3); 128 [$(C_3H_7)_2$-$(C_2H_4)N$]; 118 (M-C_3H_7); 114 (M-CH_2SH, 100%); 86 (C_4H_8S or $C_3H_7NHC_2H_4$); 72 (114-C_3H_6); 70 ($C_3H_5NCH_3$); 61 (SC_2H_5); 58 (C_2H_2S or $CH_3CHNHCH_3$); 47 (SCH_3); 44 (58- CH_2); 41 (C_3H_5) and 27 (C_2H_3).

16. Bis-(2-Diisopropylaminoethyl) disulfide (**10**): M^+=320 (not seen) 192 [(M-$(C_3H_7)_2NC_2H_4$]; 160 ($(C_3H_7)_2NC_2H_4S$); 144 ($(C_3H_7)C_2H_3NC_2H_4S$]; 128 [$(C_3H_7)_2(C_2H_4)N$]; 114 ($(C_3H_7)_2NCH_2$], 100%); 102 [$(C_3H_7)_2NH_2$]; 86 (C_4H_8S or $C_3H_7NHC_2H_4$); 70 ($C_3H_5NCH_3$); 72 ($CH_3NHC_3H_6$); 70 ($C_3H_5NHCH_2$); 58 (C_2H_2S or $CH_3CHNHCH_3$); 44 ($C_2H_4NH_2$); 41 (C_3H_5) and 27 (C_2H_3).

Of the twenty odd compounds that can be considered to have been formed from the breakdown of the organophosphorus nerve agent **VX**, 2-diisopropylaminoethyl vinyl sulfide (**1**) is unique, for the presence of the vinyl moiety makes it prone to further reactions. The synthesis of this reactive compound thus poses additional problems. Three different approaches were developed for the synthesis of 2-diisopropylaminoethyl vinyl sulfide (**1**). Of these, one was selected for the actual synthesis of (2-diisopropylaminoethyl) vinyl sulfide (**1**) based on the report that thiols and sulfides are formed when organometalic reagents are reacted with elemental sulfur[14]. Of the compounds listed in **Fig. 1**, four compounds: 2-diisopropylaminoethanethiol (**11**), bis(2-diisopropylaminoethyl) disulfide (**13**), bis(2-diisopropylaminoethyl)sulfide (**5**) and 2-diisopropylaminoethyl vinyl sulfide (1) have been detected in an aged VX sample[8a]. The origin and the formation of these three compounds is rationalized in **Fig. 2.** Compound **4** must have been formed via the halogen exchange reaction. There are precedents for this in the literature[15]. The mercaptan (**11**) must have been oxidized to give the disulfide **13.** Extrusion of sulfur from the disulfide (**13**) would thus lead to the sulfide, **5.** The presence of the vinyl sulfide (**1**), vinyl disulfide (**14**) and vinyl trisulfide (**15**) in the reaction mixture appears to give a clue to the free radical nature of the mechanism of the reaction. Of course, other mechanisms, such as the single electron transfer process, are possible. In fact, we have recently shown that the reactions of organolithium reagents with disulfides proceed via the single electron transfer process[16]; Grignard reagents are complex mixtures containing free radical species [17]. Compound **15** must have arisen from free radical reactions. Compounds **14** and **15** owe their origin to compound **1** and are formed via free radical processes (**Fig. 2**).

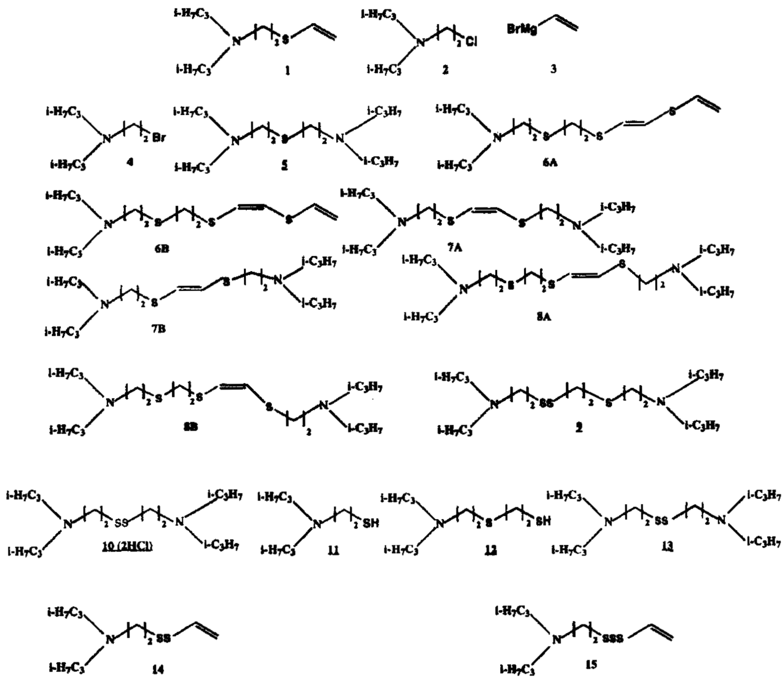

FIGURE 1 Structures of the Compounds Cited in the Narrative

The two compounds whose M$^+$ ions were not seen in their mass spectra have been identified as 2-diisopropylaminoethyl vinyl di- (**14**) and -trisulfides (**15**) (see procedure **A** in experimental section). The mass spectra of compounds **14** and **15** are strikingly similar to the mass spectral fragmentation of 2-diisopropylaminoethyl vinyl sulfide (**1**). In addition, mass spectrum of one compound shows an ion at m/e=64 and the other at m/e=96, corresponding to two and three sulfur atoms respectively. These consideration led to the assignment of structures **14** and **15** to these two compounds. Diisopropylaminoethanethiol (**11**), formed during the course of the reaction, can conceivably be converted into (diisopropylaminoethyl)disulfide (**13**) via two routes, namely (i) direct oxidation of **11** and (ii) dimerization of diisopropylaminoethanethiyl radical (**16, Fig. 2**), which could have been formed under the reaction conditions. It is known that the Grignard reagent is a heterogeneous mixture containing among others free radical species[17] and on treatment with sulfur generally gives thiols and sulfides[1b]. Thus, hydrogen abstraction from the mercaptan (**11**) by free radicals can generate the said thiyl radicals (**16**). which simply dimerizes to yield compound **13.** In turn, compound **13,** can undergo two types of cleavages. Firstly, it can suffer homolytic fission of the sulfur-sulfur bond to regenerate the thiyl radicals (**16**), which can then react with vinylthiyl radicals (**17**) to give (diisopropylaminoethyl) vinyl disulfide (**14**). Secondly, the fission of the carbon-sulfur bond can occur to furnish the perthiyl radicals (**18**). which then can add to the vinylthiyl radicals (**17**) to form (diisopropylaminoethyl) vinyl trisulfide (**15**). Another option open to the perthiyl radical would be to react with diisopropylaminoethylthiyl radical (**16**) to yield bis(diisopropylaminoethyl) trisulfide (**19**), which via the extrusion of two sulfur atoms forms (diisopropylaminoethyl)sulfide (**5**). Such fissions have been reported [15–17 and references cited therein] and there are precedents for such an extrusion of sulfur[18]. The proposed mechanism provides an acceptable rationale for the formation of the various sulfur containing compounds and stands supported by their GC-MS characterization.

Five compounds, namely **6A** or **6B** (M^+=305, r.t.=14.02 min); **7A** and **7B** (M^+=346, r.t.=16.35 min and M^+=346, r.t.=16.56 min) and **8A** and **8B** (M^+=406, r.t.=18.34 min and M^+=406, r.t.=18.58 min) represent cis and trans isomeric pairs. In the first case, only one of the two isomers is present in the reaction product. It was not possible to definitely identify which one of the two isomers is present, based on the mass spectral fragmentation behavior alone. The mass spectra of compounds **7A** and **7B** are very similar. The same is true of isomers **8A** and **8B.** Mass spectral fragmentation behavior alone was not of much help in their characterization.

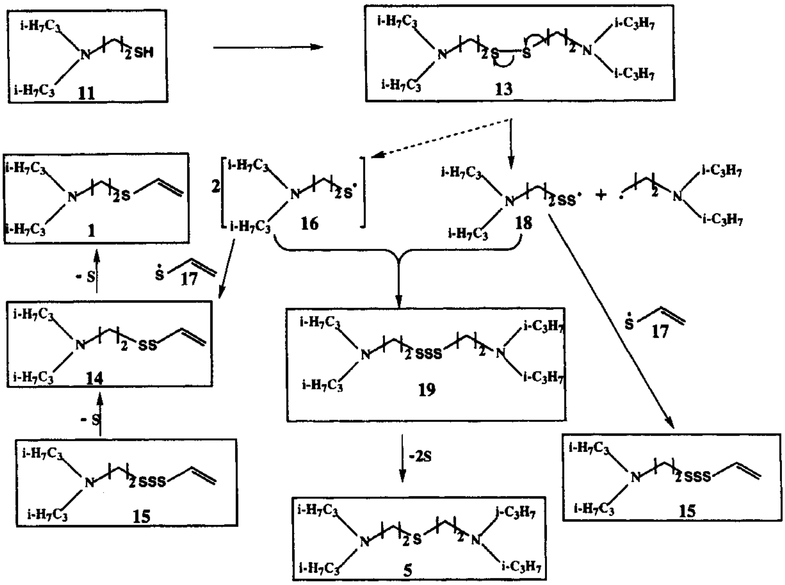

FIGURE 2 Origin of the Polysulfides

Attempts to purify **7A, 7B, 8A** and **8B** via vaccum distillation of the reaction product ended up in their decomposition.

EXPERIMENTAL

All solvents were dry and freshly distilled. Mass spectra were obtained using a Finnigan TSQ-7000 GC/MS/MS equipped with a 30 m × 0.25 mm. i.d. DB-5 capillary column (J and W Scientific, Folsom, CA) or a Finnigan 5100 GC/MS equipped with a 15 m × 0.25 mm. i.d.Rtx-5 capillary column (Restek, Bellefonte, PA). The conditions on 5100 were: oven temperature 60–270° C at 10° C/min, injection temperature was 210°, interface temperature 230° C, electron energy 70 eV, emission current 500 μA and scan time 1 sec. The conditions on the TSQ-7000 were: oven temperature 60–270° C at 15° C/min, injection temperature 220°, interface temperature 250° C, source temperature 150°, electron energy 70 eV (EI) or 200 eV (CI) and emission current 400 μA (EI) or 300 μA (CI) and scan time

0.7 sec. Data was obtained in both the electron ionization mode (range 45–450 da) and chemical ionization mode (mass range 60–450 da). Ultrahigh purity methane was used as the CI agent gas with a source pressure of 0.5 Torr (5100) or 4 Torr (TSQ-7100). Routine GC analyses were accomplished with a Hewlett-Packard 5890A gas chromatograph equipped with a J and W Scientific 30 m × 0.53 mm i.d. DB-5 column (J and W Scientific, Folsom, CA). The NMR spectra (^{1}H, and ^{13}C) were recorded in $CDCl_3$ with TMS as the internal standard on a Varian VXR-400S spectrometer at 100 MHz and 376 MHz respectively.

Synthesis of 2-(diisopropylaminoethyl) vinyl sulfide (1)

(**A**): Stoichiometric amounts of 2-diisopropylaminoethyl chloride (**2**) dissolved in dry benzene and vinyl magnesium bromide (**3**) were simultaneously added dropwise with stirring at O°C and under argon to a suspension of sulfur in dry benzene contained in a flame dried three-necked flask carrying a reflux condenser and a nitrogen inlet system. The temperature of the coolant circulating through the condenser was maintained at – 5° C. The reaction mixture was stirred at – 5° C for 2 hours and stirred over night at room temperature, treated with a saturated solution of ammonium chloride, the organic layer separated, the aqueous layer extracted with ether, the solutions mixed, washed successively with water and a saturated solution of sodium chloride, dried over anhydrous sodium sulfate and solvent evaporated under reduced pressure. Routine GC analysis of the residue showed it to be a mixture of two components. However, the GC-MS analysis of the product showed it to consist of: (1) starting material, (**2**, 62.5%), 2-(diisopropylaminoethyl) vinyl sulfide (**1**, 37%), (3) 2-diisopropylaminoethyl bromide (**4**, 1.4%) (4) two additional compounds with no M^+ peaks but with mass spectral fragmentation pattern comparable to that of compound **1** (see Results and Discussion).

(**B**): With a view to increase the yields of 2-diisopropylaminoethyl vinyl sulfide (1), the above reaction conditions were slightly modified. In that, the addition of the reagents was carried out at room temperature using dry benzene as a co-solvent. The reaction mixture was maintained at 46–50° C for 150 minutes and processed as before. GC-MS analysis of the reaction mixture showed it to consist of: (a) 2-(diisopropylamino)ethyl chloride (**2**, 1.0%, M^+=163, r.t.=2.31 min.); (b) (2-diisopropylaminoethyl) vinyl sulfide (**1**, 54.3%, M^+=187, r.t.=5.20 min.); (c) an unknown with no molecular ion peak; (d) bis 2-diisopropylaminoethyl sulfide (**5**, M^+=288, 23.5%, r.t.=11.51 min.); (e) (diisopropylaminoethylthio)(ethylthioethyleno)] vinyl sulfide (**6A** or **6B**, M^+=305, 2.3%, r.t.=14.02 min.); (f) bis-(2-diisopropylaminoethylthio)ethylene (**7A** or **7B**, M^+=346, 2.9%, r.t.=16.35 min.); (g) bis-(2-diisopropylaminoethylthio)ethylene (**7A** or **7B**, M^+=346, 6.3%, r.t.=16.56 min.); (h) [2-(diisopropylaminoethylthio)(ethylthio)] [2-diisopropylaminoethylthio]ethylene (**8A** or **8B**): M^+=406, 4.8%, r.t.=18.34 min.) and (i) 2-(diisopropylaminoethylthio)(ethylthio)] [2-diisopropylaminoethylthio]ethylene (**8A** or **8B**): M^+=406, 3.8%, r.t.=18.58 min.) After the work-up as described above and vacuum fractionation a 96.5 % pure sample of 2-diisopropylaminoethyl vinyl sulfide (**1**) was obtained.

^{13}C-NMR 2-(Diisopropylaminoethyl) vinyl sulfide (**1**): 6: $N(CH_3)$ [20.8]; CH [48.4]; N CH_2 CH_2 [44.6 and 32.7] and $SCH=CH_2$ [133.0 and 109.3].

^{1}H-NMR: 2-(Diisopropylaminoethyl) vinyl sulfide (**1**): δ: NCH [3.22 (septet, J=6.7 Hz)], $(CH_3)_2$ [1.22 (d. J=6.7 Hz)], NCH_2CH_2 [2,87, s]; SCH [dd, 6.55, (J= 10.2, 16.5, HZ), and $=CH_2$ [d, 33.7, (J=10.2 Hz); d, 5.27, (J=16.5 Hz)].

Synthesis of [2-(Diisopropylaminoethylthioethyl)] [2'-(diisopropylaminoethyl)] disulfide (9)

To a suspension of 2'-diisopropylaminoethyl disulfide hydrochloride (**10**, 2 g., 5.08 mmol) in dry dichloromethane (8 ml) cooled to −15° C, sulfuryl chloride (0.7 g., 5.08 mmol) was added dropwise with stirring. After the addition was over, the reaction mixture was stirred for an additional 20 min. and then treated dropwise with a solution of (2-diisopropylaminoethylthio)ethanethiol (**12**, 2.25 g., 10.2 mmol) in dry dichloromethane (10 ml). The reaction mixture was stirred for 60 min. and left stirring over night at room temperature. Then, it was treated with a solution of 10 ml of sodium hydroxide (20.5 mmol), the organic layer was separated, washed twice with water, dried over anhydrous $MgSO_4$, the solvent removed under reduced presssure, the residue distilled under high vacuum and the distillate analyzed by GC-MS and NMR. The GC-MS examination showed the product to consist of four components (**Fig. 1**); namely (a) diisopropylaminoethylthiol (**11**, M^+=161, 23.8%, r.t.=4.55 min.); (b) (2-diisopropylaminoethylethylthio)ethanethiol (**12**, M^+=221, 18.1%, r.t.=9.28 min.); (c) bis(diisopropylaminoethyl) disulfide (**13**, M^+=320, 31.2%, r.t.= 12.55 min.) and (d) (2-diisopropylaminoethylthioethyl)(2'-diisopropylaminoethyl) disulfide (**9**, M^+=380. 26.9%, r.t.=16.15 min.)

^{13}C-NMR: 2-Diisopropylaminoethylthioethyl-2'-diisopropylaminoethyl disulfide (**9**) 6: $N(C_3H_7)_2$ [48.8]; CH_2N [45.8]; CH_2SCH_2 [33.7 and 31.4]; CH_2SSCH_2 [40.2 and 38.6]; CH_2N [45.8] and $N(C_3H_7)_2$ [48.8].

^{13}C-NMR: (Diisopropylaminoethylthio)ethanethiol (**12**): 6: $N(CH_3)$ [21.3]; CH [48.9]; N CH_2 CH_2 [46.0 and 33.9] and SCH_2CH_2 [36.7 and 25.3].

^{1}H-NMR: (Diisopropylaminoethylethylthio)ethanethiol (**12**): 6: NCH [2.82 (septet, J=6.64 Hz)], $(CH_3)_2$ [0.83 (d. J=6.6 Hz)], NCH_2CH_2 [2,43, m and 2.32, m]; SCH_2CH_2 [2.58, m and 2.53, m] and SH [1.71].

CONCLUSION

Four compounds present in the reaction product of the synthesis of (2-diisopropylaminoethyl) vinyl sulfide (**1**), (a) 2-diisopropylaminoethanethiol (**11**). (b) bis-(2-diisopropylaminoethyl) sulfide (**5**), (c) bis-(2-diisopropylaminoethyl) disulfide (**13**) and (d) (2-diisopropylaminoethyl) vinyl sulfide (**1**) are also present in the aged **VX** sample.

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