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SUBSTITUTION OF CHLORIDE ION IN BIS(2-CHLOROETHYL) SULFIDE (HD) BY VARIOUS OXYGEN ANIONS

by

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ABSTRACT

The chemical warfare agent bis(2-chloroethyl) sulfide, (HD: Mustard Gas) reacts with the potassium salts of benzohydroxamic acid, phenol and 2,3-butanedione monoxime in aqueous ethanol to give solid crystalline products in greater than 80% yields. These products have been isolated, purified and characterized. Analysis shows that both chloride atoms of HD have been substituted by the respective oxygen anion group in the products. These results indicate that, in this system, nucleophilic substitution of mustard is preferred over the elimination mechanism.

RÉSUMÉ

L'agent de guerre chimique bis(Chloro-2-éthyl) sulfure (HD:gaz moutarde) réagit avec les sels de potassium de l'acide benzohydroxamique, du phénol et du butanedione-2,3 monoxime un milieu éthanol aqueux pour donner des produits cristallins avec des rendements supérieurs à 80%. Ces produits ont été isolés, purifiés et caractérisés. Les analyss ont démontrées que les deux atomes de chlore du composé HD ont été substitués par les nucléophiles mentionnés ci-haut. Ces résultats démontrent que, dans le solvant utilisé, la réaction de substitution nucléophile sur le gaz moutarde est favorisée par rapport à la réaction d'élimination.

EXECUTIVE SUMMARY

This reports describes a study of the reactions of a chemical-warfare agent, mustard, and three nucleophiles in a reactive non-aqueous solvent, ethanol. These nucleophiles bring about the rapid conversion of mustard to innoculous products in this solvent and, therefore, merit consideration as decontaminating agents. These nucleophile/non-aqueous solvent systems also are not corrosive to skin and eyes and allow for the possibility of developing safe personal decontaminants for the Canadian Forces.

In this particular study, the extent of reaction and the products of reaction of mustard and the individual nucleophiles have been determined. These provide valuable insights into the mechanism by which these nucleophiles decompose mustard, and suggest a definitive study, based on the kinetics of reactions between mustard and each nucleophile, to elucidate the mechanism.

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1.0 INTRODUCTION

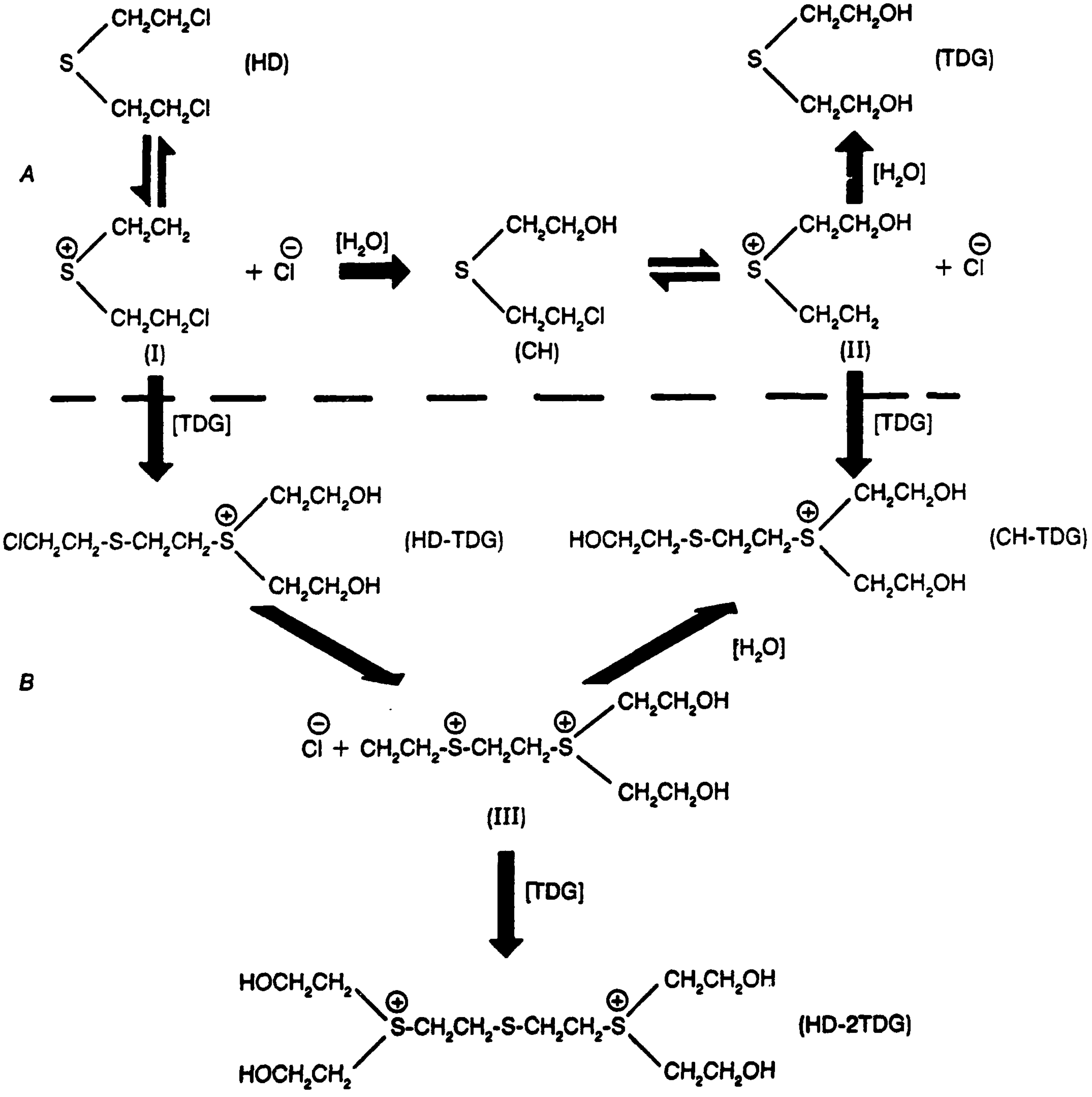
Because of the obvious need to decontaminate the soldier under conditions of chemical warfare, a wide variety of substitution reactions have been studied with the aim of producing non-toxic products and which, therefore, would be suitable for decontamination. The hydrolysis reaction of the classical chemical warfare agent, bis(2-chloroethyl) sulfide, (otherwise known as mustard gas or by its code name, HD) has been studied extensively over the years. In 1949 Bartlett and Swain (1) proposed that the hydrolysis of HD proceeds by two consecutive first-order reactions with rate limiting formation of two sulfonium ion intermediates (I) and (II), in each step. This mechanism is illustrated in the upper part (A) of Scheme 1 (2).

The first reaction results in the substitution of one chloride ion by a hydroxide ion to produce 2-hydroxyethyl ethyl sulfide (Mustard chlorohydrin:CH). In the subsequent reaction the second chloride ion is displaced by another hydroxide ion to form bis(2-hydroxyethyl) sulfide (thiodiglycol:TDG). The lower half (B) of Scheme 1 illustrates the possibility of intermolecular reactions of molecules of HD and CH with thiodiglycol which could lead to the formation of "dimeric" sulfonium chlorides such as HD-TDG, CH-TDG and HD-2TDG.

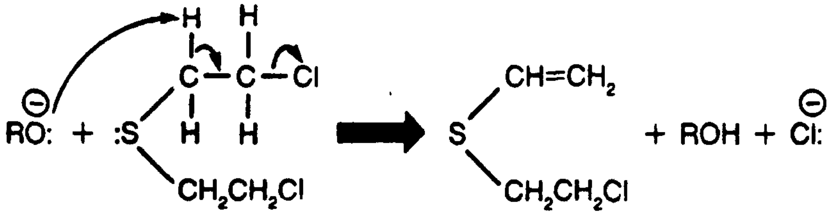
The most recent kinetic studies of the hydrolysis of CH at 25°C gave linear first-order plots which yielded first-order rate constant values (k_1) of 4.33×10^{-3} s^{-1} (1), 4.20×10^{-3} s^{-1} (3), and 3.72×10^{-3} s^{-1} (4), which are all in approximate agreement. In contrast, studies of the hydrolysis of HD at 25°C yielded non-linear first order plots. The observed curvature was attributed to the difference in the rate of hydrolysis of CH and HD, the hydrolysis of HD being slower (1). The first-order rate constants for the hydrolysis reaction of HD have been calculated from the experimental data to be 2.58×10^{-3} s^{-1} (1), 2.96×10^{-3} s^{-1} (2), and 2.90×10^{-3} s^{-1} (3), again in reasonable agreement. The rate of the hydrolysis reaction of both HD and CH was shown to be independent of pH over a wide range (1).

Recently, the hydrolysis reaction of HD has been reexamined and the mechanism proposed by Bartlett and Swain has been verified (5,6). It has also been reported (7) that the sulfonium ion intermediates HD-2TDG and CH-TDG have been directly identified during the hydrolysis of HD using NMR spectroscopy.

Scheme 1

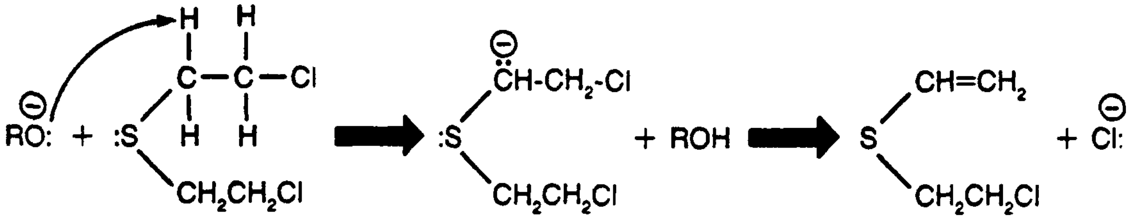


[1a]



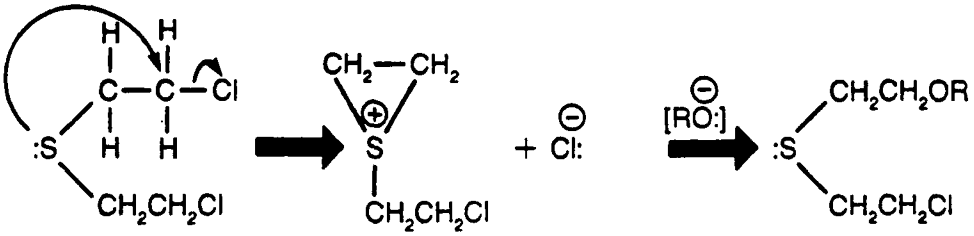
(E2)

[1b]



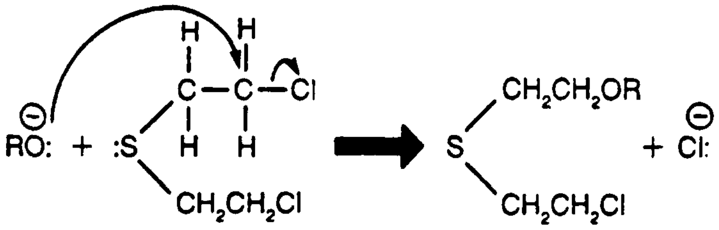
(E1CB)

[2a]



(SN1)

[2b]



(SN2)

While much attention has been paid to the substitution of chloride ion from HD by hydroxide ion there has been little investigation into the reactions of mustard with other bases or other nucleophiles in aqueous media and even less in non-aqueous media. In 1920 the reactions of _bis_(2-chloroethyl)sulfide, _bis_ (2-chloroethyl)sulfoxide, and _bis_(2-chloroethyl)sulfone with compounds such as phenoxide, thiophenoxide, alcohols, thioalcohols, aromatic amines, carboxylic acid, and iodides were reported (8). The products of these substitution reactions were isolated and characterised. The reaction of mustard chlorohydrin with the amino acids cysteine and valine also has been reported, although the products of these reactions were not identified (9). A report in a Polish journal in 1972 describes the reaction product of HD with the potassium salt of benzhydroxamic acid (10).

The above studies, as well as investigations into the reactions of related substituted ß-thioethyl chlorides (11), indicate that mustard can react with a potential nucleophile in either one of two ways. The first possibility is that the reaction proceeds by an elimination (E2 or E1CB) reaction (eq. 1a,b). The second possibility, and the one of most interest, is that the reaction proceeds by nucleophilic substitution (eq. 2a,b). This could occur by the SN1 mechanism with anchiomeric assistance or by direct nucleophilic displacement (SN2).

For the reaction of mustard with a nucleophile the mechanistic pathway will be determined by such factors as solvent media, temperature, and the nature of the nucleophile. Studies, both in-house and under contract, are currently in progress to gain a better understanding of how these factors influence the reaction of mustard and to incorporate this information into the development of a decontaminant system for the destruction of all CW agents.

This technical note reports the results of the nucleophilic substitution reactions of the potassium salts of benzohydroxic acid, phenol and 2,3-butanedione monoxime upon bis(2-chloroethyl) sulfide.

2.0 EXPERIMENTAL

2.1 ß,ß-disubstituted ethyl sulfide products

2.1.1 Bis[2-,O-(N-benzoylhydroxylamino)ethyl] sulfide (1)

Benzohydroxamic acid (2.03 g; 0.0148 mol) was added with stirring to 15 ml of an aqueous 0.831m KOH solution, 0.0125 mol, in a 100-ml 3-necked round-bottom flask. The excess benzohydroxamic acid was added to ensure that very little KOH remained in the solution. The potassium salt of benzohydroxamic acid began to precipitate so a further 25 ml of H_2O were added to the solution. The mixture was heated to 45°C and a further 2 ml of H_2O were added to give a clear solution. A solution of HD (0.643g; 0.00404 mol) in 5 ml of EtOH was added dropwise to the solution over a period of 15 min. A precipitate formed upon addition of the HD and the mixture was stirred for a further 1.5 h at 40-45°C. The mixture was left to stand overnight after the addition of 25 ml of H_2O. The precipitate was filtered, washed with cold water, then dried in a vacuum oven to yield 1.17g (80.4%) of the product. A portion of the product was recrystallized from Chloroform (mp. 139-139°C; lit. (10) 139.5-140.5°C).

2.1.2 Bis(2-phenoxyethyl) sulfide (2)

A solution of potassium phenoxide was prepared in a 3-necked round-bottom flask by adding a solution of sublimed phenol (1.87g; 0.0199 mol in 20 ml of ethanol) to 20 ml of a KOH solution (0.831M

0.0166 mol). The solution was stirred continuously and over a period of 35 min a solution of HD (0.880g; 0.00554 mol) in 10 ml of ethanol was added by way of a dropping funnel. Within a few minutes of the final addition of HD, the solution became cloudy. A water-cooled condenser was attached to the flask and the solution was warmed to 35°C for 2 h. The reaction solution was cooled in ice and left to stand overnight. The white solid which formed was filtered and washed with cold 50% EtOH-H_2O followed by washing with cold EtOH. The solid was dried over $CaCl_2$ in a dessicator under reduced pressure (water-pump evacuated). The total product yield was 86%. The product was recrystallized from chloroform (mp 55°C; lit (8) 54.2°C).

2.1.3 <u>Bis</u>[2-(2,3-butanedione oximino)ethyl] sulfide (<u>3</u>)

Method 1. The 2,3-butanedione monoxime (2.01g; 0.0199 mol) was added to a stirred solution of KOH (20 ml; 0.831 M; 0.0166 mole). A clear yellow solution resulted. The HD (0.879g; 0.00553 mole) in 5 ml of EtOH was added dropwise over 15 min, after which an oil began to separate from solution. The solution was warmed to 35°C and a further 10 ml of EtOH were added. The mixture was stirred for 2 h (an insoluble fraction persisted) and then cooled to 15°C. The bulk of the solvent was removed by rotary evaporation. The remaining oil and solvent were extracted with CH_2Cl_2 (3x5 ml). The CH_2Cl_2 extracts were combined and the solvent removed under vacuum (water pump). The residual oil (1.10 g:70%) was analysed by gas chromatography (see below) and was found to contain four components identified as[1]: HD (11.5%); 2-butanedione oximino ethyl - 2'-chloroethyl sulfide (32.6%); 2 butanedione oximino ethyl-2'-sthoxyethyl sulfide (1.6%) and <u>bis</u>[2-(2,3 butanedione oximino)ethyl] sulfide (54.3%)

Method 2. Potassium 2,3-butanedione monoximate (13.1g; 0.0941 mol) a product of Raylo Chem. Co. was weighed in a Dri-Lab (Vacuum Atmospheres Co.) into an Erlenmyer flask. To this, 175 ml of EtOH were added and the insoluble material was filtered off. HD (4.9g; 0.0308 mol) in 5 ml of EtOH was added dropwise to the oximate solution over a period of 1.5 h. To this solution was added 25 ml of water, after which the solution began to cloud. The solution was left to stir overnight. The mixture was then concentrated on the rotary evaporator to approximately 100 ml. To this, 50 ml of water were added and left for ca. 60 h. The oil which settled to the bottom of the flask was removed by pipette. The solution was again concentrated, the oil layer removed and the remaining aqueous solution was extracted with CH_2Cl_2. The oil was then combined with the CH_2Cl_2 solution and dried with anhydrous $MgSO_4$. The solution was filtered and the CH_2Cl_2 removed on the rotary evaporator. The crude yield was 8.04g or 89%.

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[1] Personal Communication, Dr. J.G. Purdon, DREO (1988)

An attempt was made to purify the resulting product mixture by a short-path distillation. Two fractions of approximately 0.5 ml each were collected, the first had a boiling point of 149-159°C and the second of 159°C, both at a pressure of 0.5 Torr. A sample of the product remaining in the distillation bulb (1.0g) was then purified by flash column chromatograpy (12). Fractions of ca. 15 ml were collected and analysed for product by TLC. The fractions containing the desired product were combined and the solvent removed to yield 0.91g of purified product. The product solidified on standing in the freezer, mp. 34-34.8°C. Anal: calcd. for $C_{12}H_{20}N_2O_4S$: C 49.98 H 6.99 N 9.71 S 11.12; found C 49.96 H 6.61 N 10.96[2] S 11.31.

2.2 Product Analysis

The CG analyses of reaction mixtures and products were performed using a Varian model 3700 gas chromatograph equipped with dual flame-photometric (FPD) and flame-ionization (FID) detectors, two CDS-111 data systems and a fused silica capillary column (DB-5-30W, 1.0μm coating, 30m x .322mm, J&W Scientific Inc.). The column effluent was split 1:1 to each detector. Solutions of the reaction mixtures and products were prepared in either EtOH or $CHCl_3$ with an excess of acetic acid added to the reaction-mixture solutions. The solutions (1μl) were injected by autosampler (Varian model 8000) directly onto a fused-silica injector body. Helium was used as a carrier gas at a flow rate of 2.4 ml/min at 250°C. Injector and detector temperatures were 220°C and 250°C respectively. In general, the column-oven program was; 100°C for 1 min, increasing 10°C or 20°C/min to 250°C and holding for 5 min.

The ^1H and ^{13}C NMR spectra were recorded with a Varian XL-200 MHz NMR instrument. All solutions were prepared using $CDCl_3$ as a solvent and TMS as internal standard except for the ^1H spectrum of 2 where CD_3OD was used. The ^{13}C spectra were proton decoupled.

IR spectra were recorded on a Perkin-Elmer 283 IR spectrophotometer. The solid products 1 and 2 were run as KBr pellets. Product 3 was run as a neat liquid film between two KBr windows.

3.0 RESULTS AND DISCUSSION

As stated in the introduction, the reaction of *bis*(2-chloroethyl) sulfide with potassium phenoxide and potassium benzohydroxamate has been reported (10,8). The purpose of this study therefore was to repeat and verify these experiments and to investigate the reaction of HD with another member of the oxime

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[2] Nitrogen analysis is not always accurate, depending on the method used. Personal Communication, Mr. G. Morris (Agriculture Canada 1988)

family, specifically potassium 2,3-butanedione monoximate. The products of the above reactions were isolated and characterized. The IR and NMR spectra of the reaction products 1, 2 and 3 are illustrated in Figures 1-4. The important characteristics of these spectra and the structural assignments are summarized in Table 1. These features are discussed below.

The IR spectrum of product 1 isolated from the reaction of HD with potassium benzohydroxamate is shown in Figure 1(A). The strong absorption band at 1660 cm^{-1} indicates the presence of the amide carbonyl group. Other IR absorptions include 3450 (NH), 3230 (monosubstituted aromatic), 1320 (monosubstituted amide) and 700-600 cm^{-1} (S-C). These absorptions are in good agreement with the reported IR absorptions of 3228, 1660, 1320 and 680 cm^{-1}. NMR spectrum given in Figure 2 indicates two triplets at 2.94 and 4.26 ppm shifted relative to TMS. The first of these triplets at 2.94 ppm was assigned to the protons α to the sulfur atom. The other (4.26 ppm) corresponds to the protons β to the sulfur. The multiplets between 7.34 and 7.78 ppm represent the aromatic protons and the singlet at 9.90 ppm indicates the presence of the lone amide proton. The chemical shift values reported in the literature are 2.87, 4.07, 7.40-7.75 and 11.6 ppm (10). These chemical shifts are reported relative to TMS, however DMSO was used as the solvent. The difference in polarity of the solvents used would account for the differences in chemical shifts, especially that of the amide proton. The correlation of the NMR, IR and melting point data indicate that product 1 is the disubstituted benzoylhydroxylaminoethyl sulfide reaction product.

The product 2, of the reaction of HD with potassium phenoxide, was isolated in good yield as a solid having a melting point of 55.0°C This is in good agreement with the literature value of 54.2°C however no further analysis of the product had been reported in the literature paper (8). The IR spectrum of this product is given in Figure 1(B). It can be seen from Figure 1 that the IR spectrum of this product is very complex. Most of the strong absorption bonds can be ascribed to the aryloxy moiety of the compound. The proton NMR spectrum (Figure 3) demonstrates one triplet at 3.00 ppm ($-SC\underline{H}_2-$) and another triplet at 4.18 ppm ($-OC\underline{H}_2-$). The two multiplets at 6.88 - 7.29 ppm correspond to the phenyl protons. The integration of these resonance signals corresponds to protons in the ratio 4:4:10 respectively. The two large signals at 3.30 and 4.85 ppm result from the presence of undeuterated methanol in the solvent. All the above are compatible with the bis (2-phenoxyethyl) sulfide structure assigned.

In the reactions of HD with phenoxide and with benzohydroxamate, the final products precipitated from solution as white crystalline solids. This was not the case for the reaction of HD with 2,3-butanedione monoximate. In the first attempt to prepare product 3 (Method 1) an oil began to separate during the reaction. Warming the reaction solution and addition of more

Table 1. NMR and IR characteristics of β,β′-disubstituted ethyl sulfide products.

Product	^{1}H-NMR (δppm)^a	^{13}C-NMR (δppm)^b	IR ($\bar{\nu}$, cm^{-1})^a
$S(CH_2CH_2O\underset{H}{N}\overset{O}{C}C_6H_5)_2$ 1	2.94 (t,4H,SCH_2) 4.26 (t,4H,OCH_2) 7.34-7.78 (mult,10H,arom) 9.90 (s,2H,NH)	30.54 (SCH_2) 76.73 (OCH_2) 127.23, 128.66, 132.14 (arom)	3450 (w,mult,NH) 3230 (m,mult,arom.) 1660 (st,C=O) 1320 (m,-NHC=O) 700-600 (m, S-C)
$S(CH_2CH_2OC_6H_5)_2$ 2	3.00 (t,4H,SCH_2) 4.18 (t,4H,OCH_2) 6.88-7.29 (mult,10H,arom)	31.67 (SCH_2) 67.94 (OCH_2) 114.64, 121.09, 129.56, 158.49 (arom)	3000 (w,mult,OAr) 1600 (st, OAr) 1500 (st, CH_2) 1460 (w,OAr) 1250 (st,C-O-Ar) 1040 (st,C-O-Ar)
$S(CH_2CH_2ON{=}\underset{CH_3}{C}\overset{O}{C}CH_3)_2$ 3	1.93 (s,6H,$\overset{N}{C}CH_3$) 2.36 (s,6H,$\underset{O}{C}CH_3$) 2.92 (t,4H,SCH_2) 4.42 (t,4H,OCH_2)	8.74 ($H_3\underline{C}C{=}N$) 24.97 ($H_3\underline{C}C{=}O$) 31.26 ($S\text{-}CH_2$) 74.62 ($O\text{-}CH_2$) 156.02 (C=N) 196.37 (C=O)	2940 (m,$CH_3C{=}(O,N)$) 1700 (st,C=O) 1620 (m,C=N) 1320 (m,CH_2) 1130 (st,$CH_3C{=}(O,N)$) 1020 (st,mult,$CH_2\text{-}O$,$CH_2\text{-}S$)

(a) s - singlet, t - triplet, arom - aromatic, mult - multiplet, st - strong, m - medium, w - weak

(b) proton decoupled

ethanol failed to dissolve this oil. This oil was removed and analysed by gas chromatography (GC). Four sulfur-containing products were found and identified by GC Mass Spectroscopy (13): HD; 2-butanedione oximinoethyl-2'-chloroethyl sulfide; 2-butanedione oximinoethyl-2'-ethoxyethyl sulfide; and <u>bis</u>[2-(2,3-butanedione oximino) ethyl] sulfide (3). In an attempt to increase the solubility of the oil and enable more complete reaction, the reaction medium was altered by the addition of water (Method 2). An oil still formed during the reaction however the relative amount of <u>3</u> was increased (approximately 81% of the amount of oil recovered). The <u>bis</u>-substituted product was purified by flash column chromatography to yield an oil which eventually solidified after standing in the freezer (mp 34-34.8°). Elemental analysis of the compound corresponded to the empirical formula $C_{12}H_{20}N_2O_4S$.

The IR spectrum (Figure 1(C)) shows a medium-strength absorption at 2940 cm^{-1} corresponding to the methyl groups attached to the carbonyl and oxime groups. Other absorptions of interest are at 1700 cm^{-1} (C=O) and 1620 cm^{-1} (C=NO). The proton NMR spectrum is shown in Figure 4. Singlet resonances at 1.93 ($C(N)\underline{CH}_3$) and 2.36 ppm ($C(o)\ \underline{CH}_3$) are observed as well as two triplet resonance signals at 2.92 ($SC\underline{H}_2$) and 4.42 ppm ($OC\underline{H}_2$)all in agreement with the assigned structure for <u>3</u>. As mentioned earlier, the structure of <u>3</u> was also confirmed by GC/MS.

All three products, <u>1</u>, <u>2</u> and <u>3</u>, isolated in this study were white crystalline solids and were obtained in very high yields. The reported yield (10) of <u>1</u> before recrystallization was 78.5% whereas the yield obtained in this study was 80.4%. Similarly the yields for <u>2</u> and <u>3</u> were approximately 80%. These high yields indicate a very high specificity for substitution of the chlorine atom by the nucleophile over either the elimination or solvolysis reactions.

4.0 <u>CONCLUSIONS</u>

The high-specificity substitution noted leads to two interesting possibilities. Firstly, if a sulfonium-ion intermediate of the type I (Scheme 1) is formed during the reaction, then it must react preferentially with the nucleophile present in solution, rather than with the solvent (i.e. H_2O or EtOH). This, of course, would be unusual in an SNI mechanism. If, on the other hand, the nucleaphile is displacing chloride by an SNZ-type mechanism, then this type of substitution must be favored strongly over either of the elimination reaction or the SNI reaction. In order to distinguish between these possibilities, detailed kinetic investigations must be conducted. Such studies are being conducted under contract at Queen's University using a mustard (HD) simulant. In-house studies using HD are planned for the future.

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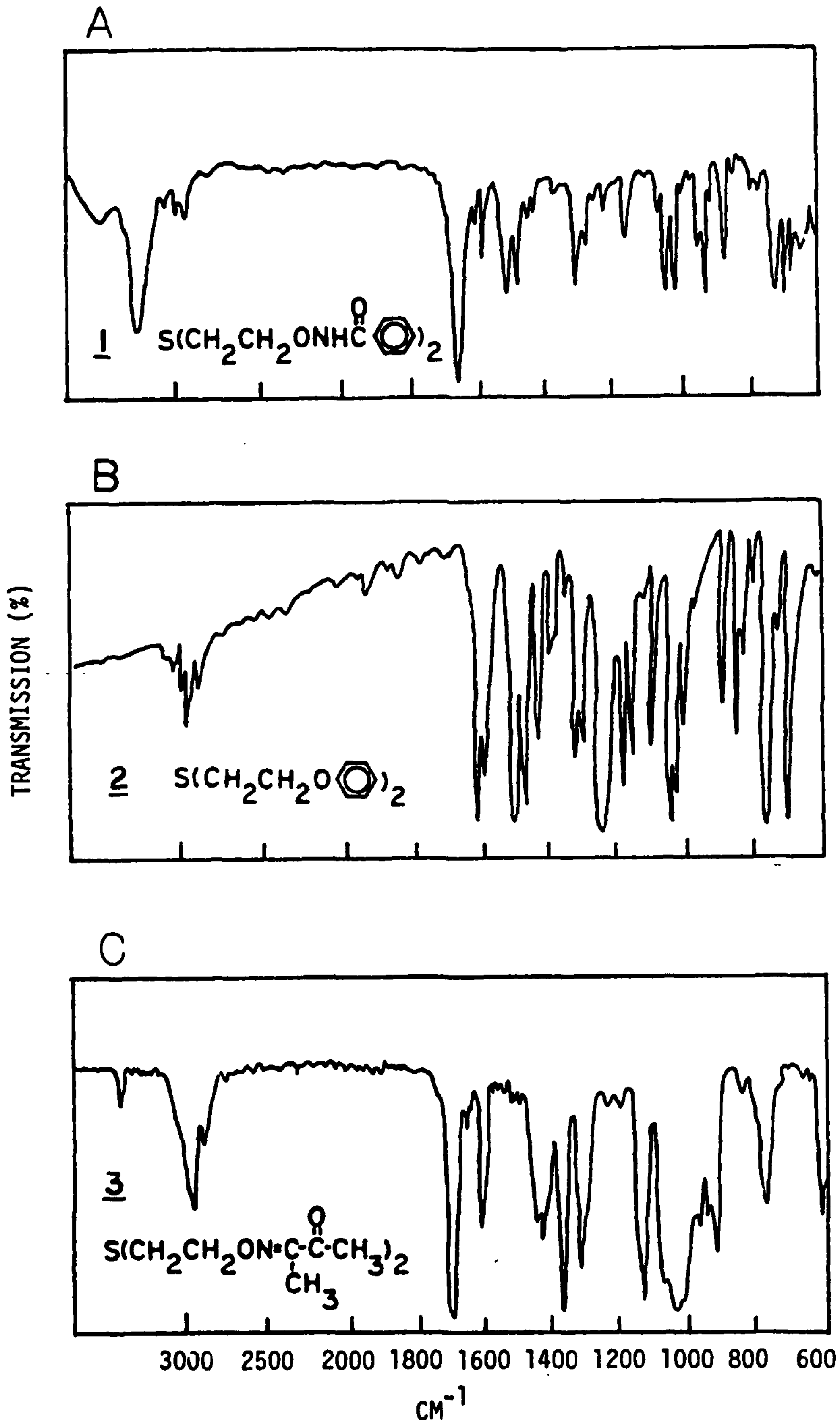
Figure 1. Infrared spectra of reaction products 1, 2 and 3.



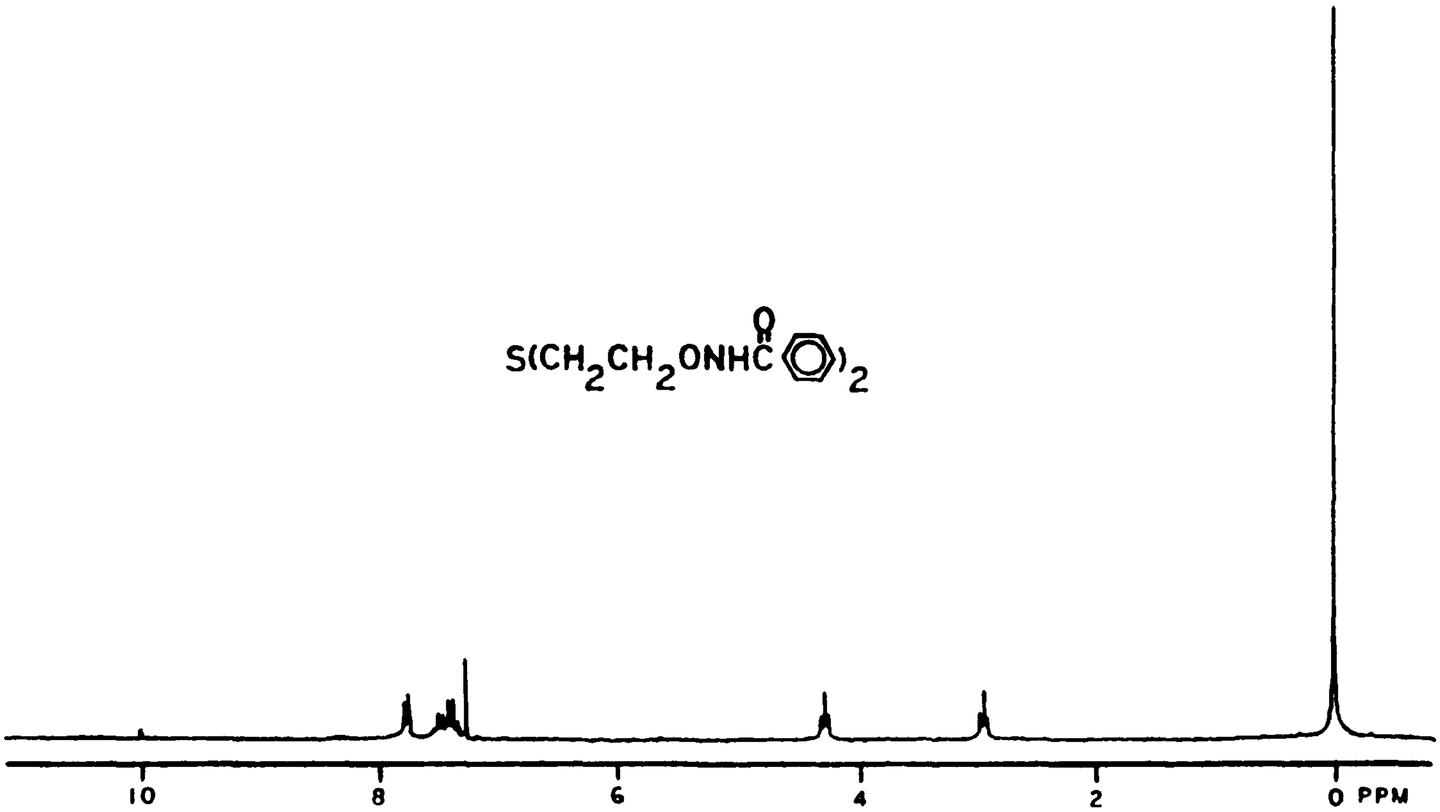


Figure 2. NMR Spectrum of Product 1

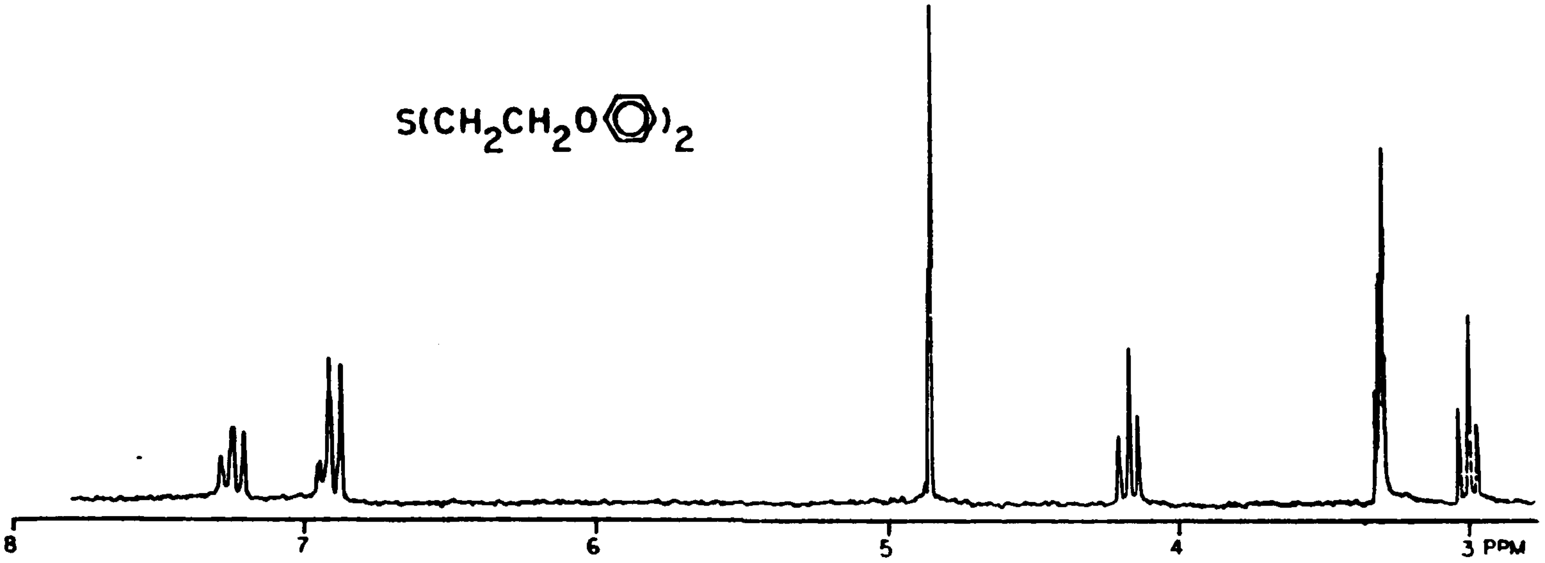
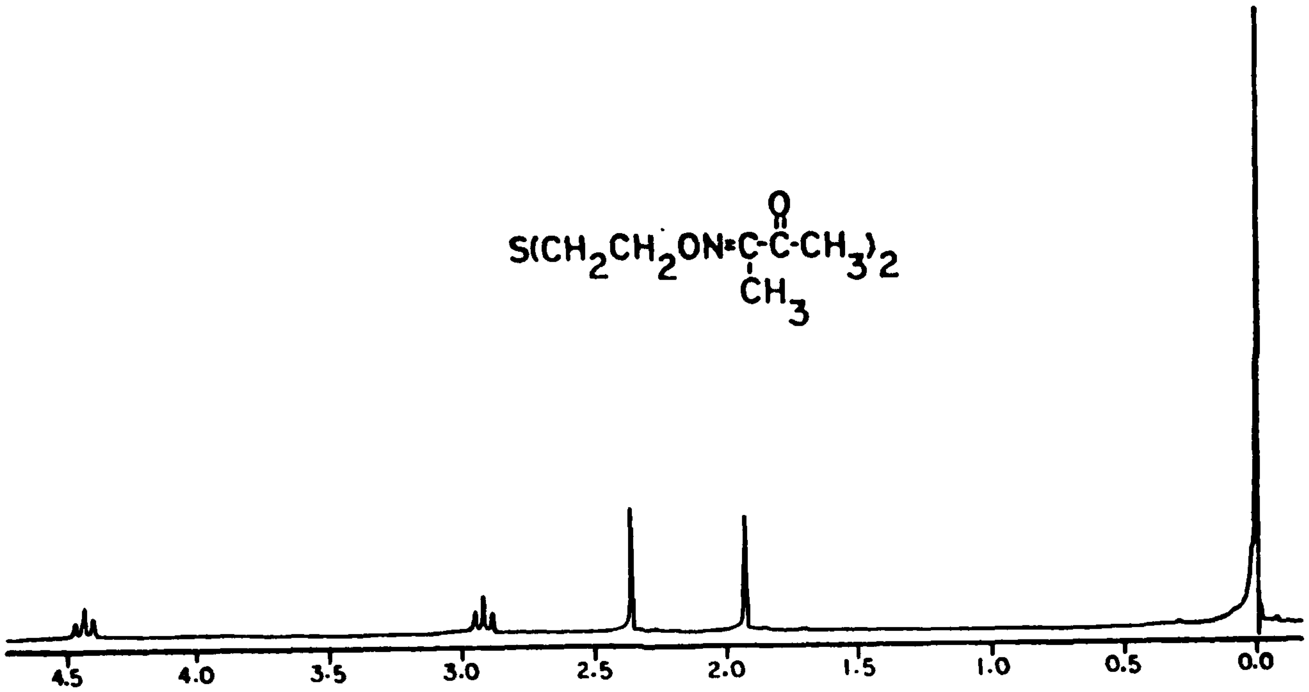


Figure 3. NMR Spectrum of Product 2.



$$S(CH_2CH_2ON{=}\underset{CH_3}{C}{-}\overset{O}{\overset{\|}{C}}{-}CH_3)_2$$

Figure 4. NMR Spectrum of Product 3.

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The chemical warfare agent bis(2-chloroethyl) sulfide, (HD: Mustard Gas) reacts with the potassium salts of benzohydroxamic acid, phenol and 2,3-butanedione monoxime in aqueous ethanol to give solid crystalline products in greater than 80% yields. These products have been isolated, purified and characterized. Analysis shows that both chloride atoms of HD have been substituted by the respective oxygen anion group in the products. These results indicate that, in this system, nucleophilic substitution of mustard is preferred over the elimination mechanism.

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MUSTARD GAS
NUCLEOPHILIC REACTIONS
NUCLEOPHILIC SUBSTITUTION
NUCLEOPHILIC ELIMINATION
SYNTHESIS
OXYANIONS
POTASSIUM BENZOHYDOXIMATE
POTASSIUM PHENOXIDE
POTASSIUM 2,3-BUTANEDIONE MONOXIMATE
NMR
IR