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Efficient Oxidation of Sulfur Mustard and Its Simulants using *N*-*tert*-Butyl-*N*-chlorocyanamide

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Abstract: *N*-*tert*-Butyl-*N*-chlorocyanamide reacts with sulfur mustard instantaneously to give a corresponding nontoxic sulfoxide in quantitative yield. The transformation is selective and takes place in semi-aqueous medium (CH_3CN/H_2O, 1:1), even at subzero temperatures.

Keywords: Decontamination, *N*-*tert*-butyl-*N*-chlorocyanamide, simulants, sulfoxides, sulfur mustard

INTRODUCTION

Bis(2-chloroethyl) sulfide, also known as sulfur mustard, HD, or yperite, is a potential chemical warfare agent first used in World War I. Large amount of this compound are still stockpiled throughout the world. Mustard is potential fatal vesicant that damages skin, eyes, and the respiratory track.[1] High toxicity of mustard is associated with the ability of the $S{-}CH_2{-}CH_2{-}Cl$ group to alkylate protein and other components of living things. 2-Chloroethyl ethyl sulfide (CEES) and 2-chloroethyl phenyl sulfide (CEPS) also contain this group and effectively simulate sulfur mustard. Until the 1980s, mustard was mainly destroyed by incineration. However, this incurs the additional hazards of transportation to the incineration site and release of toxic compounds during the process. Various oxidizing agents have also

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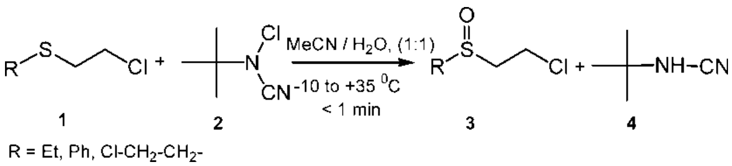


Scheme 1.

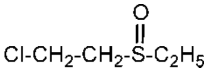
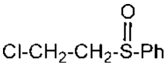
been used for the decontamination reaction such as hypochlorites,[2] peracids of the oxone type,[3] oxaziridines,[4] peroxides,[5] magnesium peroxyphthalate (MMPP),[6] and microemulsion reaction media.[7] More recently, methods of photocatalytic gas-phase destruction[8] and catalytic aerobic oxidation[9] of mustard simulant CEES have also been investigated. Among all these methods, hypochlorites and DS2[2] (diethylenetriamine 70 % + ethyleneglycol, monomethyl ether 28% and 2% sodium hydroxide) are frequently used for decontamination of mustard, but there are some disadvantages in using bleach as a decontaminant because a large amount of bleach is required for the oxidation of the agents, and most important, both are corrosive to many surfaces. Also, bleach is not effective at low temperatures.

RESULTS AND DISCUSSION

During the course of our study on chemical transformations of some organic compounds with *N*-*tert*-butyl-*N*-chlorocyanamide **2**,[10] we discovered that the quantitative conversion of sulfides to their corresponding sulfoxides **3** occurs efficiently. The oxidation took place between 0–35°C with ease (Scheme 1).

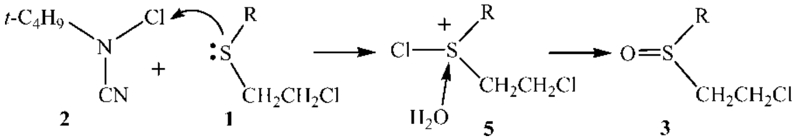
With a ratio of 1 : 1 for substrate/oxidant, the major product was the corresponding sulfoxides **3** with no evidence of sulfones formation. The results are summarized in Table 1. *tert*-Butyl cyanamide **4** was recovered in quantitative

Table 1. Selective oxidation of mustard and its simulants in CH_3CN/H_2O (1:1) by **2**

Entry	Substrate	Product	Yield (%)[a]
1	$Cl\text{-}CH_2\text{-}CH_2\text{-}S\text{-}C_2H_5$	 $Cl\text{-}CH_2\text{-}CH_2\text{-}\overset{\overset{O}{\|}}{S}\text{-}C_2H_5$	97
2	$Cl\text{-}CH_2\text{-}CH_2\text{-}S\text{-}Ph$	 $Cl\text{-}CH_2\text{-}CH_2\text{-}\overset{\overset{O}{\|}}{S}\text{-}Ph$	95
3	$(Cl\text{-}CH_2\text{-}CH_2\text{-})_2S$	$(Cl\text{-}CH_2\text{-}CH_2\text{-})_2S{=}O$	95

Note: All products had satisfactory spectroscopic data and were compared with authentic samples.

[a] Isolated yield.



Scheme 2. Mechanism of sulfoxides formation of SM and its simulants.

yield and was recycled to obtain the reagent **2**. The sulfur in mustard is believed to be oxidatively less reactive than that in alkyl sulfide, essentially because of the presence of two large electron-withdrawing chlorine atoms; however, our observation revealed that **2** was capable of oxidizing these sulfides smoothly.

The stability of **2** was also evaluated with respect to chlorine content. Oxidant was indeed very stable at 35°C for 6 months.

The mechanism of sulfoxide formation is shown in Scheme 2.

EXPERIMENTAL

Sulfur mustard (caution: highly toxic) and its stimulant were prepared by known methods. *N*-*tert*-Butyl-*N*-chlorocyanamide was synthesized by the reported method.[11]

Oxidation Procedure

N-*tert*-Butyl-*N*-chlorocyanamide (1.0 mmol) was added slowly to a stirred solution of sulfides (1.0 equiv.) in acetonitrile–water (1 : 1) (10 mL). After completion of reaction, as monitered by gas chromatography, water (10 mL) was added to reaction mixture which was then extracted with methylenechloride gas chromatography (GC) (3 × 10 mL). The organic layer was washed with water (2 × 10 mL), and dried over anhydrous Na_2SO_4, and evaporated. The residue was crystallized with methylene chloride–light petroleum to give the sulfoxides.

In summary, oxidative decontamination of sulfur mustard and its simulants using *N*-*tert*-butyl-*N*-chlorocyanamide has been described. *N*-*tert*-butyl-*N*-chlorocyanamide–based preparations can be used as effective decontamination formulations for sulfur mustard, even at lower temperatures where other methods become inoperable, because the reaction of oxidant **2** and sulfur mustard is instantaneous at two different temperatures (−10 to +35°C).

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