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Degradation of 2,2'-Dihalodiethyl Sulfides(Mustards) By N,N-Dichloro-4-methylbenzenesulphonamide in Aprotic Medium

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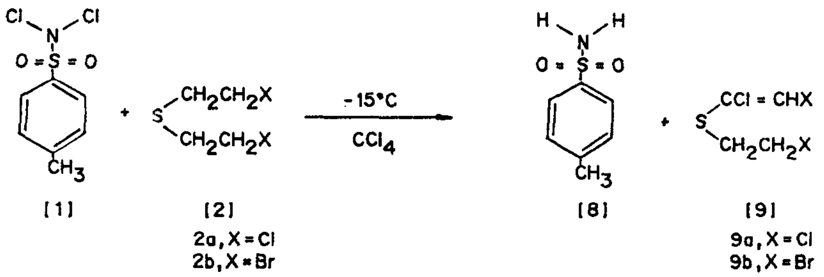
ABSTRACT:- "N,N-Dichloro-4-methylbenzenesulphonamide"(Dichloramine-T) reacts with 2,2'-dihalodiethyl sulfide instantaneously, even at sub-zero temperature, to yield p-toluenesulphonamide, 2-haloethyl 1-chloro-2-halovinyl sulfide and hydrogen chloride. A homolytic mechanism is proposed for the reaction. The positive chlorine compound (dichloramine-T) can serve as an excellent decontaminant against mustard, especially in situations where use of aqueous medium is precluded.

Bis(2-haloethyl) sulfides (mustards) are known to be environmentally persistent, cytotoxic alkylating agents. The chloro analogue, in particular, is one of the most abused chemical warfare agents. Hence decontamination of this and analogous compounds has evinced considerable interest.[1] Besides oxidative and hydrolytic degradation of mustards,[1-4] reaction with organic chloramines can also be exploited for their rapid degradation.[5] Monochloramines have been reported to react with sulfides to yield sulfilimines.[5] However, their reaction rate is greatly affected by the temperature and pH of the reaction medium.[6,7]

We observed that dichloramine-T reacts with mustards vigorously and degrades them almost instantaneously, even at sub-zero temperature, in aprotic medium. This high reactivity of dichloramine-T over monochloramines is attributed to its high chlorine releasing potential in a homogeneous phase since both the toxic sulfides and dichloramine-T are soluble in the organic medium used.

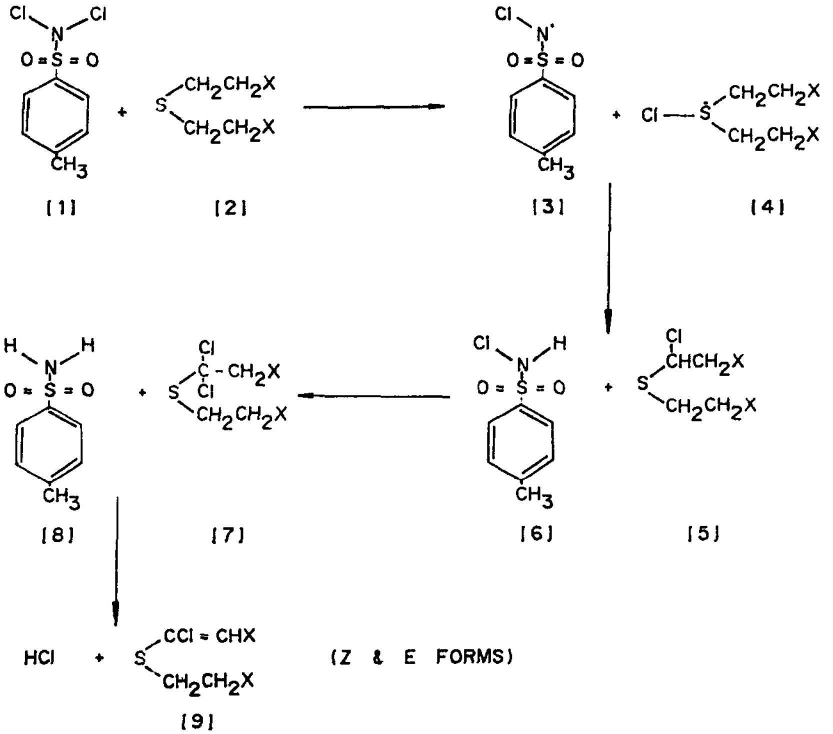
The reaction was carried out at -15°C in carbon tetrachloride.[8] Dichloramine-T, in slight excess, was found to react with bis(2-chloroethyl) sulfide[2a] and its bromo analogue[2b] very fast to yield 2-haloethyl 1-chloro-2-halovinyl sulfide[9][9] as the major product (> 80%), with evolution of HCl gas. It is of interest to note that [1] is quantitatively converted to p-toluenesulphonamide [8](Scheme-A).

The remaining products (< 20%) are believed to be tetra- and penta- chlorinated sulfides based on GCMS data. Nevertheless, their characterisation was not possible because of failure to resolve the complex mixture.



(SCHEME - A)

The reaction most likely follows a homolytic pathway as illustrated in Scheme-B.



(SCHEME - B)

Dichloramine-T[1] chlorinates the α-carbon of 2,2'-dihalodiethyl sulfide[2] to produce 2,2'-dihalo-1-chlorodiethyl sulfide [5]. The second substitution presumably forms 1,1-dichloro-2,2'-dihalodiethyl sulfide[7], owing to the inductive effect of chlorine. The intermediate [7], being unstable,[10] loses a molecule of hydrogen chloride to yield 2-haloethyl 1-chloro-2-halovinyl sulfide [9a] or [9b].

The proposed mechanism is consistent with the generation of p-toluenesulphonamide, evolution of HCl and formation of [9a] or [9b].

The study reveals that dichloramine-T works as an excellent decontaminant against mustard even at sub-zero temperatures, especially in a scenario where use of aqueous medium is undesirable. Further, this reagent also has synthetic potential, in that it can be employed for selectively chlorinating one substituent of dialkyl sulfides.

NOTES AND REFERENCES

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8. Typical experimental procedure:

   To a stirred and cooled solution of sulfide (0.04 moles) in CCl_4 (20 ml) at -15°C, was added solution of dichloramine-T (0.045 moles) in CCl_4 (20 ml). A vigorous exothermic reaction took place with formation of white precipitate and evolution of HCl gas. The cooled mixture was filtered and precipitate was washed and analysed,which was found to be p-toluenesulphonamide M.P. 136-137°C. From the filtrate the crude product was isolated by column chromatography over silica gel. The purified product was rechromatographed employing similar conditions and finally vacuum distilled, yield 80%, B.P. 9a:76°C at 1.5 mm Hg. and 9b: 82°C at 0.75 mm Hg.
9. Analytical data:

   9a-colourless liquid

   ^{1}HNMR (90 MHz) ($CDCl_3$) δ ,3.23(t,2H,$S\underline{CH_2}$ CH_2Cl); δ 3.65(t,2H,$SCH_2\underline{CH_2}Cl$); δ 6.50 and 6.74 (two, s, 1H, SCCl=$\underline{CCl\text{-}H}$ Z and E).

   IR(neat)3040 & 3060(SCCl=CCl-H,Z and E);2960(CH_2CH_2Cl), 1580(SC=C),700(C-Cl) cm^{-1}.

   Mass(EI),m/z-190[M^+,$(ClCH_2CH_2SCCl{=}CHCl)^+$], 192$(M+2)^+$,194$(M+4)^+$,196$(M+6)^+$;m/z-155$(M-Cl)^+$,157$(155+2)^+$,159$(155+4)^+$;m/z-141$(M-CH_2Cl)^+$,143$(141+2)^+$,145$(141+4)^+$; Halogen pattern with required intensity ratio was observed.

   Anal.Calcd.for $C_4H_5Cl_3S$:C,25.1;H,2.6;Cl,55.6;S,16.7.Found: C,25.2;H,2.65;Cl,55.8; S,16.8.

9b-Colourless liquid
^{1}HNMR (90 MHz) ($CDCl_3$) δ ,3.30(t,2H,$S\underline{CH_2}CH_2Br$); δ 3.51(t,2H,$SCH_2\underline{CH_2}Br$); δ 6.63 and 6.94(two,s,1H,SCCl=$\underline{CBr\text{-}H}$ Z and E).
IR(neat) 3050 and 3020 (SCCl=CBr-H Z and E);2960(SCH_2CH_2Br),1580 (SC=C), 700(C-Cl), 600(C-Br)cm^{-1}.
Mass (EI) m/z-278[M^+,$(BrCH_2CH_2SCClCHBr)^+$],280$(M+2)^+$, 282$(M+4)^+$; m/z-199 $(M-Br)^+$ 201$(199+2)^+$, 203$(199+4)^+$,205$(199+6)^+$;m/z-171 $(M-CH_2CH_2Br)^+$,173$(171+2)^+$,175$(171+4)^+$.
Halogen pattern with required intensity ratio was observed.
Anal. Calcd. for $C_4H_5Br_2ClS$: C,17.13;H,1.78;S,11.42; combined halogens, 69.7. Found: C,17.2;H,1.69; S,11.50; combined halogens, 69.9.

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