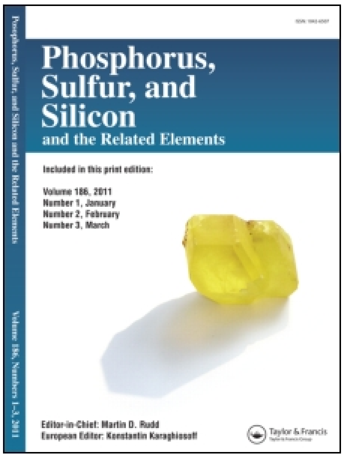

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THE REACTION OF DIMETHYL SULFOXIDE AND SYM-DICHLORO-BIS(2,4,6-TRICHLOROPHENYL) UREA

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THE REACTION OF DIMETHYL SULFOXIDE AND SYM-DICHLORO-BIS(2,4,6-TRICHLOROPHENYL) UREA

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ABSTRACT

Sym-dichloro-bis(2,4,6-trichlorophenyl) urea reacts explosively with dimethyl sulfoxide to yield phosgene, formaldehyde, methane, sulfur dioxide, ethylene chloride, methylene dichloride, chlorinated disulfides, and insoluble bis(2,4,6-trichlorophenyl) urea. The products, other than bis(2,4,6-trichlorophenyl) urea, are separated and characterized by means of gas chromatography and mass spectrometry. A homolytic mechanism is proposed for the reaction.

I. Introduction

In these laboratories an extensive investigation is presently being conducted on the thermal stability of sym-dichloro-bis(2,4,6-trichlorophenyl) urea (1) in the presence of metal oxides. While scanning a collection of solvents for 1, it was observed that a violent reaction occurred with dimethyl sulfoxide (DMSO) accompanied by a flash of flame and the evolution of a great deal of heat. Therefore, 1 should be included among those chlorinating agents that are dangerous[1] in the presence of DMSO. The synthesis of 1 is described elsewhere,[2] and its usefulness as a chlorinating agent other than for dialky sulfides has not been investigated.

A survey of the literature shows that sulfoxides have been successfully chlorinated at the alpha carbon by using common chlorinating agents such as chlorine, 1-chlorobenzotriazole,[3] nitrosyl chloride,[4] phenyliodionium dichloride,[5] sulfuryl chloride,[6] tert-butylhypochlorite,[7] *p*-toluene-sulfonyl chloride,[8] and N-chlorosuccinamide.[9] The mechanism for chlorination was generally believed[10-14] to be heterolytic involving a chlorine attack on the sulfur atom followed by an alpha proton extraction by a suitable base such as pyridine or the acetate ion and a simultaneous migration of the chlorine from sulfur to the alpha carbon. However, the presence of an added base catalyst was not always necessary for the chlorination to oc-

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cur[7,8,10,15]. In addition to an ionic mechanism F. Jung, *et al.*,[10] suggest that a free radical reaction is possible as an alternative mechanism.

1,2-dichloroethane was used as a solvent medium in an attempt to utilize **1** as a chlorinating agent for DMSO and simultaneously avoid a violent reaction by limiting the reaction temperature to the boiling point of the solution. Isolation and characterization of the products revealed that the reaction was not a straightforward chlorination of DMSO as has been reported for other chlorinating agents.[3–9]

II. Experimental Section

Solutions containing equal molar quantities of **1** and DMSO were slowly mixed by means of a dropping funnel while agitating with a mechanical stirrer. Bis(2,4,6-trichlorophenyl) urea (**4**) precipitated *quantitatively* (analysis by Schwarzkopf Microanalytical Laboratory, Woodside, N.Y.: C, 37.4%, H, 1.6%, N, 6.9%, Cl, 51.0%; theoretical C, 37%, H, 1.4%, N, 6.7%, Cl, 51%). The remaining reaction products were analyzed by injecting 2 µl of the filtrate into a Varian Aerograph model 2740 gas chromatograph equipped with a 48 in by $\frac{1}{8}$ inch column packed with chromosorb 101 (Johns Manville, 80–100 mesh). Helium was used as a carrier gas at a flow rate of 30 ml per minute. The gas chromatograph was also equipped with a hydrogen flame ionization detector and a 50/50 splitter valve so that part of the effluent gases could flow into a duPont model 21-492 mass spectrometer. The results are tabulated in Tables I and II for reaction products.

III. Results and Discussion

In solution, commercially available DMSO reacts rather fast with **1**, and the reaction is complete within about three to five seconds. Infrared spectra (ν_{OH} at 3310 cm^{-1} and 3480 cm^{-1}) of the sulfoxide indicated the presence of an alcohol impurity. Doubly distilled DMSO reacted so violently, when the 1,2-dichloroethane solutions of the reagents were mixed, that this reagent had to be added dropwise to avoid an uncontrollable explosion. The presence of the impurities apparently functioned as radical traps or played a role in base catalysis[3–14] for the chlorination reaction. This note deals exclusively with the reaction of purified DMSO and **1**. In reviewing the array of products (see Tables I, II) obtained from this reaction and noting the very fast reaction rate it is difficult to rationalize a heterolytic mechanism that will uniquely justify the formation of all the compounds produced by this reaction.

It is believed that a homolytic cleavage occurs in the nitrogen-chlorine bond of **1**, similar to that reported for N-halosuccinimide,[16–20] yielding the radical **2** (see Scheme). **2** then extracts a hydrogen atom from DMSO

TABLE I

Gas Chromatographic and Mass Spectra Data for G. C. Column Temperature of 250°C

Retention time (min.)	Product	Relative amounts %		Mass data spectral peak assignments										
3.4	CH_3SOCH_3	3.8	m/e	78	65	64	63	62	61	50	49	48	47	29
			%	100	35	20	36	38	87	7	12	38	58	35
6.3	C_2Cl_4	(a)	m/e	164	129									
			%	100	91									
9.2	CH_3SSCH_2Cl	13	m/e	128	94	93	79	64	49	47	46	45		
			%	12	43	18	100	7	7	11	9	24		
17.5	CH_3SSCCl_3	(b) 35	m/e	195	146	122	104	83	78	77	49			
			%	3	7	5	3	100	3	8	4			
21.9	$CHCl_2SSCH_2Cl$	32	m/e	195	126	81	79	65	64	48	47	46	45	
			%	2	43	65	60	12	30	13	100	29	50	
25.5	CH_3SSCCl_3	(b) 16	m/e	195	146	122	104	83	78	77	49			
			%	60	100	47	89	100	27	72	32			

(a) Not included in the integration.

(b) Two isomers of Trichloromethyl disulfide were obtained.

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TABLE II

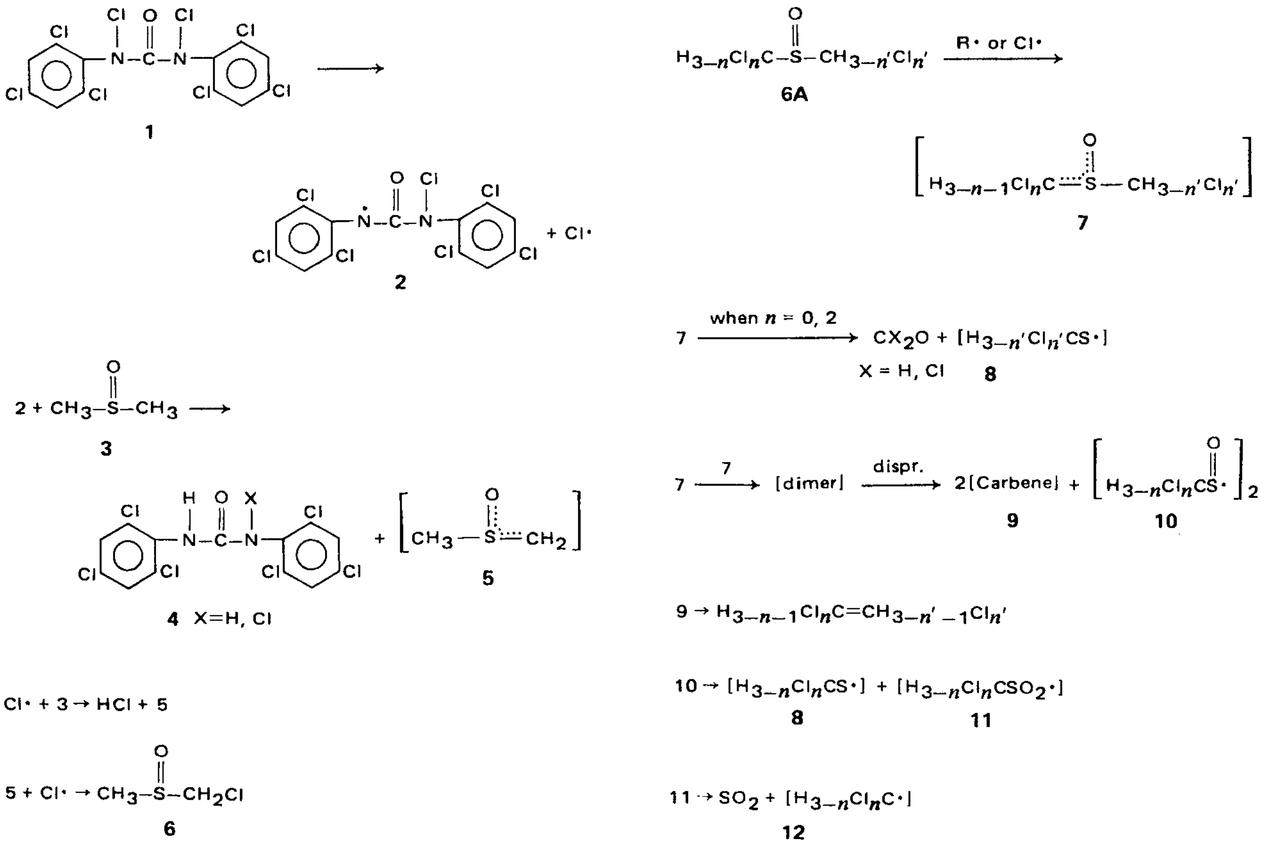
Gas Chromatographic and Mass Spectra Data for G. C. Column Temperature of 65°C

Retention time (min.)	Product	Relative amounts %	Mass data						
0.6	CH_4	2.8		(a)					
3.0	CH_2O	1.1	m/e	30	29				
			%	93	100				
4.6	SO_2	2.5	m/e	64	48				
			%	100	73				
7.5	C_2H_3Cl	85	m/e	62	27				
			%	100	30				
13.2	CCl_2O	5.9	m/e	98	63	35			
			%	7	100	24			
21.4	CH_2Cl_2	2.3	m/e	84	49				
			%	49	100				
26.0	$CHCl_3$	(b)	m/e	118	117	73	48	47	35
			%	4	9	100	12	32	9

(a) Verified to be methane by the retention time.

(b) Not included in the integration because its G. C. peak was within the solvent front.

SCHEME



to yield **4**, and the methyl-methylene sulfoxide radical (**5**) which is stabilized by means of π electrons.[21–24] **5** is also produced by atomic chlorine extracting a hydrogen atom from 3 to yield hydrogen chloride. **5** combines with chlorine by means of a terminal radical reaction producing alpha chlorination, **6**. A repetition of this mechanism leads to multiple substitution of the alpha protons which is expressed in the scheme by the general equation **6a–7**.

In order to justify the formation of disulfides and sulfur dioxide two alternate mechanisms must be occurring. For the first case, **6a** reacts with a radical hydrogen atom extractor to form the generalized radical 7. When n is zero or two, oxygen migrates causing the carbon to be oxidized and the sulfur to be reduced[25,26] yielding an alkyl sulfide radical, **8**, a propagating step, along with formaldehyde or phosgene. The second case involves a less probable mechanism whereby two radicals of 7 combine to form a dimer which then disproportionates into two carbene radicals, **9**, and dimerized alkyl sulfoxide radicals, **10**. **9** reacts to form the alkenes. **10** disproportionates to form an alkyl sulfide radical, **8**, and an alkyl sulfonyl radical, **11**.[27] **11** now disproportionates to form sulfur dioxide and an alkyl radical, **12**.[28–31] Radical **12** extracts a proton, and when n is three chloroform is formed, and when n is zero methane is formed. Radicals **8** combines to form the disulfide products.[32,33]

Perhaps this mechanism is extremely over-simplified because it ignores the participation of the solvent in the overall free-radical process. The scheme does justify all the products observed. What this study reveals is that a free radical chlorination of DMSO leads to the formation of several products, whereas base-catalyzed chlorination produces alpha proton substitution exclusively.

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