

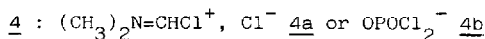
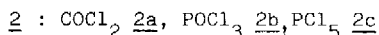
DIMETHYLSULFOXIDE ADDUCTS
WITH CHLORINATED LEWIS ACIDS AND WITH CHLORINE : NMR INVESTIGATIONS

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Abstract : The structure and mechanism of formation of the ionic species formed in the reaction of dimethylsulfoxide with COCl_2 , POCl_3 , PCl_5 , $\text{Cl}_2\text{CHOCH}_3$, $(\text{CH}_3)_2\text{N}=\text{CHCl}^+$, Cl^- or OPOCl_2^- , and Cl_2 are studied by proton, carbon and phosphorus NMR.

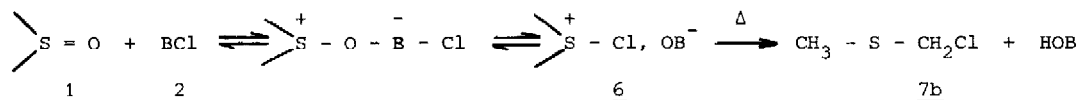
Lewis bases such as carboxamides, phosphoramides and sulfoxides are known to act as catalysts in halogenation reactions using acid chlorides or chlorine. The carboxamides have been extensively used, and usually react with acid chlorides to give chloroiminium salts (1a) which are powerful chlorination agents (1b). Hexamethylphosphoramide (HMPT) has been tried out in the catalysis of chlorination reactions in some specific cases (2a), and recently, chlorophosphonium salts were proved to be the active intermediates of these reactions (2b, c). Sulfoxides and namely, dimethylsulfoxide (DMSO) were claimed to facilitate the chlorination of alcohols (3a) with thionyl chloride and other acid chlorides (3b). A number of sulfur-containing salts were then postulated to be intermediates in the chlorination reaction, but their structures have not been definitively proved. Using proton and carbon NMR spectroscopies, we have established the structure of salts formed in the reaction of DMSO 1 with acid chlorides 2, dichloromethylmethylether 3, chloroiminium salts 4 and chlorine 5.



The NMR results, i.e. proton and carbon chemical shifts and one-bond carbon-proton coupling constants are given in the Table.

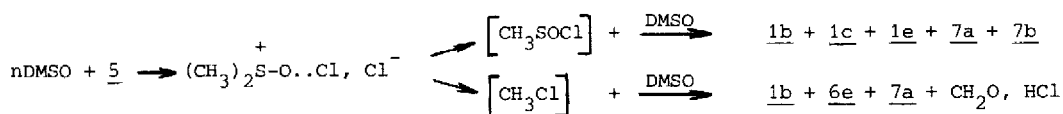
The acid chlorides give chlorosulfonium salts 6 $(\text{CH}_3)_2\text{SCl}^+$, Cl^- (6a), OPOCl_2^- (6b), PCl_6^- (6c) according to whether COCl_2 , POCl_3 or PCl_5 is used in the reaction. It should be noted that the compound 6c is obtained with an excess of PCl_5 from POCl_3 elimination ; moreover another salt $(\text{CH}_3)_2\text{SCl}^+$, ClO^- (6d) which is formed in a small proportion from PCl_3 elimination is also evidenced.

Above 273 K, the sulfonium salts 6 are unstable and rearrange into chloromethylmethylsulfide 7b via a Pummerer transposition :

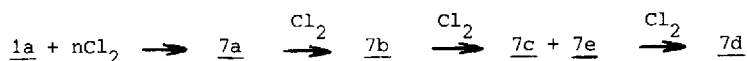


It is interesting to note that dichloromethylmethylether 3 and chloroiminium salts 4 react in the same way with DMSO to yield the chlorosulfonium salt 6a or 6b and methylformiate or N,N-dimethylformamide respectively. The structure of these salts is inferred from the observation of their NMR spectra which show a behaviour comparable to those of iminium (4) and phosphonium salts (2c). The signals of 6a (or 6b) in the uncoupled carbon spectra appear as a quartet, denoting methyl groups. The proton and carbon chemical shifts and the $^1\text{J}^{13}\text{C-H}$ values increase in 6a with respect to the corresponding values observed in $(\text{CH}_3)_2\text{S}$ (7a) as expected from the electron deficiency of the sulfur atom in the salt.

The products obtained in the reaction of chlorine with DMSO are manifold and their relative proportion depends on the DMSO/Cl₂ ratio. When an excess of 1a is used, two different kinds of products are observed : the first series of compounds corresponds to oxidized forms of sulfur such as DMSO, HCl 1b, CH₃SO₂CH₃ 1c, CH₃SO₂SCH₃ 1d, CH₃SO₂Cl 1e. The second group of products contains alkylsulfides and chloroalkylsulfides CH₃-S-CH₃ 7a, CH₃-S-CH₂Cl 7b, CH₃-S-CHCl₂ 7c, CH₃-S-CCl₃ 7d, CH₂Cl-S-CH₂Cl 7e. These various compounds originate from a sequence of disproportionation reactions of the unstable adduct $(\text{CH}_3)_2\text{S-O}\cdot\text{Cl}$, Cl⁻ and of its degradation products, as suggested some time ago (5) in the case of the reaction of Br₂ with 1. A methylsulfonium salt 6e is finally obtained in the last sequence of reactions



The chloroalkylsulfide 7b is readily oxidized to the sulfide sulfone 1d by SMO (6). When an excess of chlorine is used with 1a, the formation of polychloroalkylsulfides is observed.



The screening constants of the proton and carbon atoms belonging to the methyl group A in compounds 1 normally decrease in the series. However, it is interesting to note that, in compounds 7, the proton resonance undergoes a paramagnetic shift in the series but the $\delta^{13}\text{C}$ values of the methyl groups seem to behave irregularly. This observation could be tentatively explained by the influence of the excess of chlorine in the solution on the basic methyl groups in 7b, 7c, 7d.

N°	Compounds Formula	$\delta^1\text{H}$ (ppm/TMS)		$\delta^{13}\text{C}$ (ppm/TMS)		$^1\text{J}^{13}\text{C-H}$ (Hz)	
		(A)	(B)	(A)	(B)	(A)	(B)
<u>1a</u>	$\text{CH}_3\text{-SO-CH}_3$ (A) (A)	2.50	-	40.4	-	138	-
<u>1b</u>	$\text{CH}_3\text{-SO-CH}_3, \text{HCl}$ (A) (A)	2.87	-	37.2	-	141	-
<u>1c</u>	$\text{CH}_3\text{-SO}_2\text{-CH}_3$ (A) (A)	2.97	-	42.6	-	138	-
<u>1d</u>	$\text{CH}_3\text{-SO}_2\text{-SCH}_3$ (A) (B)	3.17	2.60	49.2	18.3	141	143
<u>1e</u>	$\text{CH}_3\text{-SO}_2\text{Cl}$ (A)	3.65	-	52.8	-	143	-
<u>6a</u>	$(\text{CH}_3)_2\text{S-Cl, Cl}$ (A)	2.9	-	24.9	-	146	-
<u>6b</u>	$(\text{CH}_3)_2\text{S-Cl, OPOCl}_2$ a (A)	2.9	-	24.5	-	146	-
<u>6c</u>	$(\text{CH}_3)_2\text{S-Cl, PCl}_6$ a (A)	3.0	-	24.5	-	146	-
<u>6d</u>	$(\text{CH}_3)_2\text{S-Cl, ClO}$ (A)	3.1	-	21.5	-	146	-
<u>6e</u>	$(\text{CH}_3)_2\text{S-CH}_3, \text{Cl}$ (A) (A)	3.0	-	24.2	-	146	-
<u>7a</u>	$\text{CH}_3\text{-S-CH}_3$ (A) (A)	2.05	-	18.0	-	138 b	-
<u>7b</u>	$\text{CH}_3\text{-S-CH}_2\text{Cl}$ (A) (B)	2.25	4.65	15.0	52.0	140 b	165 b
<u>7c</u>	$\text{CH}_3\text{-S-CHCl}_2$ (A) (B)	2.40	6.70	14.0	75.7	142 c	188 d
<u>7d</u>	$\text{CH}_3\text{-S-CCl}_3$ (A) (B)	2.60	-	22.2	107.3	140	- e
<u>7e</u>	$\text{CH}_2\text{Cl-S-CH}_2\text{Cl}$ (B) (B)	-	4.70	-	46.0	-	165 b

TABLE - NMR parameters of sulfoxides, sulfones, sulfides and chlorosulfonium salts.

(Positive values of shifts indicate a low screening with respect to that of TMS)

Conditions : solvent CH_2Cl_2 or CDCl_3 , concentration $\underline{c} = 2 \text{ mol.l}^{-1}$ temperature 273 K or 298 K, cell 8 mm (no degassing).

^1H and ^{13}C spectra were recorded at 2.4 T in the CW mode (^1H : sweep rate 500 Hz s^{-1} , B_1 intensity 50 dB) or in the FT mode (^{13}C flip angle 15.10^{-6} s , 90° flip angle $45 \cdot 10^{-6} \text{ s}$, acquisition time 0.8 s, 8192 data points, FID multiplication SE 0.6).

a : $\delta^{31}\text{P}/\text{H}_3\text{PO}_4$ $\text{OPOCl}_2^- = -8 \text{ ppm}$, $\text{PCl}_6^- = -290 \text{ ppm}$.

b, c, d, e : $^3\text{J}^{13}\text{CNH} = 5 \text{ Hz}$, 4 Hz , 6 Hz , 7 Hz .

The salts were synthesized according to the general procedure described previously (1a) : For COCl_2 , POCl_3 , PCl_5 , dichloromethylmethylether, a solution of acid in CH_2Cl_2 is added slowly under dry nitrogen atmosphere to the DMSO in the same solvent cooled at 273 K. For chloroiminium salts and chlorine a solution of the acide species in CH_2Cl_2 is previously prepared and then DMSO is added.

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