

Studies on Chlorosulphites: Part I—Preparation & Structure of N-Alkyl/N-2-Chloroethyl-pyridinium/picolinium Chlorosulphites

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N-Methyl/ethyl/n-butyl/2-chloroethyl-pyridinium/ α -, β - and γ -picolinium chlorosulphites have been isolated and their structure elucidated through elemental analyses, UV, IR and PMR spectral data, molar conductances, molecular weight determinations as well as by metathetical reactions. All the data reveal that these compounds exist as $[BR]^+ [SO_2Cl]^-$ (B = base). These compounds may serve as sources of chlorosulphite anion.

Reactions of methyl/ethyl chlorosulphites with pyridine and aniline are reported^{1,2} to lead to a mixture of products in each case. Our earlier attempts³ to isolate N-alkylated organic nitrogen base chlorosulphites even under mild conditions failed (in some cases, evolution of sulphur dioxide was observed). Our continued attempts finally led us to the successful preparation of the title chlorosulphites, the structures of which could be arrived at on the basis of elemental analyses, molar conductance and spectral data (UV, IR and PMR). We have also investigated the possibility of using the title compounds as sources of chlorosulphite ions.

Materials and Methods

Methyl/ethyl/n-butyl/2-chloroethyl-chlorosulphites were prepared by the literature procedures^{2,4}. Pyridine, α -, β - and γ -picolines (all BDH, pure) were distilled before use.

Infrared spectra were recorded as thin films or as nujol mulls on a Perkin-Elmer model 621 or 377 spectrophotometer. UV spectra were recorded in dichloromethane in the concentration range of 1.2×10^{-4} to 1.6×10^{-3} M on a Hitachi 330 spectrophotometer. PMR spectra were recorded on a Varian EM 390 (90 MHz) instrument using TMS as an external reference; chemical shifts are expressed in δ (ppm).

Molecular weights were determined by cryoscopic technique⁵ in freshly distilled formamide. Conductances of millimolar solutions of compounds were measured in freshly distilled DMF⁶ and conductivity water using a dip-type cell (cell constant = 0.52 cm^{-1}).

Reaction between alkyl/2-chloroethyl chlorosulphites and pyridine/ α -, β - or γ -picoline

To a pre-cooled (-5°C) solution of methyl/ethyl/n-butyl or 2-chloroethyl chlorosulphite (1 mol) in dry ether was added a pre-cooled (-5°C) solution of

pyridine/ α -, β - or γ -picoline in the same solvent in three to four lots under dry N_2 atmosphere. The mixture was stirred for 30 min. A slightly coloured heavy layer was obtained in each case. The upper layer was removed using hypodermic syringe through a septum and the lower layer was repeatedly extracted with ether. The liquid compound so obtained, was dried *in vacuo* (20-50 mm Hg). The complete removal of the solvent was monitored by PMR spectroscopy. Whereas the compounds obtained in the reaction of methyl chlorosulphite with α - and γ -picolines were solids and could be recrystallised from dichloromethane-ether mixture, (m.ps. 72 and 66° respectively), the other compounds were obtained as viscous oils. Attempts to distil these compounds under reduced pressure (~ 0.02 mmHg) were unsuccessful.

Metathetical reactions

To a solution of N-methyl- γ -picolinium chlorosulphite (2.07g, 10 mmol) in dry dichloromethane/acetoneitrile (20 ml) was added dropwise with stirring, under dry N_2 atmosphere, sodium tetraphenylboride (1.75 g, 10 mmol) in acetonitrile or potassium iodide (1.66 g, 10 mmol) in DMF. Immediately, a cream coloured solid started separating out in each case. The reaction mixture was stirred for 2-3 hr. The solid so obtained was filtered, washed, dried *in vacuo* and analysed.

With sodium tetraphenylboride, the solid obtained (yield 70 %) analysed for $NaSO_2Cl$ (Found : Na, 19.2; S, 26.4; Cl 28.8. $NaSO_2Cl$ requires Na, 18.7; S, 26.1; Cl, 28.9%); with potassium iodide the solid obtained (28%) analysed for KSO_2Cl (Found : S, 22.9; Cl, 24.9. KSO_2Cl requires S, 23.1; Cl, 25.6 %).

Results and Discussion

The N-alkyl/N-2-chloroethyl-pyridinium/picolinium chlorosulphites are light coloured, soluble in dichloromethane, chloroform,

Table 1—Characterization Data of the Products of Reaction of Alkyl Chlorosulphites with Pyridine and α -, β - and γ -Picolines

Compound	Colour & state (m.p. °C)	Found (Calc %)			Mol.wt found (calc)	λ_M (ohm ⁻¹ cm ² mol ⁻¹)
		N	Cl	S		
1. $[\alpha\text{-CH}_3\text{C}_3\text{H}_4\text{NCH}_3]^+ [\text{SO}_2\text{Cl}]^-$	White solid (72)	6.6 (6.7)	17.0 (17.1)	15.5 (15.4)	103.0 (207.5)	63
2. $[\beta\text{-CH}_3\text{C}_3\text{H}_4\text{NCH}_3]^+ [\text{SO}_2\text{Cl}]^-$	Brown viscous liquid	6.2 (6.7)	16.7 (17.1)	15.2 (15.4)	100.5 (207.5)	58.6
3. $[\gamma\text{-CH}_3\text{C}_3\text{H}_4\text{NCH}_3]^+ [\text{SO}_2\text{Cl}]^-$	Yellow solid (66)	6.2 (6.7)	16.9 (17.1)	15.2 (15.4)	110.0 (207.5)	58.2
4. $[\text{C}_3\text{H}_5\text{NCH}_2\text{CH}_3]^+ [\text{SO}_2\text{Cl}]^-$	Light yellow liquid	6.5 (6.7)	17.4 (17.1)	15.1 (15.4)	95.0 (207.5)	65.9
5. $[\alpha\text{-CH}_3\text{C}_3\text{H}_4\text{NCH}_2\text{CH}_3]^+ [\text{SO}_2\text{Cl}]^-$	Dark brown liquid	5.9 (6.3)	16.2 (16.0)	15.0 (14.4)	112.0 (221.5)	69.3
6. $[\beta\text{-CH}_3\text{C}_3\text{H}_4\text{NCH}_2\text{CH}_2\text{Cl}]^+ [\text{SO}_2\text{Cl}]^-$	Dark brown liquid	5.6 (5.4)	27.1 (27.7)	12.3 (12.5)	134.0 (256.0)	57.4
7. $[\text{C}_3\text{H}_5\text{NC}_4\text{H}_9]^+ [\text{SO}_2\text{Cl}]^-$	Light yellow liquid	5.6 (5.9)	15.2 (15.0)	13.8 (13.5)	125.0 (235.5)	61.4

formamide and DMF etc. and are insoluble in ether, *n*-hexane and carbon tetrachloride. These are hygroscopic in nature and slowly lose sulphur dioxide on standing. Analytical and other characterization data of the compounds are listed in Table 1. Conductances of their millimolar solutions in DMF and their molecular weights determined in formamide cryscopically suggest them to be 1:1 electrolytes.

UV spectra

The UV spectra of all the compounds in dichloromethane exhibit a charge transfer (CT) band in the region of 262-265 nm (ϵ 4000 to 5000). The UV spectra are found to be independent of the cations. Therefore, the CT band may be considered characteristic of chlorosulphite anion.

Infrared spectra

Some major infrared spectral absorptions are discussed below :

Alkyl/2-chloroethyl chlorosulphites show $\nu_{\text{as}}\text{SO}$, $\nu_{\text{s}}\text{SO}$ and δSO_2 bands at 1310, 1200 and 540 cm^{-1} respectively³. All these absorptions undergo shift to lower wavenumbers in the IR spectra of the products obtained with the reaction of these chlorosulphites with tertiary nitrogen bases and appear at 1260-40, 1140-1100 and 525-520 cm^{-1} respectively in the products. The $\nu\text{SO}(\text{C})$ in the chlorosulphites occur in the region of 980-900 cm^{-1} . The absence of these bands in the products suggest the cleavage of $\text{SO}(\text{C})$ bond on reaction of chlorosulphite with tertiary nitrogen bases. The characteristic $\nu\text{C}=\text{C}$ and $\nu\text{C}=\text{N}$ modes of pyridine and α -, β - or γ -picoline^{7,8} which appear at around 1600, 1500, 1490, 1440 cm^{-1}

respectively undergo shift to higher wave numbers ($\Delta\nu = 15\text{-}35 \text{ cm}^{-1}$) in the products⁷. Typical absorptions (medium to weak) attributed to pyridinium and picolinium⁸ ions are observed between 2500 and 1700 cm^{-1} . These are infact overtones or combination bands⁸.

PMR spectra

In the PMR spectrum of $\text{CH}_3\text{SO}_2\text{Cl}$, the methyl protons appear as a singlet at δ 4.0(3H). In the PMR spectra of the products obtained in the reaction of $\text{CH}_3\text{SO}_2\text{Cl}$ with α -, β - or γ -picoline $[\alpha\text{-}/\beta\text{-}/\gamma\text{-CH}_3\text{C}_3\text{H}_4\text{N-CH}_3]^+$, the N-methyl protons appear as singlets (3H) at 2.8, 2.6 and 2.7 respectively. The three-proton singlets at 4.25, 4.5 and 4.65 respectively are assigned to the α -, β - and γ -methyls. The pyridine ring protons appear as four-proton multiplet around 8.6 ppm.

The PMR spectrum of $\text{C}_2\text{H}_5\text{SO}_2\text{Cl}$ exhibits the methyl and methylene protons as triplet and a multiplet (2H) at δ 4.7 and 1.6 respectively. In the PMR spectrum of N-methylpyridinium chlorosulphite or N-ethyl- α -picolinium chlorosulphite, these signals undergo downfield shift and appear as triplets (3H) at 1.9 and 1.8 and as a quartet (2H) at 5.2 respectively. The ring protons (4H) appear as multiplets at 9.1 and 8.8 respectively. In addition, α -methyl proton in the case of α -picolinium derivatives appear as a singlet at 3.2 ppm.

In 2-chloroethyl chlorosulphite, the PMR signals are identified at 3.8 (2H) and 4.7 (2H) as triplet and multiplet corresponding to $\text{ClCH}_2\text{—}$ and $\text{—CH}_2\text{O}$ protons respectively, whereas, in 2-chloroethyl- β -picolinium-chlorosulphite, these signals appear as triplets at 4.3(2H) and 5.5 (2H) respectively. The ring

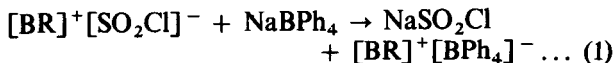
protons appear at 8.5(4H) as a multiplet. The β -methyl protons appear as a singlet at 2.7 (3H).

The PMR spectrum of *n*-butyl chlorosulphite exhibits signals as triplet at 1.1(3H) and multiplets at 1.7(4H) and 4.6(2H) corresponding to CH_3 , CH_2 and $-\text{CH}_2\text{O}-$ protons respectively. In *n*-butylpyridinium chlorosulphite these signals undergo downfield shift and appear as a triplet at 0.8(3H) and as multiplets at 1.4(2H), 1.8(2H) and at 5.1 ppm(2H) as a triplet.

All the above data point to the fact that the compounds are ionic in nature and have the general composition $[\text{BR}]^+[\text{SO}_2\text{Cl}]^-$ (where B = pyridine, α -, β - or γ -picoline and R = CH_3 , C_2H_5 , $\text{C}_2\text{H}_4\text{Cl}$ or *n*- C_4H_9 group).

The formation of these ions are further confirmed by metathetical reactions (1) and (2), where in NaSO_2Cl and KSO_2Cl precipitate out. Both these compounds do not react with water and are stable at room temperature. Elemental analyses, UV, IR and TGA/DTA data confirm the above composition of these compounds. Molar conductances in water reveal them to be 1:1 electrolytes possibly constituted of K^+/Na^+ , $(\text{SO}_2\text{Cl})^-$ ions. Thus organic nitrogen

tertiary base chlorosulphites may serve as a possible source of isolable chlorosulphite anion.



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