156. *The Interaction of Alkyl Chlorosulphinates and Pyridine in Ethereal Solution.*

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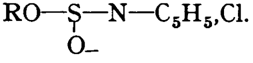
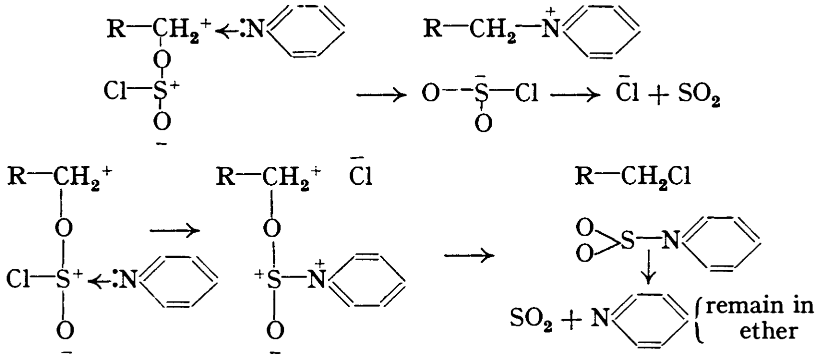
CONSIDERABLE interest attaches to the use of pyridine with thionyl chloride in effecting the replacement of the alcoholic hydroxylic group by a chlorine atom (see Silberrad, *J. Soc. Chem. Ind.*, 1926, **45**, 37, 55; Clark and Streight, *Trans. Roy. Soc. Canada*, 1929, **23**, III, 77), and the suggestion has been made by Kenyon, Lipscomb, and Phillips (J., 1930, 415) that the pyridine not only facilitates the formation of the intermediate chlorosulphinate, but also aids its decomposition into the chloride by forming an unstable pyridinium chloride,  $RO{-}\underset{\underset{O_{-}}{\uparrow}}{\overset{+}{S}}{-}\overset{+}{N}{-}C_5H_5,\overset{-}{Cl}$. During a study of Walden inversion reactions involving the replacement of the hydroxyl group in ethyl *d*-lactate by a chlorine atom (Gerrard, Kenyon, and Phillips, unpublished), it was observed that when ethyl *d*-α-chlorosulphinoxypropionate was added to pyridine in cold ethereal solution, a pale yellow oil separated, leaving in the ether but a third of the theoretical yield of ethyl *d*-α-chloropropionate. From the analysis of the picrate yielded by the oil, the latter appeared to consist chiefly of a salt of 2-carbethoxypyridinium hydroxide. Furthermore, when a chlorosulphinate, RO·SOCl, is added to an ethereal solution of an alcohol, R'OH, and pyridine, a precipitate of pyridine hydrochloride is produced, and an almost theoretical yield of the sulphite, $RR'SO_3$, can be obtained from the ethereal solution (Voss and Blanke, *Annalen*, 1931, **485**, 258; Gerrard, Kenyon, and Phillips, *loc. cit.*). It appeared to be of interest, therefore, to examine the interaction of alkyl chlorosulphinates and pyridine itself in cold ethereal solution.

It is now shown that when the alkyl chlorosulphinate, RO·SOCl, is mixed with pyridine in cold dry ether, a yellow oily mixture of 1-alkylpyridinium chloride and 1-alkylpyridinium chlorosulphinate separates in quantity, leaving in the ether about a 40% yield of the alkyl chloride. With 1 mol. of the chlorosulphinate per mol. of pyridine, nearly a third of the base remained in the ether at the end of the reaction; but with 0·5 mol. of the base, no pyridine remained in the ether, and the yield of alkyl chloride was somewhat larger. The aqueous washings of the ethereal solutions at the end always contained a considerable amount of sulphur dioxide, but scarcely any chloride ion.

To account for these observations it is suggested that there are two distinct mechanisms by which pyridine reacts with the chlorosulphinate:



From a consideration of the arrangement of electrons in the chlorosulphinate molecule, it seems probable that there are two points where positive charges tend to polarise. It is conceivable that the lone pair of electrons on the nitrogen atom of the pyridine molecule could be accommodated at either of these points. If attachment took place at the carbonium point, the C—O link would be disturbed, and, following the scission indicated, the pyridinium cation would be formed. On the other hand, if attachment took place at the sulphur atom, the release of the chlorine anion might be followed by a scission at the C—O link resulting in the formation of the unstable complex, $SO_2NC_5H_5$, which decomposes into pyridine and sulphur dioxide. The re-formed pyridine is then available for further reaction by either of the two mechanisms proposed.

It is not likely that the alkylpyridinium compound is formed by the addition of the alkyl chloride to the unchanged pyridine; for this combination proceeds very slowly in ethereal solution at room temperature. *iso*Amyl chloride mixed with pyridine in dry ether gave no deposit after three months, even when the solution had been saturated with dry sulphur dioxide.

In contrast to chlorosulphinates, the chlorides of carboxylic acids do not give quaternary pyridinium compounds; *e.g.*, acetyl chloride and benzoyl chloride yield additive compounds with pyridine, but with water these decompose readily into dehydracetic acid and benzoic anhydride respectively (Minunni, *Gazzetta*, 1892, **22**, ii, 213; Wedekind, *Ber.*, 1901, **34**, 2070).

The isolation and identification of the alkylpyridinium compounds were effected in the first place by the precipitation from aqueous solution of their sparingly soluble *ferrocyanides*, $(C_5H_5NR)_2,H_2Fe(CN)_6,2H_2O$. At the dilution used, pyridine does not give a precipitate with potassium ferrocyanide (compare Cumming, J., 1922, **121**, 1287; 1923, **123**, 2457), so this affords an excellent means of separating the quaternary compounds from adventitious pyridine.

EXPERIMENTAL.

The chlorosulphinates were prepared as usual by adding the alcohol (1 mol.) slowly with vigorous shaking to freshly distilled, cooled thionyl chloride (1·3 mols.), keeping the product in a desiccator for 4 hours, and distilling it at low pressure. The products were redistilled until pure and were used immediately.

General Procedure.—A solution of the appropriate chlorosulphinate in dry ether at — 10° was mixed with a cold solution of pyridine in dry ether, and the mixture was at once filtered rapidly from a small amount of white solid which always separated. The stoppered flask containing the filtrate was replaced in the freezing mixture and allowed to warm to room temperature. Within a few minutes after the mixing, there was an evolution of heat, and a pale yellow oil began to separate. At the end of 12 hours most of the oil had formed, but the deposition usually continued for a further 48—60 hours. The absence of chlorosulphinate at the end was indicated by the non-production of a white precipitate of pyridine hydrochloride on the addition of an alcohol (followed, if necessary, by pyridine) to a test portion of the ethereal solution.

The ether was decanted from the oil, washed successively with water, potassium carbonate solution, dilute hydrochloric acid, water, potassium carbonate solution, and finally dried over sodium sulphate prior to distillation through a 12-bulb column. From the residue thereby obtained, the alkyl chloride was isolated in the cases of *n*-butyl, *iso*amyl, and *iso*butyl chlorides. The aqueous extract of the ether contained a considerable amount of sulphur dioxide; but the first water and carbonate washings were practically free from chloride ion. When molecular proportions of the chlorosulphinate and pyridine had been used, the aqueous extract of the ether yielded on steam-distillation from alkaline solution about a third of the original quantity of pyridine, this estimation being effected by Schulze's method (*Ber.*, 1887, **20**, 3391).

The oils were miscible with water and alcohol in all proportions, sulphur dioxide being freely evolved on the addition of dilute mineral acid. When placed in a vacuum, the oils lost sulphur dioxide, rapidly at first, but retained some of it even after a month. The sulphur dioxide was estimated by distilling a weighed amount of oil from a solution of phosphoric acid in a stream of carbon dioxide, the distillate being absorbed in water kept slightly coloured with standard iodine solution added from a burette. Ionised chlorine was determined by the Volhard method. Very little pyridine, 0·5 g., was obtained when the oils were steam-distilled from alkaline solution, and the aqueous residues on acidification and treatment with potassium ferrocyanide solution gave the yellow ferrocyanides of the quaternary pyridinium compounds. These analyses indicated the oils to be mixtures of the alkylpyridinium chloride and chlorosulphinate.

The *alkylpyridinium ferrocyanides* were prepared by the slow addition of *N*-hydrochloric acid to an aqueous solution of the oil and potassium ferrocyanide. The yellowish crystalline precipitate was filtered off, washed well with water, and dried over calcium chloride in a desiccator. Oxidation frustrates attempts to obtain a further crop of crystals from the mother-liquor. Furthermore, if too much acid is added, a white precipitate is produced, and this appears to consist of $C_5H_5NR,H_3Fe(CN)_6,H_2O$.

In Table I are recorded the quantities of alkyl chlorosulphinate and pyridine used, together with the yields of oils and alkyl chlorides. Table II contains the data for the 1-alkylpyridinium ferrocyanides not previously described; and in Table III is recorded other evidence of the existence in the oils of 1-alkylpyridinium compounds, the data given being in accord with those

TABLE I.

Interaction of alkyl chlorosulphinates and pyridine.

RO·SOCl.					
R.	Wt., g.	C_5H_5N, g.	Vol. of Et_2O, c.c.	Yield of oil, %.	Yield of RCl, %.
CH_3	22·9	15·8	90	57·5	—
C_2H_5	25·7	15·8	60	72·2	—
,,	25·7	7·9 (0·5 mol.)	60	51·4	—
n-C_3H_7	28·5	15·8	70	76·6	—
n-C_4H_9	31·4	15·8	60	62·5	15·5
,,	31·4	7·9 (0·5 mol.)	60	45·8	49·7
iso-C_5H_{11}	17	7·9	40	52	32·9
,,	17	4 (0·5 mol.)	40	43·3	43·2
,,	17	2 (0·25 mol.)	40	17·3	47·9
iso-C_3H_7	28·5	15·8	70	61	—
iso-C_4H_9	31·3	15·8	70	55·8	23·2

published in the literature. For 1-methylpyridinium picrate, Ostermayer (*Ber.*, 1885, **18**, 592) gave the m. p. as 34°, whilst Decker and Kaufmann (*J. pr. Chem.*, 1911, **84**, 425) record m. p. 109—110° (needles) and m. p. 113—114° (rhombohedra); Kohn and Grauer (*Monatsh.*, 1913, **34**, 1751) give m. p. 107—110°.

The yields are calculated on the weight of chlorosulphinate, and the yields of oil are calculated on the weights of alkylpyridinium compound possible.

TABLE II.

1-*Alkylpyridinium ferrocyanides*, $(C_5H_5NR)_2,H_2Fe(CN)_6,2H_2O$, *obtained from the oils by addition of potassium ferrocyanide and hydrochloric acid solutions.*

		Analyses, %.*				
R.	Yield, %.	C.	H.	N.	Fe.	Remarks.
Me	60·8	49·4	5·0	25·5	12·9	Orange-yellow; brown at 150°, does not melt.
		49·3	5·0	25·5	12·8	
				25·5	12·9	From 1-methylpyridinium iodide.
Et	74·8	51·3	5·5	24·0	12·0	Orange; brown at 143°; m. p. 150—151° (decomp.).
		51·5	5·4	24·0	12·0	
		51·3	5·5	24·0	12·2	From 1-ethylpyridinium iodide.
Pr	72·1			22·6	11·3	Orange-yellow; darkens at 140°, m. p. 143° (decomp.).
				22·7	11·3	
Bu	92·7	55·0	6·4	21·8	10·8	Chrome-yellow; turns brown at 163°, decomp. without melting at 165°.
		55·2	6·5	21·5	10·7	
iso-Amyl	94	56·7	6·9	20·3	10·2	Yellow.
		56·7	6·9	20·4	10·2	
iso-Propyl	—				11·4	Orange; decomp. 145°.
					11·3	
iso-Butyl	—				10·8	Yellow; decomp. 150°.
					10·7	

* The second line in each case gives the theoretical values.

TABLE III.

Derivatives of oils.

R.	Derivative.	Analyses.
Me	Picrate, m. p. 109°	N, 17·4 (Calc. for $C_{12}H_{10}N_4O_7$: N, 17·4%).
	Chloroaurate, m. p. 247°	
Et	Picrate, m. p. 89°	N, 16·8 (,, ,, $C_{13}H_{12}N_4O_7$: N, 16·7%).
	Chloroaurate, m. p. 141—142°	
	Chloroplatinate, m. p. 201° (orange-red crystals)	
Pr	Chloroaurate, m. p. 128° (yellow crystals)	Au, 42·9 (,, ,, $C_8H_{12}NAuCl_4$: Au, 42·8%).
Bu	Chloroplatinate, m. p. 202°	*B*, 136·5 (,, ,, $C_5H_5N{\cdot}C_4H_9$: *B*, 136·0).
	Chloroaurate, m. p. 117°	
iso-Amyl	Chloroplatinate, m. p. 203°	*B*, 149·8 (,, ,, $C_5H_5N{\cdot}C_5H_{11}$: *B*, 150).
	Chloroaurate, m. p. 139°	
iso-Pr	Chloroaurate, m. p. 144°	Au, 42·7 (,, ,, $C_8H_{12}NAuCl_4$: Au, 42·8%).
iso-Bu	Chloroaurate, m. p. 139—140°	*B*, 138 (,, ,, $C_5H_5N{\cdot}C_4H_9$: *B*, 136).

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