21. *Studies on the Esters of Sulphurous, Chlorosulphinic, and Chlorosulphonic Acids. Part I.*

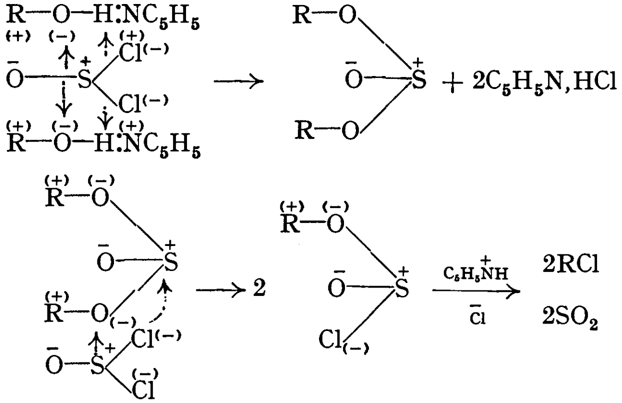
By William Gerrard.

Confusing statements in the literature concerning the sequence of reactions taking place between thionyl chloride and a hydroxylic compound in the presence of pyridine, and the necessity for precise knowledge of this sequence in a more extensive investigation, led to the detailed examination described herein. Pyridine in the Darzens procedure facilitates the formation of the sulphite, R_2SO_3, and not the chlorosulphinate, RO·SOCl; the latter is formed by the second half of the thionyl chloride used and is decomposed catalytically by the pyridine hydrochloride present to form the chloride, RCl, and sulphur dioxide.

Search for a convenient method of indicating the presence of thionyl chloride in specimens of chlorosulphinate led to the examination of the interaction between aliphatic chlorosulphinates and formic acid, which was found to result in the formation of the corresponding formate without the evolution of carbon monoxide.

In an investigation which is still in progress, it became necessary to have a clear conception of the mechanism of the replacement of a hydroxyl group by a chlorine atom through the agency of thionyl chloride in the presence of pyridine (Darzens, *Compt. rend.*, 1911, **152**, 1314), and in view of the somewhat confusing statements in the literature (Carré and Libermann, *Compt. rend.*, 1931, **192**, 1738; 1932, **195**, 799; 1933, **196**, 275, 865, 1419, 1807; 1934, **198**, 274; Silberrad, *Review J. Soc. Chem. Ind.*, 1926, **45**, 37, 55) it seemed desirable to examine the reactions in detail.

It is now shown that the slow addition of thionyl chloride (1 mol.) to a mixture of the hydroxylic compound R·OH (1 mol.) and pyridine (1 mol.) results in the precipitation of a good specimen of pyridine hydrochloride during the addition of the first half of the thionyl chloride, but no further change is apparent during the addition of the second half of the reagent. The reaction mixture then consists of the sulphite R_2SO_3 (0·5 mol.), white crystalline pyridine hydrochloride (1 mol.), and unchanged thionyl chloride (0·5 mol.). If the liquid is filtered and worked up, good yields of the sulphite R_2SO_3 and pyridine hydrochloride result. On the other hand, if the mixture is heated on a steam-bath (Darzens' procedure), the second half of the thionyl chloride reacts with the sulphite and forms the chlorosulphinate RO·SOCl, which is then catalytically decomposed by the pyridine hydrochloride to the chloride RCl and sulphur dioxide. This has been verified by warming the appropriate chlorosulphinate (alkylchlorosulphinates and ethyl α-chlorosulphinoxypropionate) with a small quantity of pyridine hydrochloride and obtaining practically theoretical yields of the chloride R·Cl and sulphur dioxide at temperatures far below those required to decompose the chlorosulphinates themselves. The chloride ions supplied by the pyridine hydrochloride are probably *the* important factor in the decomposition. The suggested mechanism involves the co-ordination of the hydrogen atom of the hydroxyl group (the signs in parentheses are intended to denote tendency) :

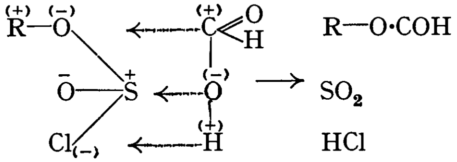


Pyridine alone reacts with alkyl chlorosulphinates and ethyl α-chlorosulphinoxypropionate to give a pyridinium compound $C_5H_5NR{\cdot}SO_2Cl$ and a considerably diminished yield of the chloride R·Cl (Gerrard, J., 1936, 688; Gerrard, Kenyon, and Phillips, J., 1937, 153). It is now shown that the use of pyridine in excess of one molecule for one molecule of thionyl chloride and one molecule of hydroxylic compound (Darzens) inhibits the decomposition of the intermediate sulphite in proportion to the amount of pyridine used. For example, thionyl chloride (1 mol.) added to *n*-amyl alcohol (1 mol.) and pyridine (2 mols.) produces a mixture of *n*-amyl sulphite (0·5 mol.), thionyl chloride (0·5 mol.), pyridine hydrochloride (1 mol.), and pyridine (1 mol.). On being refluxed on a steam-bath, this mixture turns black owing to the interaction of the excess of pyridine and thionyl chloride to form 4-pyridylpyridinium dichloride (Koenigs and Greiner, *Ber.*, 1931, **64**, 1049), which leaves insufficient thionyl chloride for attack on the sulphite, much of which is recovered unchanged. The discoloration which occurs when the reaction mixture in the Darzens procedure is heated is due to the interaction of the slight excess of pyridine with the thionyl chloride.

In the investigation mentioned in the first paragraph of this paper, it was further necessary to have some method for showing the presence or absence of unchanged thionyl chloride in a chlorosulphinate which cannot be distilled without decomposition. The chlorosulphinates, RO·SOCl, examined gave with formic acid in the cold a steady evolution of hydrogen chloride and sulphur dioxide, but *no* carbon monoxide, and left the corresponding formate, $H{\cdot}CO_2R$, in contrast with the interaction of formic acid with thionyl chloride and acyl chloride, R·COCl :

$$SOCl_2 + H{\cdot}CO_2H = SO_2 + 2HCl + CO$$
$$R{\cdot}COCl + H{\cdot}CO_2H = R{\cdot}CO_2H + HCl + CO$$

(Meyer and Turnau, *Monatsh.*, 1913, **34**, 69 ; Moureu, *Compt. rend.*, 1894, **119**, 337 ; *Monatsh.*, 1907, **28**, 153). The mechanism suggested is :



The action of thionyl chloride on phenol was examined by Carius (*Annalen*, 1859, **111**, 93), but no definite compound was isolated. Tassinari (*Gazzetta*, 1890, **20**, 362) and Voswinkel (*Pharm. Z.*, 1895, **40**, 241) obtained many products, but identified only $(C_6H_4{\cdot}OH)_2S$. Carré and Libermann (*Compt. rend.*, 1933, **196**, 275) examined the reaction further and suggested the scheme :

$$3C_6H_5{\cdot}OH + 2SOCl_2 \longrightarrow (C_6H_4{\cdot}OH)_3SCl + SO_2 + 3HCl \longrightarrow (C_6H_4{\cdot}OH)_2S + C_6H_4Cl{\cdot}OH$$

(compare Courtot and Tung, *Compt. rend.*, 1935, **200**, 1541). The implication has developed and a definite suggestion has been made (Carré and Libermann, *Compt. rend.*, 1932, **195**, 799) that phenyl chlorosulphinate, PhO·SOCl, cannot be made directly from phenol and thionyl chloride as in the preparation of alkyl chlorosulphinates. This, however, is not so. The present author has prepared pure phenyl chlorosulphinate in this way.

EXPERIMENTAL.

Interaction of Thionyl Chloride, in the Presence of Pyridine, with n-*Butyl Alcohol,* n-*Amyl Alcohol, and Ethyl Lactate.*—(a) *Equimolecular quantities.* (i) n-*Butyl alcohol.* Thionyl chloride (60 g. ; 1 mol.) was added slowly to a well-stirred mixture of *n*-butyl alcohol (37 g. ; 1 mol.) and pyridine (40 g. ; 1 mol.) at 0°. The product consisted of crystalline pyridine hydrochloride (1·0 mol.), which separated during the addition of the first 0·5 mol. of thionyl chloride, and a colourless supernatant liquid containing *n*-butyl sulphite (0·5 mol.) and unchanged thionyl chloride (0·5 mol.). The pyridine hydrochloride was washed with dry ether and placed on a porous plate in a vacuum desiccator; yield, 55 g., 96% (Found : Cl, 29·9. Calc. : Cl, 30·7%). The filtrate, mixed with the ethereal washings and worked up, yielded practically nothing but *n*-butyl sulphite, b. p. 116°/19 mm., $d_{4°}^{18·8°}$ 0·9939 (Found : S, 16·3. Calc. : S, 16·4%) ; yield, 38·8 g., 80%. When the experiment was made in ethereal solution (100 c.c.), a better specimen of pyridine hydrochloride (Cl, 30·5%) and a larger yield of *n*-butyl sulphite (87%) were obtained. The mixture of *n*-butyl sulphite (0·5 mol.), thionyl chloride (0·5 mol.), and pyridine hydrochloride (1·0 mol.) which resulted from the addition of thionyl choride (23·8 g. ; 1 mol.) to *n*-butyl alcohol (14·8 g. ; 1·0 mol.) and pyridine (15·8 g. ; 1·0 mol.) as previously described, was heated on a steam-bath for 3 hours (Darzens' procedure). The product gave *n*-butyl chloride, b. p. 77°, $d_{4°}^{18°}$ 0·8875 ; yield, 17·4 g., 94%.

(ii) n-*Amyl alcohol.* Thionyl chloride (15 g. ; 1 mol.) was added to a mixture of *n*-amyl alcohol (11 g.; 1 mol.) and pyridine (10 g.; 1 mol.) as described in (a i) and the same phenomena were observed. Filtration of the reaction mixture yielded pyridine hydrochloride (14·0 g., 97·2%), and from the filtrate *n*-amyl sulphite was obtained, b. p. 137°/20 mm., $d_{4^\circ}^{16^\circ}$ 0·9821; yield, 83% (Found: S, 14·4. Calc.: S, 14·4%).

(iii) *Ethyl lactate.* Thionyl chloride (35·6 g.; 1 mol.), added to a mixture of ethyl lactate (35·4 g.; 1 mol.) and pyridine (23·7 g.; 1 mol.) as described in (a ii), gave the same result. Crystalline pyridine hydrochloride (yield, 95%) was obtained and from the filtrate practically nothing but α-carbethoxyethyl sulphite was isolated, b. p. 161°/14 mm.; yield, 35·6 g., 84% (Found: S, 11·4. Calc.: S, 11·4%).

(b) *With excess of pyridine.* (i) n-*Butyl alcohol.* Thionyl chloride (23·8 g.; 1 mol.), added to a mixture of *n*-butyl alcohol (14·8 g.; 1 mol.) and pyridine (31·6 g.; 2 mols.) as in (a i), precipitated pyridine hydrochloride only during the addition of the first 0·5 mol. The precipitate was pasty owing to the presence of excess of pyridine, and difficult to filter, but after much washing with dry ether, and long standing in a vacuum desiccator, it weighed 22·5 g., 98% (Found: Cl, 29·6%). The ethereal solution of the filtrate required much washing, and gave, after being dried with sodium sulphate, *n*-butyl sulphite, b. p. 114°/17·5 mm. (11·5 g., 60%), but no *n*-butyl chloride could be isolated. In a second experiment the same quantities of reactants were mixed as described and heated on a steam-bath for 4 hours. The pyridine hydrochloride darkened and became fluid. The cooled product consisted of white crystalline pyridine hydrochloride mixed with a dark brown oil and covered with a colourless liquid, which on being decanted and worked up gave *n*-butyl chloride, b. p. 77°, $d_{4^\circ}^{17\cdot5^\circ}$ 0·8880 (5·7 g., 60·1%) and *n*-butyl sulphite, b. p. 114°/18 mm., $d_{4^\circ}^{18^\circ}$ 0·9940 (5·9 g., 30·5%) (Found: S, 16·3%). The dark brown oil contained SO_2, 11·5; Cl, 20·3%, and was probably a product of the interaction of pyridine and thionyl chloride. In a third experiment, with the same quantities of reactants except that 47 g. of pyridine (3 mols.) were used in 40 c.c. of dry ether, the same phenomena were observed. The mixture, after being kept for 18 hours at room temperature, gave *n*-butyl sulphite, b. p. 110°/13 mm.; yield, 15·3 g., 80% (Found: S, 16·2%). In a fourth experiment, the reaction mixture was heated on a steam-bath for 4 hours. The colourless supernatant liquid, decanted from the brown oil and solid, gave, on being worked up, *n*-butyl chloride, b. p. 77°, $d_{4^\circ}^{18\cdot3^\circ}$ 0·8870 (3·1 g., 33%), and *n*-butyl sulphite, b. p. 116°/19 mm., $d_{4^\circ}^{18^\circ}$ 0·9941 (11·5 g., 59%). A mixture of the same quantities of reagents, but with 64 g. of pyridine (4 mols.) in 100 c.c. of dry ether, was filtered from pyridine hydrochloride (21·8 g., 95%) (Found: Cl, 30·7%), and refluxed for one hour, during which operation a dark brown oil (14·1 g.) was deposited. The ethereal solution gave *n*-butyl sulphite, b. p. 114°/18 mm. (14·9 g., 77%).

(ii) n-*Amyl alcohol.* Thionyl chloride (15 g.; 1 mol.), added to a mixture of *n*-amyl alcohol (11 g.; 1 mol.) and pyridine (20 g.; 2 mols.) in the way described, gave on standing for 24 hours and being refluxed on a steam-bath for 4 hours, a dark brown mass, which, on being cooled, separated into a crystalline mass mixed with a dark brown oil, and a colourless liquid. This liquid yielded *n*-amyl chloride, b. p. 108°, $d_{4^\circ}^{20^\circ}$ 0·8833 (3·3 g., 24%), and *n*-amyl sulphite, b. p. 137°/20 mm., $d_{4^\circ}^{16^\circ}$ 0·9820 (9·7 g., 69%).

(iii) *Ethyl lactate.* Thionyl chloride (35·6 g.; 1 mol.), added to a mixture of ethyl lactate (35·4 g.; 1 mol.) and pyridine (47·4 g.; 2 mols.) as described, gave a product which, on being heated on a steam-bath for 6 hours, yielded a black crystalline mass and a discoloured liquid. From the liquid, ethyl α-chloropropionate, b. p. 43°/15 mm., $d_{4^\circ}^{15^\circ}$ 1·0855 (20 g.), and α-carbethoxyethyl sulphite, b. p. 161°/14 mm. (10 g.), were obtained.

Decomposition of (a) n-*Butyl Chorosulphinate and* (b) *Ethyl α-Chlorosulphinoxypropionate by Pyridine Hydrochloride.*—(a) *n*-Butyl chlorosulphinate (15·8 g.) was mixed with pyridine hydrochloride (1·5 g.) and slowly heated; at 50° the evolution of sulphur dioxide was appreciable. The temperature was maintained at 60—63° for 2 hours, the mixture remaining practically colourless. The cooled product consisted of crystalline pyridine hydrochloride and an almost colourless liquid. Dry ether was added and decanted; it yielded *n*-butyl chloride, b. p. 77°, $d_{4^\circ}^{18^\circ}$ 0·8875 (8·9 g., 96%) (Found: Cl, 38·2. Calc.: Cl, 38·4%). The sodium hydroxide solution used for the absorption of the gas evolved contained 5·95 g. of sulphur dioxide (theo., 6·4 g.) but no chloride ion.

(b) Ethyl α-chlorosulphinoxypropionate (20 g.) was mixed with pyridine hydrochloride (1 g.) and treated as in (a). The evolution of sulphur dioxide was appreciable at 80° and rapid at 90°. The ethereal extract of the residue gave ethyl α-chloropropionate, b. p. 143—144°, $d_{4^\circ}^{15^\circ}$ 1·0855 (12·5 g., 91%) (Found: Cl, 25·8. Calc.: Cl, 26·0%). The absorption vessel contained 5·6 g. of sulphur dioxide, but no chloride ion. The wash-water of the ethereal extract contained 0·4 g. of sulphur dioxide. In a study of the Walden inversion, Frankland and Garner (J., 1914, **105**,

1101) heated 30 g. of ethyl α-chlorosulphinoxypropionate with 7 g. of pyridine hydrochloride and obtained ethyl α-chloropropionate in 80% yield.

Interaction between Formic Acid and Esters of Chlorosulphinic Acid.—(a) *Ethyl α-chlorosulphinoxypropionate.* 20 G. of ethyl α-chlorosulphinoxypropionate ($\alpha_D^{18°}$ — 22·8°) were mixed with 4·6 g. of formic acid (100%). A slow but steady reaction was appreciable at room temperature, bubbles of gas were disengaged from the liquid, and hydrogen chloride and sulphur dioxide were evolved, but no carbon monoxide could be detected. After 2 hours, the liquid was warmed to 60° during 1 hour and finally to 100° during a few minutes. The product was *ethyl α-formoxypropionate* (13·3 g., 91%), b. p. 69—70°/18 mm., $\alpha_D^{18°}$ — 6·38°, $d_{4°}^{22°}$ 1·0733, $d_{4°}^{43°}$ 1·0504 [0·8725 g. required 20·7 c.c. of 0·5764N-potassium hydroxide for hydrolysis, whence equiv., 73·1. $CH_3{\cdot}CH(O{\cdot}CHO){\cdot}CO_2Et$ requires equiv., 73]. The solution of sodium hydroxide in the absorption vessel contained 5·6 g. of sulphur dioxide and 3·3 g. of chloride ion, quantities in accordance with the yield of formate. Ethyl α-chlorosulphinoxypropionate, mixed with thionyl chloride and then treated with formic acid as described, gave an initial vigorous reaction, and a volume of carbon monoxide in proportion to the thionyl chloride added was evolved together with hydrogen chloride and sulphur dioxide.

(b) n-*Butyl chlorosulphinate.* 15·6 G. of *n*-butyl chlorosulphinate, mixed with 4·6 g. of formic acid as described, gave *n*-butyl formate, b. p. 106·5—107°, $d_{4°}^{14°}$ 0·8996 (0·7871 g. required for hydrolysis 13·38 c.c. of 0·5764N-potassium hydroxide, whence equiv. 101·9. Calc., 102); yield 9·0 g., 90%.

(c) iso*Butyl chlorosulphinate.* 15·6 G. of the ester and 4·6 g. of formic acid gave *iso*butyl formate, b. p. 97—98°, $d_{4°}^{0°}$ 0·8859; yield, 8·7 g., 87% (0·6230 g. required for hydrolysis 10·9 c.c. of 0·560N-potassium hydroxide, whence equiv., 101·9).

(d) *Ethyl chlorosulphinate.* 25·7 G. (1 mol.) of the ester, mixed with 9·2 g. of formic acid, gave ethyl formate, b. p. 54°, $d_{4°}^{0°}$ 0·9386; yield 13·1 g., 88% (0·8250 g. required 19·24 c.c. of 0·5764N-potassium hydroxide, whence equiv., 74·1. Calc., 74·0).

(e) iso*Amyl chlorosulphinate.* 17·0 G. of the ester and 4·6 g. of formic acid gave *iso*amyl formate, b. p. 123—124°, $d_{4°}^{0°}$ 0·8935; yield, 88%.

Phenyl Chlorosulphinate.—Phenol (47 g.; 1 mol.) in 60 c.c. of dry ether was added dropwise to thionyl chloride (120 g.; 1 mol. + large excess) in 20 c.c. of dry ether in a flask fitted with delivery and exit tubes for the passage of dry carbon dioxide (to agitate the contents and carry off hydrogen chloride) and cooled in ice–salt at −5°. There was no apparent reaction during the addition of the phenol (1 hour). The flask was kept overnight at room temperature, then attached to a water-pump, and warmed to 50° during 1½ hours; at the end of this time the pressure was 20 mm. The product distilled remarkably well, b. p. 100·5—101°/18 mm., $d_{4°}^{13°}$ 1·3640, $d_{4°}^{33°}$ 1·3409, $n_D^{25°}$ 1·5580; yield, 80·1 g., 90%. (Found: S, 18·1; Cl, 20·1%. Calc. for PhO·SOCl: S, 18·1; Cl, 20·1%). The product was a colourless liquid which was hydrolysed readily by water to phenol, sulphur dioxide, and hydrogen chloride. Trunel (*Compt. rend.*, 1935, **200**, 2186), in a dipole-moment determination, gives $d_{4°}^{25°}$ 1·349 and $n_D^{25°}$ 1·5583, but no other experimental details are recorded.

The method now described is much more convenient than that of Battegay and Denivelle (*Compt. rend.*, 1931, **192**, 492; *Bull. Soc. Ind. Mulhouse*, 1932, **98**, 51), who added sodium phenoxide to thionyl chloride in toluene; their product had b. p. 94—96°/13 mm.

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