

45. Studies on the Esters of Sulphurous, Chlorosulphinic, and Chlorosulphonic Acids. Part II.

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The decomposition of phenyl chlorosulphinate, $\text{Ph}\cdot\text{O}\cdot\text{SOCl}$, and certain typical aliphatic chlorosulphinates, in the presence of the tertiary bases pyridine, quinoline, dimethylaniline and in that of their hydrochlorides, has been examined with special reference to the fate of the base or its hydrochloride. It is shown that, not only is the decomposition mechanism in presence of the base quite different from that in presence of the hydrochloride, but there is a fundamental difference between the modes of decomposition of the aromatic and the aliphatic chlorosulphinates. Experiments have been extended to the determination of the fate of the base during the interaction of carbonyl chloride, phosphorus trichloride, or phosphorus oxychloride with hydroxy-compounds in the presence of pyridine. The interaction between pyridine and quinoline and the chlorosulphonate of a typical hydroxy-ester has also been studied, and evidence of the formation of the chlorosulphinates of *isopropyl*, *sec.*-butyl, and β -octyl alcohols and of ethyl mandelate by the direct action of thionyl chloride has been obtained. A general theory is submitted to account for the experimental results of other workers in this field.

THE purpose of this series of papers is the precise formulation of the mechanisms of the replacement of a hydroxy-group by a chlorine atom through the agency of thionyl chloride, sulphuryl chloride, carbonyl chloride, and the chlorides and oxychloride of phosphorus in (a) the absence and (b) the presence of the tertiary bases pyridine, quinoline, and dimethylaniline and their hydrochlorides. An experimental survey of the field has now been made with special reference to the fate of the base and the hydrochloride.

Thionyl Chloride, Hydroxy-compound, and Tertiary Base.—It was shown in Part I (Gerrard, J., 1939, 99) that addition of thionyl chloride to a mixture of pyridine (1 mol.) and hydroxy-compound (*n*-butyl or *n*-amyl alcohol or ethyl lactate; 1 mol.) resulted in the formation of pyridine hydrochloride and an excellent yield of the sulphite, R_2SO_3 , when 0.5 mol. of the reagent had been added. The further addition of the thionyl chloride converted the sulphite into the chlorosulphinate, $\text{R}\cdot\text{O}\cdot\text{SOCl}$, the pyridine hydrochloride playing no part in this phase of the operation. When the resulting mixture was heated, the chlorosulphinate was catalytically decomposed by the hydrochloride, which was left unchanged at the end, sulphur dioxide being emitted and an excellent yield of the chloride, RCl , being formed. Excess of pyridine beyond 1 mol. diminished the yield of chloride. It is now shown that addition of thionyl chloride (0.5 mol.) to an ethereal solution of pyridine (1.0 mol.) and (a) β -octanol, (b) ethyl mandelate, or (c) phenylmethylcarbinol results in the immediate precipitation, even at -10° , of pure pyridine hydrochloride (1 mol.) in nearly 100% yield. β -Octyl sulphite was obtained in good yield, but the isolation of the sulphites of (b) and (c) was not attempted in this instance. There is definite evidence that the production of pyridine hydrochloride and sulphite, R_2SO_3 , is, in general, rapid and quantitative, even at -10° . When results contrary to this are obtained [compare Ritchie (J., 1935, 1054), who could obtain only a 25% yield of α -carboethoxyethyl sulphite], it is probably because insufficient mixing is allowing local heat production, the consecutive reactions $\text{R}_2\text{SO}_3 \longrightarrow \text{RO}\cdot\text{SOCl} \longrightarrow \text{RCl}$, and even direct action of

the thionyl chloride on the hydroxy-compound, as well as possible interaction between the base and both the chlorosulphinate and thionyl chloride. It has always been assumed that in such experiments pyridine hydrochloride was formed; but there does not appear to be any record of systematic analysis, and in many experiments the hydrochloride must have been contaminated with appreciable amounts of other pyridine compounds.

Excellent yields of α -carbethoxyethyl sulphite and *n*-butyl sulphite as well as quinoline hydrochloride and dimethylaniline hydrochloride were produced by addition of thionyl chloride to ethereal solutions of the appropriate hydroxy-compound and base. The hydrochlorides of these bases were also produced in the case of phenol. The rapidity and definiteness of this reaction would appear to rule out the probability of the formation of a complex between the pyridine and the thionyl chloride; it is better to postulate that the co-ordination of the hydroxyl hydrogen atom with the nitrogen atom of the base, $\text{ROH}:\text{NC}_5\text{H}_5$, facilitates the appropriately oriented collision with the thionyl chloride molecule.

The Decomposition of Chlorosulphinates in the Presence of Tertiary Bases and their Hydrochlorides.—In Part I (*loc. cit.*) it was shown that pure alkyl chlorosulphinates and ethyl α -chlorosulphinoxypropionate (compare also Frankland and Garner, J., 1914, 105, 1101) decomposed when heated with pyridine hydrochloride, and gave rise to the chloride, RCl , in excellent yield; sulphur dioxide was evolved steadily and left the pyridine hydrochloride unchanged. The same chlorosulphinates reacted with pyridine itself, in ethereal solution, even below room temperature, giving rise to a considerably diminished yield of chloride, RCl , the pyridinium compound, $\text{C}_5\text{H}_5\text{N}(\text{R})\cdot\text{O}\cdot\text{SOCl}$, and probably pyridine-sulphur dioxide, $\text{C}_5\text{H}_5\text{N}:\text{SO}_2$ (Gerrard, J., 1936, 688; Gerrard, Kenyon, and Phillips, J., 1937, 153). It is now shown that for these typical chlorosulphinates and for phenyl chlorosulphinate the mechanism of the decomposition effected by pyridine, quinoline, and dimethylaniline is quite different from that of the decomposition effected by the hydrochlorides of these bases. In the absence of ether, the aliphatic chlorosulphinates reacted rapidly with pyridine in the cold, the products being the same as those obtained in ethereal solution. With quinoline the reaction was somewhat slower, but still fairly rapid, and similar types of compounds were produced, the quinolinium compound being in decidedly smaller yield. The slower reaction with quinoline is probably due to the bulkier appendage, which decreases the probability of suitably oriented collisions (cf. Winkler and Hinshelwood, J., 1935, 1147). Dimethylaniline reacted vigorously with *n*-butyl chlorosulphinate even at -5° , and readily with ethyl α -chlorosulphinoxypropionate, producing a low yield of chloride, RCl , some sulphite, R_2SO_3 , and products not yet identified. The fate of the base is probably largely determined by the reactivity of the hydrogen atom in the *p*-position. The chlorosulphinates of β -octanol and ethyl mandelate behaved with pyridine in ethereal solution as did *n*-butyl chlorosulphinate.

When *n*-butyl chlorosulphinate or ethyl α -chlorosulphinoxypropionate was heated with quinoline hydrochloride or dimethylaniline hydrochloride, excellent yields of the chloride, RCl , were produced, sulphur dioxide was *steadily* evolved, and the hydrochloride of the base was recovered quantitatively.

Not only does the mechanism of the decomposition of phenyl chlorosulphinate by means of a tertiary base differ distinctly from that of the decomposition by means of the hydrochloride of the base, but it also differs widely from that of the decomposition of aliphatic chlorosulphinates effected by corresponding reagents. Phenyl chlorosulphinate did not react in the cold with pyridine or quinoline whether ether was present or not, but it reacted explosively with these bases at 122° , and was decomposed vigorously by their hydrochlorides at 98° and 108° respectively (see p. 224). Although the chlorosulphinate reacted explosively within a minute of being mixed with dimethylaniline, no such reaction occurred when it was heated in the presence of the hydrochloride of the base, slow evolution of gas occurring at about 50° .

Carré and Libermann (*Bull. Soc. chim.*, 1933, 53, 1050, 1075; 1936, 3, 1064) claim to have determined the decomposition temperatures of chlorosulphinates "en présence d'une molécule de pyridine"; but it is remarkable that in not a single experiment described was pyridine as such present. Their technique was to mix, in the cold, the hydroxy-

compound (1.0 mol.) with pyridine (1.0 mol.) and thionyl chloride (1.0 mol.) and to heat this mixture until the manometer mercury began to fall more rapidly than by thermal expansion of air in the apparatus. After mixing, the system consisted of pyridine hydrochloride, more or less pure depending on the exact procedure during the mixing (no data were given), the sulphite, R_2SO_3 , and 0.5 mol. of thionyl chloride, which, during the heating process, would convert the sulphite into chlorosulphinates with a velocity as yet unknown. No reference was made to the remarkable behaviour of phenyl chlorosulphinates in contrast with that of the aliphatic chlorosulphinates. Without giving further details, the authors merely state that they have verified in a large number of cases that the temperatures of decomposition found by the technique described are the same if the decomposition is effected with the chlorosulphinate " *préparé à part.*" and then treated with a molecular proportion of pyridine.

Thionyl Chloride and Hydroxy-compounds.—The reaction between these reagents may take various courses according to the exact method of experiment. Whereas Stähler and Schirm (*Ber.*, 1911, **44**, 319) obtained an 85% yield of ethyl chlorosulphinate by the addition of thionyl chloride to the alcohol in the cold, and Voss and Blanke (*Annalen*, 1931, **485**, 258) obtained a 68% yield by the reverse order of addition, Carré and Libermann (*loc. cit.*) record yields of 95% for ethyl and other chlorosulphinates so prepared, yet they could not obtain *isopropyl* chlorosulphinate, and concluded that the chlorosulphinates of secondary alcohols were not formed by the direct interaction of the alcohol and thionyl chloride. Voss and Blanke (*loc. cit.*), however, obtained a 46% yield of *isopropyl* chlorosulphinate in this way, and the author, repeating his preparation of this compound (J., 1936, 688), obtained an excellent yield and also secured a fair yield of *sec.*-butyl chlorosulphinate. Carré and Libermann (*Compt. rend.*, 1933, **196**, 275; *loc. cit.*) also declared that phenyl chlorosulphinate cannot be made by the interaction of thionyl chloride and phenol, the product being $(C_6H_4 \cdot OH)_3SCl$: yet the author (J., 1939, 99) prepared phenyl chlorosulphinate in 85–90% yields from these reagents. The same workers claim to have prepared the chlorosulphinates of β -octanol and phenylmethylcarbinol by the action of thionyl chloride on the corresponding sulphite (products were not distilled), and they state that the chlorosulphinates are *not* formed by the action of thionyl chloride on the alcohols themselves: "direct chlorination" is assumed to occur. Since the formation of the "intermediate chlorosulphinate" is a vital link in the Walden inversion theories of Kenyon, Phillips, and their co-workers, the preparation of β -octyl chlorosulphinate from β -octanol and thionyl chloride was a matter of considerable interest to them; but despite repeated attempts, Kenyon, Lipscomb, and Phillips (J., 1930, 417) failed to prepare it. It should be possible to do so, however, because Hunter (J., 1924, **125**, 1389) prepared β -octyl sulphite by adding thionyl chloride (0.5 mol.) to β -octanol (1.0 mol.) in light petroleum, and therefore, according to Carré and Libermann—though in contradiction to their other statement—the chlorosulphinate should result from the continued addition of the thionyl chloride beyond the 0.5 mol. Evidence is now presented to show that β -octyl chlorosulphinate can be obtained by the action of thionyl chloride on the alcohol as well as on the sulphite. Evidence of the formation of ethyl α -chlorosulphinoxyphenylacetate was also obtained, but the results with phenylmethylcarbinol are uncertain.

Other confusing conclusions, *e.g.*, of Meyer (*Monatsh.*, 1901, **22**, 415), McKenzie and Barrow (J., 1911, **99**, 1910, 1915), Hoering and Baum (*Ber.*, 1908, **41**, 1918), and Carré and Libermann (*Compt. rend.*, 1935, **200**, 1215; *Bull. Soc. chim.*, 1935, **2**, 1166) concerning thionyl chloride and mandelic acid, and also the difference between Frankland and Garner (*loc. cit.*) and Blaise and Montagne (*Compt. rend.*, 1922, **174**, 1173, 1553) concerning lactic acid, suggest that there are several fundamental modes of interaction due to collisions oriented by the electronic condition of the different parts of the molecules of the two reactants, the probability of such collisions depending on the exact procedure, as well as on the nature of the hydroxy-compound.

Thionyl Chloride and the Walden Inversion.—It has been shown by McKenzie and Barrow (*loc. cit.*) that addition of ethyl *l*-mandelate (1 mol.) to cold thionyl chloride (2 mols.) results in the formation of ethyl *l*-phenylchloroacetate, $\alpha_{5461} - 91.3^\circ$. Kenyon, Lipscomb,

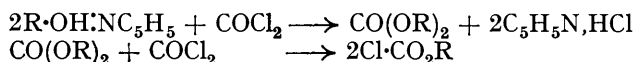
and Phillips (J., 1930, 415) assume that this takes place without inversion through the decomposition of the postulated intermediate chlorosulphinic acid giving rise to a carbonium anion: $C_6H_5 \cdot CH(O \cdot SOCl) \cdot CO_2C_2H_5 \longrightarrow C_6H_5 \cdot \overset{+}{C}H \cdot CO_2C_2H_5 + SO_2 + Cl^-$. "If pyridine were present," they state, "it could facilitate the formation of the chlorosulphinic acid, and also aid its decomposition by combining with it to form the unstable intermediate complex, $RO \cdot SO \cdot NC_5H_5Cl$, a pyridinium chloride." "When the chlorosulphinic acid decomposes in the presence of pyridine," a Walden inversion occurs. Pyridine, however, does not facilitate the formation of the chlorosulphinic acid, but the sulphite, and the formation of the above complex does not appear to be necessary for inversion, because Kenyon, Lipscomb, and Phillips obtained an inversion ($\alpha_{5461} + 41.2^\circ$) when thionyl chloride (1 mol.) was added to an ethereal solution of ethyl *l*-mandelate (1 mol.) and pyridine (1 mol.), followed by warming on a steam-bath for 30 minutes. In these circumstances the pyridine as such ceased to function when 0.5 mol. of thionyl chloride had been added; during the subsequent warming the reaction $R_2SO_3 + SOCl_2 \longrightarrow 2R \cdot O \cdot SOCl$ took place, and this product underwent slow decomposition in the *absence* of pyridine, but with pyridine hydrochloride in the system as a *separate phase*. The incomplete decomposition of the chlorosulphinic acid in these circumstances, followed by subsequent hydrolysis during the working up, would account for the occurrence of a not inconsiderable amount of ethyl *l*-mandelate in the product (yields not stated). This system is equivalent to the toluene-phenylmethylcarbinyl chloroformate-quinoline hydrochloride system of Houssa and Phillips (J., 1932, 1232, 1st expt.), in which the chloroformate is considered as decomposing in the *absence* of tertiary base. Furthermore, McKenzie and Clough (J., 1910, 97, 2564) added *l*-phenylmethylcarbinol to thionyl chloride and obtained *l*- α -chloroethylbenzene, and for the same reasons as in the example of ethyl *l*-mandelate, Kenyon, Phillips, and Taylor (J., 1931, 382) assumed that no inversion occurred, but they obtained the *d*-chloride (1st expt.) when thionyl chloride (2 mols.) was added to the *l*-alcohol (1 mol.) and pyridine (1 mol.), followed by heating, *i.e.*, in circumstances in which there was no pyridine to form the pyridinium complex. Although it appears certain that the chloride, RCl , is formed by the decomposition of the chlorosulphinic acid when pyridine has been used in the system, it is by no means probable that the chlorosulphinic acid is an essential intermediate when thionyl chloride is used alone. A study of the magnitude of the rotatory powers of the specimens of chlorides produced indicates the occurrence of inversion and non-inversion reactions together, but in different proportion. It was remarked by McKenzie and Clough (*loc. cit.*) that "the presence of a phenyl group in other compounds causes group displacement to be accompanied by racemisation to a degree which is generally considerable." "Racemisation" in the carefully conducted experiments with thionyl chloride is probably due to occurrence of non-inversion and inversion reactions, rather than to the actual change of configuration of the chloride when formed. For instance, *l*-phenylmethylcarbinol with thionyl chloride alone gave *l*-chloride, $\alpha_{5461} - 63.3^\circ$ (McKenzie and Clough); with 1 mol. of pyridine (decomposition of chlorosulphinic acid in *absence* of base, but in presence of the hydrochloride), *d*-chloride, $\alpha_{5461} + 17.3^\circ$ (Kenyon, Phillips, and Taylor) was produced; with 2 mols. of pyridine (free base present after formation of sulphite), the *d*-chloride, $\alpha_{5461} + 36.3^\circ$ (*idem*) was formed. Under the same three sets of conditions, ethyl *l*-mandelate and thionyl chloride afford respectively *l*-chloride, $\alpha_{5461} - 91.3^\circ$ (McKenzie and Barrow, *loc. cit.*); *d*-chloride, $\alpha_{5461} + 41.2^\circ$ (Kenyon, Lipscomb, and Phillips); *d*-chloride, $\alpha_{5461} + 122.0^\circ$.

Chlorosulphonates and Tertiary Bases.—Willcox (*Amer. Chem. J.*, 1904, 32, 446) obtained dimethylaniline-sulphur trioxide, $C_6H_5 \cdot N(CH_3)_2 \cdot SO_3$, in 83.3% yield, together with ethyl chloride and a little quaternary compound, by mixing chloroform solutions of ethyl chlorosulphonate and the base below 0° . Baumgarten (*Ber.*, 1926, 59, 1166) obtained similar results with pyridine, the compound $C_5H_5N \cdot SO_3$ being produced in 85% yield. The reaction has now been extended to ethyl α -chlorosulphonoxypropionate and to quinoline; when ethereal solutions of the ester and pyridine were mixed at -10° , a crisp white precipitate, consisting almost entirely of pyridine-sulphur trioxide, began to form immediately, whereas the ethereal solution afforded a good yield of chloride, RCl . In a similar way *quinoline-sulphur trioxide*, $C_9H_7N \cdot SO_3$, was obtained.

The sulphur atom in the chlorosulphonate is preponderantly positive, and the lone pair of electrons on the nitrogen atom of the base will make oriented collision at that point highly probable. The velocity of precipitation of the quinoline-sulphur trioxide was smaller than with pyridine, probably for reasons already mentioned. It is remarkable that the positively charged sulphur atom in the chlorosulphonate appears to hinder the reactivity of the chlorine atom: whereas the chlorosulphinatc gave an excellent yield of pyridine hydrochloride when added to an ethereal solution of the hydroxy-compound and pyridine, the chlorosulphonate still gave pyridine-sulphur trioxide.

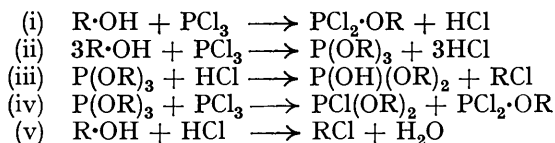
In line with the chlorosulphinatc, phenyl chlorosulphonate did not appear to react with either pyridine or quinoline in the cold. Denivelle (*Compt. rend.*, 1934, **199**, 211) apparently found it necessary to use the drastic process of heating phenyl chlorosulphonate, phenol (for example), and pyridine in a sealed tube at 120° to prepare phenyl sulphate. In interesting contrast with the chlorosulphinatc, phenyl chlorosulphonate appears to react slowly with dimethylaniline; on warming the mixture, an alcohol-soluble oil was produced which exhibited indicator properties. Denivelle (*Bull. Soc. chim.*, 1936, **3**, 2143) concluded that phenyl chlorosulphonate is without apparent immediate action in the cold on a benzene solution of dimethylaniline. He referred to an oil which separates in the course of two days; but he neither isolated the product nor mentioned the indicator effect.

Carbonyl Chloride, Hydroxy-compound, and Tertiary Base.—The slow addition of a toluene solution of carbonyl chloride (0.5 mol.) to ethyl lactate (1 mol.) and pyridine (1 mol.) in toluene at -10° produced the immediate precipitation of pyridine hydrochloride. Without any warming, almost theoretical yields of pyridine hydrochloride and α -carboethoxyethyl carbonate were obtained. From this, and from a study of other relevant experiments by, e.g., Hunter (*loc. cit.*) and Ritchie (*loc. cit.*), it is clear that the action of carbonyl chloride on a hydroxy-compound in the presence of pyridine is strictly analogous to that of thionyl chloride as already described:



Therefore the statement (Houssa and Phillips, J., 1932, 1232) that "when only one molecular proportion of quinoline was used, it was converted into quinoline hydrochloride by the hydrogen chloride liberated during the formation of the chloroformate" is not a correct description of the mechanism. Then again the statement by Carré and Libermann (*loc. cit.*) that "les chloroformiates d'alcoyle qui, à l'état de pureté, sont plus stables que les chlorosulphites, deviennent au contraire moins stables en présence de pyridine," is fallacious. The authors repeatedly refer to pyridine, whereas it was the hydrochloride that was present. When properly compared, it will be found that the chlorosulphinates are quite as reactive towards pyridine as are the chloroformates; and, as a first approximation, it is highly probable that the chloroformates are more stable when heated with pyridine hydrochloride than are the chlorosulphinates.

Phosphorus Trichloride or Oxychloride, Hydroxy-compounds, and Pyridine.—A study of the experiments of Raillon (J., 1854, **7**, 216), Menshutkin (*Annalen*, 1866, **139**, 343), Schiff (*ibid.*, 1857, **102**, 334), Wichelhaus (*ibid.*, 1868, Suppl. **6**, 257), Chambon (*Jenaische Z.*, 1876, **10**, 97), Geuther (*ibid.*, p. 104), Kowalewsky (*Chem. Centr.*, 1897, **68**, 333), Jaroschenko (*ibid.*, p. 334), Milobendzki and Sachnowski (*Chem. Polski*, 1917, **15**, 34), and Balarew (*Z. anorg. Chem.*, 1917, **99**, 187; **101**, 225) shows that the action of the chlorides and oxychloride of phosphorus on hydroxy-compounds involves even more possible mechanisms than that of thionyl chloride. Highly probable mechanisms are of the types:



The mechanism or mechanisms followed will depend upon the nature of the group R and the exact procedure. In the presence of pyridine, however, when efficient mixing is

ensured, the primary action is the formation of the ester, phosphite or phosphate, the addition of the phosphorus chloride beyond $\frac{1}{3}$ mol. then giving rise to the types shown in (iii) and (iv).

Addition of an ethereal solution of phosphorus trichloride (0.33 mol.) to an ethereal solution of pyridine (1 mol.) and *n*-butyl alcohol, β -octanol, or ethyl mandelate (1 mol.) resulted in almost quantitative precipitation of pyridine hydrochloride. The further addition of the trichloride produced no heat effect and no apparent change. Phosphorus oxychloride gave similar results; but the precipitation of the hydrochloride was definitely slower, as would be expected from the presence of the positive charge on the phosphorus atom, which diminished the reactivity of the chlorine atoms.

A satisfactory explanation of the experimental results of Houssa and Phillips (J., 1931, 108) is thereby furnished. Addition of a mixture of β -octanol (1 mol.) and pyridine (2 mols.) in ether to phosphorus trichloride (1 mol.) in ether probably resulted in the precipitation of pyridine hydrochloride (1 mol.), leaving in solution β -octyl phosphite (0.33 mol.), pyridine (1 mol.), and phosphorus trichloride (0.66 mol.). When this mixture was warmed for 10 minutes, a reaction of type (iv) would occur with an unknown velocity. The action of pyridine on these chlorides (of which lower members, *e.g.*, *n*-butyl, are stable to distillation) is now under examination. Apparently the pyridine did not effect a conversion into β -chloro-octane, for none was found in the ultimate product. Treatment of the ethereal solution with water doubtless resulted in the hydrolysis of these chlorides, $\text{PCl}_2(\text{OR}) \longrightarrow \text{P}(\text{OH})_2(\text{OR})$ and $\text{PCl}(\text{OR})_2 \longrightarrow \text{P}(\text{OH})(\text{OR})_2$, and these esters were in fact the main products isolated by the authors. An analogous argument explains their results with phosphorus oxychloride, with which "only a trace of β -chloro-octane was produced, the main products being a neutral phosphoric ester and a mixture of acid phosphoric esters." Phosphorus pentachloride, however, did give some β -chloro-octane (actual amount not stated), a result to be expected from the reaction $4\text{ROH} + \text{PCl}_5 + 4\text{C}_5\text{H}_5\text{N} \longrightarrow \text{RCl} + \bar{\text{O}}-\overset{\dagger}{\text{P}}(\text{OR})_3 + 4\text{C}_5\text{H}_5\text{N}\cdot\text{HCl}$. Kenyon, Phillips, and Taylor (*loc. cit.*) carried out their phenylmethylcarbinol-phosphorus halide experiments in absence of ether and in the presence of 1 mol. of pyridine per mol. of alcohol. If the reaction proceeded by the course $\text{R}\cdot\text{OH} \longrightarrow \text{P}(\text{OR})_3 \longrightarrow \text{PCl}(\text{OR})_2 + \text{PCl}_2(\text{OR})$, then the production of a 70% yield of chloride indicates that the chlorophosphites in this case are much less stable and are decomposed at 50° in the presence of pyridine hydrochloride, in which circumstances it is not clear how the pyridine complex formulated by the authors can be formed.

The conclusions of Boyd and Ladhams (J., 1928, 215) can be profitably examined in the light of these arguments.

EXPERIMENTAL.

Interaction of Phenyl Chlorosulphinic with Tertiary Bases and their Hydrochlorides.—
(a) *With pyridine in ethereal solution.* Phenyl chlorosulphinic, prepared as described in Part I (*loc. cit.*) (23.75 g., 1 mol.), in 30 c.c. of dry ether (the ether used throughout was dried) was treated with pyridine (10.7 g., 1 mol.) in 20 c.c. of ether at -10° . Apart from the immediate precipitation of about 0.3 g. of pyridine hydrochloride, no reaction took place even on 3 days' standing at room temperature. The addition of phenol (12.2 g., 1 mol.) in 20 c.c. of ether at -10° then precipitated 9.2 g. of pyridine hydrochloride, and the filtered ethereal solution yielded phenyl sulphite, *b. p.* $178^\circ/15$ mm. (18.5 g.) (Found: S, 13.5. Calc.: S, 13.7%), thus showing the presence of the chlorosulphinic in the reaction mixture.

(b) *With pyridine in absence of ether.* The chlorosulphinic (17.6 g., 0.1 mol.) showed no sign of reaction on being mixed with pyridine (7.9 g., 0.1 mol.) at -5° . The mixture was then heated gently in a small flask attached to an upright condenser fitted at the top with a tube leading to a guard-tube containing calcium chloride, a reversed empty wash bottle, and to a three-way tap leading either to a manometer or to a wash-bottle containing an aqueous solution of potassium hydroxide and thence to the top of a separating funnel attached at the bottom to another funnel for levelling purposes. At 122° (reproducible in several experiments) there was a sudden rise in pressure, the manometer tap was shut, and the absorption tap opened. The reaction was almost explosive and subsided in a few seconds; the alkali absorbed about 0.03 mol. of sulphur dioxide, but no hydrogen chloride. The liquid in the flask thickened immediately, and on cooling became an amber-coloured gum, which, on trituration with water,

yielded a pale brown solid (10.5 g.) and an aqueous solution containing pyridine hydrochloride (0.095 mol.). The brown solid was insoluble in the common organic solvents, but readily soluble in dilute sodium hydroxide, forming a dark brown solution, from which it was reprecipitated by dilute hydrochloric acid, the mother-liquor being colourless. The solid was free from chlorine and nitrogen (Found: C, 56.6; H, 3.4; S, 15.6%). It appeared to form a benzoate, a pale brown solid, insoluble in a solution of sodium hydroxide, but very soluble in chloroform, from which it could not be crystallised.

(c) *With quinoline.* The chlorosulphinate (8.8 g., 0.05 mol.) was mixed with quinoline (6.5 g., 0.05 mol.) and heated as described. Similar phenomena were observed. The decomposition occurred at 122°, the alkali absorbed 1.17 g. of sulphur dioxide, but no hydrogen chloride, and the thick gum which remained yielded on trituration a pale brown solid (6.1 g.), having properties apparently identical with those of the solid obtained in (b), and an aqueous solution of quinoline hydrochloride (nearly 0.05 mol.).

(d) *With dimethylaniline.* This base and the chlorosulphinate reacted explosively within 1 min. after mixing at 16°, the volatile products being emitted in white clouds, leaving a dark greenish-black residue lining the flask.

(e) *With pyridine hydrochloride.* The chlorosulphinate (17.6 g., 0.1 mol.) was mixed with pyridine hydrochloride (11.5 g., 0.1 mol.) and heated as described. The hydrochloride remained solid, but dissolved gradually as the temperature was raised, and at 90° the mass became homogeneous. At 98° an explosive reaction occurred, 4 g. of a mixture of hydrogen chloride and sulphur dioxide being evolved almost in equimolar ratio. The residue, a stiff brown gum, was triturated with water, but instead of the brown solid, an ether-soluble gum was obtained, and the aqueous liquid contained pyridine hydrochloride (0.1 mol.), excess chloride ion (0.187 g.), and sulphur dioxide (0.128 g.). The gum weighed 12.5 g. when dried, was soluble in the common organic solvents, and in aqueous sodium hydroxide, from which it was reprecipitated by hydrochloric acid.

(f) *With quinoline hydrochloride.* The chlorosulphinate (8.8 g., 0.05 mol.) and the hydrochloride (0.05 mol.) were heated as described. The latter softened at about 85°, gave a homogeneous liquid at 103°, and reacted as described at 108°. 1.567 G. of a mixture of hydrogen chloride and sulphur dioxide (in almost equimolar ratio) were evolved, and the residue of thick brown gum yielded, on treatment as in (e), quinoline hydrochloride (0.05 mol.) and thick brown oil (7.1 g.) having similar properties to that obtained in (e).

(g) *With dimethylaniline hydrochloride.* The chlorosulphinate (5.4 g.) and the hydrochloride (4.8 g.) were heated as in (f). Evolution of gas started at 50°, and from 65° to 120° it was steady but slow. 0.93 G. of hydrogen chloride and sulphur dioxide in equimolar ratio was evolved. Trituration of the residue with water yielded an ether-soluble oil (2.9 g.) similar to that in (f), an aqueous solution of dimethylaniline hydrochloride, and a white solid (1.5 g.), m. p. 122°.

The characterisation of the thick oils and brown solids produced in the foregoing experiments will be reported later.

The Interaction of Thionyl Chloride and Phenol in the Presence of Tertiary Bases in Ethereal Solution.—(a) *With pyridine.* Thionyl chloride (80 g., 0.5 mol.) in 50 c.c. of ether was added slowly to a mixture of phenol (129 g., 1 mol.) in 200 c.c. of dry ether and pyridine (107 g., 1 mol.), at -5° (vigorous shaking throughout is essential for a good yield). 153 G. (Calc. 155 g.) of pyridine hydrochloride were precipitated (Found: Cl, 30.7. Calc.: Cl, 30.8%). The ethereal solution yielded phenyl sulphite, b. p. 178°/15 mm. (141.8 g., 91%). Richter (*Ber.*, 1916, 49, 2340) prepared phenyl sulphite by these reagents in carbon disulphide, and used 1 mol. of pyridine, not a "little" pyridine (Silberrad, *J. Soc. Chem. Ind.*, 1926, 45, 37, 55).

(b) *With quinoline.* Thionyl chloride (6 g., 0.5 mol.) in 20 c.c. of dry ether, added to quinoline (12.9 g., 1 mol.) and phenol (9.4 g., 1 mol.) in 50 c.c. of ether at -5°, gave quinoline hydrochloride (15.9 g.) (Found: Cl, 20.9. Calc.: Cl, 21.4%) and phenyl sulphite, b. p. 177—179°/16 mm. (9.6 g.). In these experiments, the phenomena during the mixing of the reagents were different from those observed with alcohols in ethereal solution. At first the hydrochloride of the base redissolved in the pyridine-phenol-ether, and then, as the phenol was converted into sulphite, the hydrochloride separated as an oil, probably containing dissolved pyridine and/or phenol, and on being vigorously shaken it crystallised. The pyridine and quinoline hydrochlorides were good specimens, but the dimethylaniline hydrochloride obtained in the corresponding experiment was discoloured.

Reaction of Phenyl Chlorosulphinate with Formic Acid.—The chlorosulphinate (17.6 g., 0.1 mol.) was mixed with formic acid (100%; 5.5 g., 0.12 mol.) in a flask attached to the absorp-

tion apparatus. The reaction proceeded steadily at room temperature, hydrogen chloride (3.45 g.), sulphur dioxide (5.77 g.), and carbon monoxide (508 c.c.) being evolved. After four hours the residue was distilled, and a colourless fraction, b. p. 77—85°/18 mm., 7.8 g., was obtained; a thick syrupy residue, 3.6 g., remained undistilled, oil-bath at 200°. Redistillation yielded a fraction, b. p. 78—83°/18 mm., 6 g., of which 0.180 g. gave with concentrated sulphuric acid in a Lunge nitrometer 27.8 c.c. (N.T.P.) of carbon monoxide, indicating 84% of phenyl formate. Auger (*Compt. rend.*, 1904, **139**, 798) showed that Seifert's product, from the interaction of phenol and formic acid in the presence of phosphorus oxychloride (*J. pr. Chem.*, 1900, **31**, 467), could not have contained more than 30% of phenyl formate, the rest being phenol, which could not be separated by distillation but was removed by benzylation.

Reaction of Phenyl Chlorosulphinic with l-Menthol in Presence of Pyridine.—The chlorosulphinic (17.6 g., 0.1 mol.) was added slowly to a well-shaken ethereal solution of *l*-menthol (15.6 g., 0.1 mol.) and pyridine (8 g., 0.1 mol.) in 50 c.c. of ether at -5°. Pyridine hydrochloride (11.4 g. Calc.: 11.55 g.) was precipitated at once (Found: Cl, 30.2. Calc.: Cl, 30.7%). Distillation of the ethereal solution under 2—3 mm. yielded fractions: (i) b. p. 70—125° (8 g.); (ii) b. p. 150—156° (9.6 g.); (iii) b. p. 156—160° (3.8 g.); residue (2.6 g.). Fraction (iii), *phenyl menthyl sulphite*, had $\alpha_D^{20} + 10.61^\circ$ ($l = 1$) (Found: S, 11.2. $C_{16}H_{24}O_3S$ requires S, 10.8%).

Preparation of Phenyl Chlorosulphinic by the Action of Thionyl Chloride on Phenyl Sulphite.—Carré and Libermann (*Compt. rend.*, 1932, **195**, 799) claim to have prepared this ester in excellent yield by the action of thionyl chloride on phenol "en présence d'une quantité équimoléculaire de pyridine," but in one place they state they could not distil their product, whereas in another place they state that they isolated "une petite quantité de chlorosulphite de phenyle." Phenyl sulphite (freshly distilled) was treated with excess of thionyl chloride and kept for 48 hours. The product on distillation gave about a 10% yield of phenyl chlorosulphinic.

Interaction of Aliphatic Chlorosulphinates with Tertiary Bases.—(a) *With pyridine in absence of ether.* (i) *n*-Butyl chlorosulphinic (15.6 g., 0.1 mol.) was mixed with pyridine (7.9 g., 0.1 mol.) at -10° in a flask which was then fitted to the absorption apparatus and immersed in water at 0°. Within a few minutes a red oil began to separate, the temperature rising meanwhile to 10°. The absorption liquid contained a little sulphur dioxide, but no chloride ion. Treatment of the product with dilute sulphuric acid gave a lower aqueous layer which contained butylpyridinium ion [yielding 19.0 g. of butylpyridinium ferrocyanide (Found: Fe, 10.75. Calc.: Fe, 10.7%)], sulphur dioxide (nearly 0.1 mol.), chloride ion (1.6 g.), and pyridine (4.8 g., 60% of original amount), whilst the upper layer gave only *n*-butyl chloride (3.9 g. 42%), b. p. 77°, $d_4^{18} 0.8873$.

(ii) Ethyl α -chlorosulphinoxypropionate (20.0 g., 0.1 mol.) was mixed with pyridine (7.9 g., 0.1 mol.) at -10°, and the flask treated as in (i), but being immersed in ice-water. The only sign of reaction was a gradual development of a pale yellow colour; but, on removal of the ice-water after 15 mins., the mixture became quite hot in 4—5 mins., forming a dark red, less mobile liquid and emitting little more than a trace of sulphur dioxide, and practically no hydrogen chloride. Addition of dry ether precipitated a dark red oil (11.3 g.) (cf. Gerrard, *loc. cit.*; Gerrard, Phillips, and Kenyon, *loc. cit.*), and the ethereal layer yielded to water 3.74 g. of sulphur dioxide, 4.5 g. of pyridine (probably as C_5H_5N, SO_2 in the ethereal solution), and 7.5 g. (55%) of ethyl α -chloropropionate, b. p. 47.5°/20 mm., $n_D^{20} 1.4170$, $d_4^{19.5} 1.0779$ (Found: Cl, 25.7. Calc.: Cl, 26.0%), but no chloride ion. The oil contained Cl, 1.403 g.; SO_2 , 2.41 g., and pyridinium compound.

(b) *With quinoline in absence of ether.* (i) *n*-Butyl chlorosulphinic (15.6 g., 0.1 mol.) and quinoline (12.9 g., 0.1 mol.) reacted at -10°. Addition of ether produced a solution, from which sulphur dioxide (4 g.), quinoline (8.3 g.), and *n*-butyl chloride (5.5 g., 60%) were obtained, and an oil (8.8 g.), from which, after treatment with aqueous sodium bicarbonate and ether extraction to remove quinoline, *n-butylquinolinium chloroplatinate*, m. p. 223—224° (decomp.), was obtained (Found: Pt, 24.9. $C_{26}H_{32}N_2PtCl_6$ requires Pt, 25%).

(ii) Ethyl α -chlorosulphinoxypropionate (20 g., 0.1 mol.) and quinoline (0.1 mol.) also reacted at -10°. Sulphur dioxide was evolved slowly as the mixture was heated to 55°, but there was no indication of a definite temperature of emission. Treatment as in (i) yielded an oil (5.5 g.), which contained quinoline and an α -carbethoxyethylquinolinium salt (*chloroplatinate*, m. p. 170—171°. Found: Pt, 22.52. $C_{28}H_{32}O_4N_2PtCl_6$ requires Pt, 22.46%), and an ethereal solution containing ethyl α -chloropropionate (10.3 g., 75%), b. p. 47.5°/21 mm., $d_4^{19.5} 1.0779$, quinoline, and sulphur dioxide in almost molecular proportions, but giving very little chloride ion with water.

(c) *With quinoline in presence of ether.* (i) Ethyl α -chlorosulphinoxypropionate (20 g., 0.1 mol.) and quinoline (0.1 mol.) were mixed in ethereal solution (200 c.c.) at -10° , and allowed to warm to 16° . An oil began to separate from the beginning, and after 24 hours the oil (4.1 g.) had the same composition as in (b, ii) (chloroplatinate, m. p. $170-171^\circ$). Found: Pt, 22.5%, and the ethereal solution resembled that above, containing ethyl α -chloropropionate (9.6 g., 70%), b. p. $47^\circ/20$ mm.

(ii) With quinoline (0.1 mol.) in ethereal solution methyl chlorosulphinate (0.1 mol.) reacted rapidly at -10° , heat being evolved, and gave 13 g. of a dirty white solid. Ethyl chlorosulphinate (0.1 mol.) reacted less rapidly, giving a white precipitate of *ethylquinolinium chlorosulphinate* (16.4 g.) tending to change to a red oil [Found: Cl, 14.2; SO₂, 22.7. C₉H₇N(C₂H₅)₂SO₂Cl requires Cl, 13.9; SO₂, 24.9%]. *n*-Propyl chlorosulphinate (0.1 mol.) gave a mixture of oil [Found: Cl, 11.0; SO₂, 22.6. C₉H₇N(C₃H₇)SO₂Cl requires Cl, 13.1; SO₂, 23.6%] and crystals (6.9 g.) (Found: Cl, 13.6; SO₂, 19.0%). Evaporation of the ether in a vacuum desiccator gave 3.6 g. of white crystals of *quinolinium sulphite*, which turned into a red sticky mass on manipulation [Found: SO₂, 19.2; Cl, 1.35. (C₉H₇N)₂H₂SO₃ requires SO₂, 19.0%]. *iso*Butyl chlorosulphinate (0.1 mol.) yielded 8.2 g. of dirty white crystals, *n*-amyl chlorosulphinate (0.1 mol.) gave 8.3 g. of oil, and *n*-butyl chlorosulphinate (0.1 mol.) gave 9.0 g. of oil.

(d) *With dimethylaniline in absence of ether.* (i) Ethyl α -chlorosulphinoxypropionate (0.1 mol.) mixed with the base (0.1 mol.) at -10° became hot in 3 mins. after removal from the cooling bath, sulphur dioxide and the chloropropionate being evolved. The residue of thick red oil was treated with water, and an indigo-blue solution with indicator properties resulted. The ethereal extract of this gave the chloropropionate (6.9 g., 50%), b. p. $47.5^\circ/21$ mm., and α -carbethoxyethyl sulphite (0.5 g.), b. p. $171^\circ/20$ mm. Addition of sodium hydroxide to the aqueous solution precipitated a sticky purple mass from which were obtained 0.4 g. of a purple solid with indicator properties, and 5 g. of a white solid, m. p. $120-124^\circ$, insoluble in water and alkali, soluble in acid, reprecipitated by alkali. This substance is being examined.

(ii) The base (12.1 g., 0.1 mol.), added slowly to *n*-butyl chlorosulphinate (0.1 mol.) at -10° , reacted vigorously when only 7 g. of the base had been added, sulphur dioxide and butyl chloride being emitted, leaving a semi-solid mass. Dilute hydrochloric acid was added, and from the upper layer *n*-butyl chloride (3.2 g.) and *n*-butyl sulphite (3.5 g.), b. p. $115^\circ/18$ mm., $d_4^{25} 0.9948$ (Found: S, 16.1. Calc. for C₈H₁₈O₃S: S, 16.4%), were obtained. On being rendered alkaline with sodium hydroxide, the aqueous solution yielded a semi-solid mass, which on crystallisation from alcohol gave a white solid, m. p. $120-124^\circ$ (3.3 g.), and dimethylaniline (2.5 g.), probably added after the reaction had commenced.

(e) *With dimethylaniline in ethereal solution.* (i) Ethyl α -chlorosulphinoxypropionate (17 g.), mixed with dimethylaniline (10.5 g.) in 200 c.c. of dry ether at -10° , began to deposit a dark oily mass on warming to room temperature. After 12 hours, the oil weighed 13 g., and the ethereal solution, on being washed with water, gave no chloride ion, much sulphur dioxide, ethyl α -chloropropionate (2.2 g.), b. p. $47.5^\circ/21$ mm., $n_D^{20} 1.4170$, $d_4^{19} 1.0780$, and α -carbethoxyethyl sulphite (3.0 g.), b. p. $173^\circ/21$ mm., $n_D^{20} 1.4400$.

(ii) *n*-Butyl chlorosulphinate (15.7 g., 0.1 mol.) and dimethylaniline (12.1 g.) in 50 c.c. of ether, mixed at -10° and allowed to warm to room temperature, gave a semi-solid dark brown mass (20.4 g.), and the ethereal solution yielded *n*-butyl chloride (3.3 g.) and *n*-butyl sulphite (3.0 g.).

(iii) Methyl, ethyl, propyl, *isobutyl*, and *n*-amyl chlorosulphinates reacted with dimethylaniline in ethereal solution below room temperature. The first mixture evolved much heat at -10° , and the oil separated rapidly.

The Decomposition of Aliphatic Chlorosulphinates in Presence of the Hydrochlorides of Quinoline and Dimethylaniline.—(a) *With quinoline hydrochloride.* Ethyl α -chlorosulphinoxypropionate (15 g., 0.075 mol.) and quinoline hydrochloride (10 g., 0.075 mol.) were mixed in a flask which was then fitted to the absorption apparatus and gently heated in a water bath. The mass became fluid at 38° , sulphur dioxide appeared slowly to be evolved at 39° , and two layers were maintained in the reaction mixture throughout. The temperature was gradually raised to 60° , and there was no indication of a definite decomposition temperature, sulphur dioxide being steadily evolved. On being cooled, the two layers persisted, the lower one consisting of quinoline hydrochloride containing dissolved sulphur dioxide and probably ethyl α -chloropropionate, the upper one being chiefly the ester. Treatment with dry ether yielded pure quinoline hydrochloride (10 g.; ca. 100%) (Found: Cl, 21.2. Calc.: Cl, 21.4%) and ethyl α -chloropropionate (9.9 g., almost theoretical), b. p. $47.5^\circ/21$ mm., $n_D^{19.5} 1.4170$, $d_4^{19.5} 1.0779$.

(b) *With dimethylaniline hydrochloride.* Ethyl α -chlorosulphinoxypropionate (10 g.,

0.05 mol.) was mixed with dimethylaniline hydrochloride (7.8 g.) as in (a). At 29° the hydrochloride liquefied. The temperature was raised slowly (1 hour) to 97°, and there was a slow evolution of sulphur dioxide (2.87 g. Calc. : 3.2 g.) but no hydrogen chloride was evolved. The ethereal extract, after being washed with water (which extracted 0.028 g. of chloride ion and some sulphur dioxide), yielded ethyl α -chloropropionate (6.5 g., almost theoretical), b. p. 47°/21 mm., $n_D^{19.5}$ 1.4178, $d_4^{19.5}$ 1.0779. The ether-insoluble residue remained molten and retained some sulphur dioxide after standing over concentrated sulphuric acid in a vacuum for 12 hours; after several hours over calcium chloride and solid potassium hydroxide, however, white dimethylaniline hydrochloride was obtained (7.5 g.) (Found : Cl, 22.2. Calc. : Cl, 22.5%), free from sulphur dioxide.

The Production of Sulphites.—(a) To ethyl lactate (236 g., 2 mols.) mixed with pyridine (160 g., 2 mols.) in 200 c.c. of ether at -10° , thionyl chloride (119 g., 1 mol.) in 100 c.c. of ether) was added dropwise with shaking. A pure white precipitate of pyridine hydrochloride began to separate at once; this was finally filtered off rapidly and washed with ether (230 g., theoretical) (Found : Cl, 30.4. Calc. : Cl, 30.7%). The ethereal solution after being washed and dried yielded α -carbethoxyethyl sulphite (258 g., 90%), b. p. 161°/13 mm., 148°/4—5 mm. (Ritchie, *loc. cit.*, gives b. p. 158—164°/4 mm.), n_D^{20} 1.4400 (Found : S, 11.3. Calc. : S, 11.4%).

Repetition of this experiment provided convincing evidence that the actual production of the sulphite was theoretical. Ritchie (*loc. cit.*) states that Frankland and Garner's method (J., 1914, 105, 1101) for the preparation of this sulphite gave uncertain results on a larger scale; but his own technique—addition of thionyl chloride to a cooled, stirred mixture of ethyl lactate and pyridine, followed by heating at 100° for 2 hours—gave a poor yield (25%). The low yield was probably due to inadequate mixing causing local heating and formation of the chlorosulphinate which reacted with the pyridine. Subsequent heating of the mixture is unnecessary.

(b) Ethyl lactate (0.1 mol.), quinoline (0.1 mol.), and thionyl chloride (0.05 mol.) as in (a) gave quinoline hydrochloride (16.3 g.) (Found : Cl, 21.0. Calc. : Cl, 21.4%), and the sulphite (13.3 g.), b. p. 162°/15 mm.

(c) Dimethylaniline (0.1 mol.) yielded the hydrochloride (15 g.) (Found : Cl, 21.9. Calc. : Cl, 22.5%), and the sulphite (13.1 g.), b. p. 162°/15 mm.

(d) The corresponding results for *n*-butyl alcohol (0.1 mol.) are : quinoline hydrochloride (16.3 g.), *n*-butyl sulphite (9 g.), dimethylaniline hydrochloride (15.5 g.), *n*-butyl sulphite (9 g.).

(e) *n*-Butyl chlorosulphinate (39.1 g., 1 mol.) was added slowly to a mixture of *l*-menthol (39 g., 1 mol.) and pyridine (19.7 g., 1 mol.) in 100 c.c. of ether. Precipitation of pyridine hydrochloride commenced immediately (Final wt., 29.1 g. Calc. : 28.8 g.) (Found : Cl, 29.5%), and the ethereal solution, after being washed and dried, yielded *l*-menthyl butyl sulphite (56 g.), b. p. 98—99°/1 mm. To separate the possible stereoisomerides, the product was distilled into four fractions : (i) $\alpha_D^{18} - 32.0^\circ$ ($l = 1$); (ii) $\alpha_D^{18} - 32.1^\circ$, d_4^{18} 1.0056 (Found : S, 11.5. $C_{14}H_{28}O_2S$ requires S, 11.6%); (iii) $\alpha_D^{18} - 32.5^\circ$, d_4^{18} 1.0025 (Found : S, 11.5%); (iv) $\alpha_D^{18} - 32.6^\circ$: it is seen that no separation had occurred.

(f) α -Carbethoxyethyl *n*-butyl sulphite (36 g.; 80%), b. p. 141—142°/19 mm. (Found : S, 13.4. $C_9H_{18}O_5S$ requires S, 13.4%) and pyridine hydrochloride (22 g.) (Found : Cl, 29.9%) were obtained from 0.2 mol. of ethyl α -chlorosulphinoxypropionate and *n*-butyl alcohol as in (e). During the distillation there was some tendency of the radicals to interchange, *n*-butyl sulphite and α -carbethoxyethyl sulphite being formed (cf. Bourgeois and Castele, *Bull. Soc. chim. Belg.*, 1927, 36, 149).

Interaction of β -Octanol and Thionyl Chloride.—Thionyl chloride (9 g., 0.5 mol.) in 10 c.c. of ether was added dropwise to β -octanol (19.5 g., 1 mol.) and pyridine (12 g., 1 mol.) in 50 c.c. of ether at -10° . The pyridine hydrochloride (16.7 g.) (Found : Cl, 30.3%) was filtered off and the filtrate divided into two equal parts. (a) Thionyl chloride (4.5 g., 0.5 mol.) was added, but there was no sign of reaction. After 18 hours pyridine (6 g., 1 mol.) was added at -10° , and a dark red oil (6 g.) containing a β -octylpyridinium compound was slowly deposited. The ethereal solution yielded β -octyl chloride (4.7 g., 43%), b. p. 66.5°/20 mm., d_4^{15} 0.8600, $n_D^{16.5}$ 1.4297. (b) After being washed and dried, this half yielded β -octyl sulphite (7.2 g.), b. p. 192—195°/22 mm., 139°/3 mm., d_4^{18} 0.9249, n_D^{16} 1.4455 (Found : S, 10.5. Calc. : S, 10.5%). Hunter (*loc. cit.*) prepared this ester (yield not stated) from the same reagents in light petroleum without the aid of pyridine, and gave b. p. 133—134°/1 mm., d_4^{17} 0.9264, n_D^{20} 1.4436.

β -Octanol (39 g., 1 mol.) in an equal volume of ether was added slowly to thionyl chloride (60 g., 1 mol. + excess) in an equal volume of ether at -10° , the liquid being agitated by a stream of dry carbon dioxide. Excess thionyl chloride was removed on the pump; the product

(67.9 g. Calc. for β -octyl chlorosulphinat: 63.6 g. Found: SO_2 , 29.1; Cl, 17.6. $\text{C}_8\text{H}_{17}\text{O}_2\text{ClS}$ requires SO_2 , 30.1; Cl, 16.7%) was pale yellow and was characterised as follows. (a) 15 G. poured on ice yielded β -octanol (7.5 g.), b. p. $85.5^\circ/20$ mm., d_4^{15} 0.8268, n_D^{17} 1.4298, but no β -octyl chloride was obtained. (b) 21.2 G. were treated with pyridine (8 g.) in ethereal solution at -10° . 9.2 G. of oil separated, and the ethereal solution yielded β -octyl chloride (6.1 g., 41%), b. p. $70^\circ/24$ mm., d_4^{15} 0.8630, n_D^{17} 1.4293. (c) 10.6 G., heated with pyridine hydrochloride at 50 – 70° for 1.5 hours, yielded β -octyl chloride (6.0 g., 81%), d_4^{15} 0.8625, n_D^{17} 1.4293, and an undistilled oil (2 g.). (d) 10.6 G. gave with formic acid (2 c.c.), SO_2 , 2.36 g.; HCl, 1.41 g. (i.e., SO_2 : HCl = 1:1, and not 1:2 as would be obtained from thionyl chloride); about 25 c.c. of carbon monoxide, and a liquid, b. p. 79 – $80^\circ/25$ mm., 5.5 g., d_4^{15} 0.8661, probably β -octyl formate.

Interaction of Ethyl Mandelate and Thionyl Chloride.—Thionyl chloride (3 g., 0.025 mol.) in ether, added to ethyl mandelate (9 g., 0.05 mol.) and pyridine in ether at -10° , produced 5.7 g. of pyridine hydrochloride (Found: Cl, 29.9%). There was no apparent action when 3 g. of thionyl chloride were added to the ethereal filtrate; but when, 12 hours later, pyridine (4 g., 0.05 mol.) was added, an oil separated (6 g.), which was not completely soluble in water, but the aqueous solution gave yellow α -carbethoxybenzylpyridinium ferrocyanide, $\text{CHPh}(\text{CO}_2\text{Et})\cdot\text{NC}_5\text{H}_5[\text{H}_3\text{Fe}(\text{CN})_6]$ (Found: Fe, 12.1. $\text{C}_{21}\text{H}_{19}\text{O}_2\text{N}_7\text{Fe}$ requires Fe, 12.25%. $\text{C}_{21}\text{H}_{19}\text{O}_2\text{N}_7\text{Fe}\cdot\text{H}_2\text{O}$ requires Fe, 11.8%). The ethereal solution yielded ethyl phenylchloroacetate (3.5 g., 36%), b. p. 138 – $139^\circ/20$ mm., n_D^{15} 1.5187 (Found: Cl, 17.1. Calc.: Cl, 17.9%).

Ethyl mandelate (18 g., 0.1 mol.) was added dropwise to thionyl chloride (20 g., 1.75 mols.) diluted with an equal volume of ether, and agitated by a stream of dry carbon dioxide at -10° . After an hour at 16° , the excess thionyl chloride was removed in a vacuum (2 hours), and 26.8 g. of colourless α -carbethoxybenzyl chlorosulphinat (Calc.: 26.3 g.) were obtained (Found, after hydrolysis with cold dilute sodium hydroxide: SO_2 , 22.8; Cl, 14.6. $\text{C}_{10}\text{H}_{11}\text{O}_4\text{ClS}$ requires SO_2 , 24.4; Cl, 13.5%).

(a) The chlorosulphinat (13.1 g., 1 mol.) in 20 c.c. of ether was treated with pyridine (4 g., 1 mol.) at -10° . A thick yellow oil (8.5 g.) separated, and all but about 1 g. dissolved in water. The aqueous solution gave a yellow ferrocyanide (Found: Fe, 12.2%). The ethereal solution deposited no oil on standing with more pyridine (4 g.). It yielded ethyl phenylchloroacetate (4.6 g., 46%), b. p. $138^\circ/20$ mm., n_D^{15} 1.5176 (Found: Cl, 17.3%).

(b) The chlorosulphinat (6.5 g., 1 mol.) was mixed with 100% formic acid (1.2 g., 1 mol.). 1.248 G. of sulphur dioxide, 0.824 g. of hydrogen chloride (SO_2 : HCl = ca. 1:1), and about 20 c.c. of carbon monoxide were evolved.

(c) The chlorosulphinat (4 g.), dissolved in ether and poured on crushed ice, yielded a mixture of mandelate and ethyl phenylchloroacetate (2.6 g.), b. p. $134^\circ/15$ mm., n_D^{17} 1.5165 (Found: Cl, 8.5%).

Interaction between Phenylmethylcarbinol and Thionyl Chloride.—The carbinol (12.2 g., 1 mol.) was added slowly to thionyl chloride (20 g., excess) diluted with 20 c.c. ether as described. After 1 hour at 16° and 2.5 hours on the pump, the product (18.5 g.) was pale yellow (Found, by cold alkaline hydrolysis: SO_2 , 15.6; Cl, 18.1. $\text{C}_8\text{H}_9\text{O}_2\text{ClS}$ requires SO_2 , 31.2; Cl, 17.4%). This α -phenylethyl chlorosulphinat (8 g.) was treated with pyridine (3 g.) at -10° in ethereal solution. There was no deposition of oil even after 24 hours' standing, followed by 1 hour's refluxing. The ethereal solution, however, gave considerable heat when treated with water, sulphur dioxide and hydrogen chloride being evolved. From the ether α -chloroethylbenzene (5 g.) was obtained, b. p. $79^\circ/19$ mm., n_D^{19} 1.5275 (Found: Cl, 24.9. Calc.: Cl, 25.2%). Thionyl chloride (4.3 g.), added to phenylmethylcarbinol (9 g.) and pyridine in ether at -10° , produced 8.1 g. of pyridine hydrochloride, which was separated. Addition of 4.3 g. of thionyl chloride produced no apparent effect, and after 24 hours, half the solution on treatment with water yielded α -chloroethylbenzene (4.7 g.), b. p. 76 – $78^\circ/15$ mm., n_D^{19} 1.5275 (Found: Cl, 23.8%); the other half gave about 0.5 g. of oil with pyridine after standing for some days, and after working up, α -chloroethylbenzene (4.2 g.), b. p. $75^\circ/14$ mm., n_D^{19} 1.5275, was obtained.

Thionyl Chloride and Secondary Alcohols.—(a) *isopropyl alcohol.* (i) By adding the alcohol (1 mol.) to thionyl chloride (1.5 mol.) agitated by a stream of dry carbon dioxide at -5° , followed by standing at room temperature for 12 hours, *isopropyl chlorosulphinat* was obtained in 75–80% yield, b. p. $55^\circ/40$ mm., d_4^{13} 1.2020 (Found: Cl, 25.0; SO_2 , 44.8. Calc.: Cl, 24.9; SO_2 , 44.9%). Voss and Blanke (*loc. cit.*) give d_4^{13} 1.2005, b. p. $34^\circ/24.5$ mm. (ii) The chlorosulphinat (28.5 g., 0.2 mol.) was mixed with formic acid (9.2 g., 0.2 mol.), kept at room temperature for 3 hours on the absorption apparatus, and then warmed at 70° for 10 minutes.

Sulphur dioxide, 11.6 g., and hydrogen chloride, 6.3 g., were evolved and the residue on distillation gave isopropyl formate, b. p. 67—68°, d_4^{17} 0.8801; yield 88% (Found, by saponification: M , 88. Calc.: M , 88). (iii) The chlorosulphinate and pyridine, mixed at -10° and removed from the cooling bath, warmed rapidly, reacted vigorously, and emitted sulphur dioxide and isopropyl chloride. (iv) The same substances when mixed in ether gave a red oil which solidified at -10° . The aqueous solution of the oil gave isopropylpyridinium ferrocyanide [Found: Fe, 11.42. $(C_3H_7 \cdot C_5H_5N)_2H_2Fe(CN)_6 \cdot 2H_2O$ requires Fe, 11.34%].

(b) By the same procedure as (a), *sec.*-butyl chlorosulphinate was obtained, b. p. 55—60°/30—35 mm. (Found, by cold alkaline hydrolysis: Cl, 20.1; SO_2 , 37.2. Calc.: Cl, 22.6; SO_2 , 40.9%). With pyridine in ethereal solution it gave an oil which yielded yellow *sec.*-butylpyridinium ferrocyanide [Found: Fe, 10.88. $(C_4H_9 \cdot C_5H_5N)_2H_2Fe(CN)_6 \cdot 2H_2O$ requires Fe, 10.72%].

The Precipitation of Pyridine Hydrochloride by the Interaction of Hydroxy-compounds and Phosphorus Halides in the Presence of Pyridine in Ethereal Solution.—(a) Phosphorus trichloride (6.8 g., 1 mol.) in 20 c.c. of ether was added slowly to a well-shaken solution of *n*-butyl alcohol (11.1 g., 3 mols.) in 80 c.c. of ether and pyridine (12 g., 3 mols.) at -10° . A crisp white precipitate of pyridine hydrochloride (Found: Cl, 30.5%) formed at once and continued to separate until addition was complete (yield, 17.3 g.; 100%). Addition at room temperature of more phosphorus trichloride to part of the ethereal filtrate had no apparent effect. An aqueous extract of the other part produced only a faint cloudiness with silver nitrate.

(b) Phosphorus oxychloride (7.7 g., 1 mol.) in 10 c.c. of ether, added slowly to *n*-butyl alcohol (11.1 g., 3 mols.) in 50 c.c. of ether and pyridine (12 g., 3 mols.), also gave the hydrochloride (16.5 g. Calc.: 17.3 g. Found: Cl, 30.1%).

(c) Phosphorus trichloride (4.1 g., 1 mol.) in 10 c.c. of ether, added to β -octanol (11.7 g., 3 mols.) and pyridine (7.2 g., 3 mols.) in 40 c.c. of ether, behaved similarly (hydrochloride, 10.0 g. Calc.: 10.35 g. Found: Cl, 30.1%). Further addition of the trichloride to the filtrate effected no apparent change.

(d) Phosphorus oxychloride (4.6 g., 1 mol.), β -octanol, and pyridine [as in (c)] reacted less rapidly (hydrochloride, 8.9 g. Calc.: 10.35 g. Found: Cl, 29.5%). Further addition of oxychloride to the filtrate produced no noticeable effect.

(e) Phosphorus trichloride (2.05 g., 1 mol.) in 10 c.c. of ether, added to ethyl mandelate (8.1 g., 3 mols.) in 40 c.c. of ether and pyridine (3.6 g., 3 mols.), also gave the hydrochloride (5.1 g. Calc.: 5.2 g. Found: Cl, 30.05%). The filtrate did not appear to react with more trichloride.

Ethyl α -Chlorosulphonoxypropionate and Tertiary Bases.—In an attempt to prepare α -carboethoxyethyl *n*-butyl sulphate by addition of *n*-butyl chlorosulphonate (17.1 g.) to an ethereal solution of ethyl lactate (11.8 g.) and pyridine (8 g.), the white granular precipitate first obtained turned into a thick paste which could not be filtered, and the decanted ether yielded, after being washed and dried, *n*-butyl chloride (4.3 g.), b. p. 70—77°, and a residue (4.6 g.) which could not be distilled. The white paste appeared to be pyridine sulphate, but since Baumgarten (*loc. cit.*) had prepared pyridine-sulphur trioxide, $C_5H_5N \cdot SO_3$, from ethyl chlorosulphonate and pyridine, and Willcox (*loc. cit.*) had prepared the corresponding dimethylaniline compound similarly, it appeared desirable, not only to include quinoline in the series, but also to extend the method of Bushong (*Amer. Chem. J.*, 1903, 30, 212) and that of Levailant (*Ann. Chim.*, 1936, 6, 461) for the preparation of alkyl chlorosulphonates to a typical hydroxy-ester. Dry chlorine was passed into α -carboethoxyethyl sulphite (75.5 g.) in a wash bottle surrounded with ice-water until the correct increase in weight for the reaction, $R_2SO_3 + Cl_2 = RCl + R \cdot O \cdot SO_2Cl$, had been obtained (6 hours). On distillation, two fractions were obtained: (i) b. p. 50—56°/23 mm., 33.1 g.; (ii) b. p. 88—95°/2 mm., 54 g. Fraction (i) yielded ethyl α -chloropropionate after being washed and dried, b. p. 47°/19 mm.; and (ii) gave ethyl α -chlorosulphonoxypropionate, b. p. 90—92°/2 mm., 43 g. (Found: Cl, 16.5. $C_5H_9O_5ClS$ requires Cl, 16.4%). The same compound (Found: Cl, 16.3%) was also prepared by adding ethyl lactate (11.8 g.) to sulphuryl chloride (14 g.) agitated by a stream of dry air and cooled at first at -10° , the temperature being allowed to rise to that of the room towards the end. The product was diluted with chloroform, washed rapidly with ice-water, dried over sodium sulphate, and worked up as usual; b. p. 90—92°/2 mm. (14 g., 65% yield).

To the chlorosulphonate (10 g.) in 30 c.c. of dry ether, pyridine (4 g.) in 10 c.c. of ether was added at -10° . A white crystalline precipitate formed immediately, and was finally collected (4.5 g.); it gave no reaction for chloride, dissolved fairly slowly in water, and gave a copious precipitate with barium chloride (Found: S, 19.6. Calc. for $C_5H_9N \cdot SO_3$: S, 20%).

Calc. for C_6H_5N, H_2SO_4 : S, 18%). The ethereal solution yielded ethyl α -chloropropionate, b. p. $48^\circ/22$ mm. (5.8 g., 85%), n_D^{20} 1.4171, d_4^{19} 1.0778.

The chlorosulphonate (11 g.) in 20 c.c. of dry ether at -10° was treated with quinoline (6.5 g.). A white crystalline precipitate (7.8 g.) formed much more slowly than with pyridine. It dissolved slowly in cold water, rapidly in hot water, gave a decided reaction for sulphate, and a slight one for chloride. After being washed quickly with ice-water, it was left for 24 hours in a vacuum desiccator over phosphoric oxide (Found: S, 15.0. *Quinoline-sulphur trioxide*, C_9H_7N, SO_3 requires S, 15.3%). If the washing with ice-water is not rapidly carried out, quinoline sulphate (Calc.: S, 14.1%) is formed: one specimen contained S, 14.0%, even after prolonged desiccation. The ethereal solution after being washed and dried yielded ethyl α -chloropropionate, b. p. $45^\circ/16$ mm., 6.2 g., n_D^{20} 1.4179.

Interaction of Carbonyl Chloride and Ethyl Lactate in the Presence of Pyridine.—Carbonyl chloride (24.8 g., 0.25 mol.) in 400 c.c. of toluene was added to a mixture of ethyl lactate (59 g., 0.5 mol.) and pyridine (40 g., 0.5 mol.) in toluene (80 c.c.) at -10° . Precipitation of pyridine hydrochloride commenced forthwith and continued until the end of the addition. It was filtered off immediately (54 g. Calc.: 57 g. Found: Cl, 30.3%). The toluene solution was washed and dried, and, after the removal of the toluene at $50-60^\circ/40$ mm., α -carbethoxyethyl carbonate (58 g., 90%) was obtained, b. p. $110-110.5^\circ/1$ mm., n_D^{16} 1.4280, $d_4^{14.5}$ 1.1280, d_4^{27} 1.1080 (Found: C, 50.2; H, 6.8. $C_{11}H_{18}O_7$ requires C, 50.4; H, 6.9%). Ritchie (*loc. cit.*) obtained poor yields of the corresponding carbomethoxy-ester from carbonyl chloride (1.0 mol.), methyl lactate (2 mols.), and pyridine (2 mols.). With 1.4 mols. of carbonyl chloride, followed by heating at 100° for 2 hours, he obtained a 40% yield of the carbonate and 20% of methyl α -chloropropionate, the latter probably being due to intermediate formation of the chloroformate owing to local excess of the carbonyl chloride. Waste of this reagent on the side reaction would explain why 0.4 mol. excess is necessary to give even a 40% yield of the desired product.

Phenyl Chlorosulphonate and Tertiary Bases.—An attempt to prepare the chlorosulphonate by addition of phenol to a cold ethereal solution of sulphonyl chloride led to formation of a mixture of chlorophenols (cf. Durrans, J., 1922, 121, 44); the compound was therefore prepared by the method of Battegay and Denivelle (*Compt. rend.*, 1932, 194, 1505). No precipitates were produced when phenyl chlorosulphonate was added to an ethereal solution of pyridine or quinoline, even when *n*-butyl alcohol was added to the resulting mixture. In absence of ether, these bases gave no indication of a reaction when they were mixed with the chlorosulphonate. Dimethylaniline, however, did appear to react; a vivid deep blue liquid was produced slowly in the cold, rapidly by heating on a water-bath. The resulting oil was insoluble in water, soluble in alcohol, giving rise to a blue solution which exhibited a "universal indicator" effect, violet (alkali) \rightarrow yellow (acid), the whole range of colours being shown and the effect being reversible.