CXXXVIII.—*The Action of Sulphur Monochloride on Salts of Organic Acids: a Convenient Method of Preparing Anhydrides.*

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Heintz (*Jahresber. Chem.*, 1856, 569) investigated the action of sulphur dichloride, SCl_2 ("chlorschwefel," SCl, in the old notation), on anhydrous salts of organic acids, and found that the reaction always takes place so that a metallic chloride and sulphate are formed and sulphur separates. He proposed a method for the preparation of benzoic anhydride based on the reaction between dry sodium benzoate and sulphur dichloride, benzoyl chloride being first formed according to the equation:

$$4C_6H_5{\cdot}CO_2Na + 3SCl_2 = 2S + Na_2SO_4 + 2NaCl + 4C_6H_5{\cdot}COCl,$$

this reacting at 150° with excess of sodium benzoate to give benzoic anhydride. Heintz used no solvent for the sulphur dichloride.

The author has found that the sodium, or better, the silver, salts of many monobasic organic acids react smoothly with sulphur monochloride in presence of such solvents as light petroleum, ether, or benzene to give the chloride of the metal and unstable derivatives of the acids, in which, apparently, sulphur replaces the hydrogen of the hydroxyl group. These compounds decompose even when kept in sealed tubes, and the products of decomposition are found to be the anhydride of the acid, sulphur dioxide, and free sulphur. The following equations may perhaps be taken as representing respectively the formation and decomposition of the benzoic acid derivative:

$$2C_6H_5{\cdot}CO_2Na + Cl_2S_2 = (C_6H_5{\cdot}CO_2S)_2 + 2NaCl.$$
$$2(C_6H_5{\cdot}CO_2S)_2 = 2(C_6H_5{\cdot}CO)_2O + SO_2 + 3S.$$

Similar unstable derivatives have been obtained from *o*-toluic, *m*-toluic, *p*-toluic, acetic, phenylacetic, and propionic acids. Those from *m*- and *p*-toluic acids are apparently the most stable. The ready formation and simple decomposition of these compounds (both reactions appear to be quantitative) afford a convenient and rapid method of preparing the anhydrides of the acids.

It was thought to be possible that more stable compounds of the same kind might be obtained from derivatives of the above acids. So far, the silver salts of salicylic, ethylsalicylic, and *o*-nitrobenzoic acids only have been examined, and it has been found that, although reactions take place between these salts and sulphur chloride, they are apparently more complex.

Among dibasic acids, oxalic, malonic, succinic, and the three phthalic acids have been studied. Of these, only the salts of succinic and phthalic acids appear to react at all readily, but no intermediate compounds have been obtained, the anhydrides alone being formed.

Metallic derivatives of imides, for example, potassium phthalimide, react with sulphur chloride. A stable compound, $C_6H_4(CO)_2NS$, has been obtained in this way, and the same compound can be prepared by the action of sulphur chloride on phthalimide in presence of pyridine.

The investigation of the action of sulphur monochloride on metallic salts and on compounds containing imino-groups is being continued.

EXPERIMENTAL.

Action of Sulphur Monochloride on Sodium Benzoate.—This reaction has been carried out repeatedly in slightly varying ways, using different solvents; the following may be taken as typical. 2·9 Grams of dry, powdered sodium benzoate were mixed with about 20 c.c. of light petroleum, and the calculated quantity (1·4 grams) of sulphur chloride dissolved in a few c.c. of the same solvent was added all at once. The mixture was then boiled on the water-bath for a hour and a-half under a reflux condenser provided with a calcium chloride tube; a slight odour of sulphur dioxide was noticed during this operation. About one gram of freshly reduced copper powder * was then added, and the boiling was continued for half-an-hour longer. The copper became black, and the solution green, but, on filtering, a clear, colourless liquid was obtained, from which crystals separated on cooling. In this way a good yield is obtained of the substance, $(Ph\cdot CO_2S)_2$, in well-defined, colourless crystals, which, however, soon turn yellow and evolve sulphur dioxide, leaving sulphur and benzoic anhydride. This decomposition takes place even in an atmosphere of carbon dioxide, and in warm weather may occur instantaneously with the formation of a liquid mass consisting of a mixture of sulphur and benzoic anhydride. The compound is easily soluble in alcohol, ether, benzene, carbon disulphide, or glacial acetic acid, more sparingly so in light petroleum. The solution in benzene may be kept for a day or two without evidence of decomposition, whilst that in glacial acetic acid soon decomposes. The substance, when dissolved in petroleum, reacts with ammonia, but no definite product other than ammonium benzoate could be obtained. It reacts also with aniline.

The sulphur was estimated in some of the freshly prepared and recrystallised substance, which had been quickly dried by warming it gently in a current of carbon dioxide:

0·5098 gave 0·7928 $BaSO_4$. $S = 21·32$.

0·39 in 13·09 benzene gave $\Delta t = -0·53$. M.W. = 281.

$C_{14}H_{10}O_4S_2$ requires $S = 20·92$ per cent. M.W. = 306.

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* The copper is not essential. It was added in one experiment to see if it would remove the sulphur and leave benzoyl peroxide, but this did not happen. The use of it was continued in after experiments, since it appeared to destroy final traces of sulphur chloride and to be better for this purpose than excess of sodium benzoate.

This compound, $(C_6H_5{\cdot}CO_2S)_2$, may be prepared more readily by shaking together dry silver benzoate and a solution of sulphur chloride in ether in the manner described below for other silver salts.

Action of Sulphur Monochloride on Silver Acetate.—Since sulphur chloride does not react readily with sodium acetate, the silver salt was employed, and after a number of preliminary experiments, the following simple method was found to give satisfactory results.

To 2·5 grams of dry silver acetate, about 20 c.c. of dry ether were added, and then 0·4 c.c. (rather less than the calculated quantity) of sulphur chloride, dissolved in a few c.c. of dry ether. The containing vessel was closed and shaken for a minute, when the mixture became warm and the yellow colour of the sulphur chloride disappeared.

After filtering, the ether was distilled off, the last traces being removed by means of a current of dry hydrogen. The compound, $(CH_3{\cdot}CO_2S)_2$, was thus obtained as a clear, faintly yellow, viscous liquid with a faintly pungent odour. Some of it, after being kept for three days in a closed flask in the ice-chest, was found to be completely decomposed into sulphur dioxide, sulphur, and acetic anhydride:

0·6248 gave 1·5984 $BaSO_4$. S = 35·14.
0·617 in 19·94 benzene gave $\Delta t = -0{\cdot}895$. M.W. = 173.
$C_4H_6O_4S_2$ requires S = 35·16 per cent. M.W. = 182.

Action of Sulphur Monochloride on Silver Propionate.—This experiment was carried out exactly as was the one with silver acetate, and a compound, $(C_2H_5{\cdot}CO_2S)_2$, was obtained, of which the properties were exactly similar to those of the compound derived from acetic acid, and decomposed similarly:

0·6910 gave 1·5436 $BaSO_4$. S = 30·68.
0·998 in 16·19 benzene gave $\Delta t = -1{\cdot}59$. M.W. = 194.
$C_6H_{10}O_4S_2$ requires S = 30·48 per cent. M.W. = 210.

Preparation of Propionic Anhydride from Silver Propionate.—To 18·1 grams of dry silver propionate in about 50 c.c. of dry ether, 4 c.c. of sulphur chloride in 20 c.c. of dry ether were added; this addition must be made gradually, as otherwise the reaction may become too vigorous. The mixture was then shaken for a minute, and after filtering off the silver chloride and removing the ether by distillation, the syrup obtained was heated on the water-bath for an hour or two until decomposition was complete. The clear liquid was then decanted and distilled, the distillation being stopped as soon as the distillate appeared yellow; 5·5 grams of the crude anhydride distilled between 160° and 170°, the greater portion above 165°. The boiling point of propionic anhydride is 168°, and the calculated yield from 18·1 grams of silver propionate is 6·5 grams.

Preparation of Propionic Anhydride from Sodium Propionate.—9·6 Grams of dry sodium propionate were boiled for an hour under reflux with 4 c.c. of sulphur chloride in presence of 40 c.c. of light petroleum, a little copper powder being added towards the end. The solution was then filtered from sodium chloride and treated as just described in the preparation from the silver salt; 4·5 grams of the crude anhydride distilled over at a little below 170°. The theoretical yield is 6·5 grams.

Action of Sulphur Monochloride on Silver Phenylacetate.—This reaction was carried out exactly in the way described in the case of silver acetate, a slight excess of the silver salt being used. The compound, $(C_6H_5\cdot CH_2\cdot CO_2S)_2$, was obtained as a pale yellow, very viscous liquid with a faint odour, which partly crystallised when cooled in ice. If heated in the steam-oven, it decomposes in a few minutes, and when kept in a sealed tube, decomposition is apparent in two days. The only products of decomposition observed were sulphur dioxide, sulphur, and phenylacetic anhydride. The last-named substance can readily be purified by recrystallisation from benzene with addition of light petroleum. It was identified by a determination of its melting point and by conversion into phenylacetic acid:

0·2826 gave 0·3930 $BaSO_4$. S = 19·10.
0·795 in 16·95 benzene gave $\Delta t = -0·78$. M.W. = 301.
$C_{16}H_{14}O_4S_2$ requires S = 19·16 per cent. M.W. = 334.

Action of Sulphur Monochloride on Silver o-*Toluate.*—This reaction was carried out much as described in the case of silver acetate, but as the product is a crystalline solid, it was precipitated by distilling off most of the ether, then adding light petroleum, and cooling in ice. The compound, $(C_6H_4Me\cdot CO_2S)_2$, is a white, crystalline, odourless solid, which decomposes in two or three hours. It resembles the benzoic acid derivative in being more stable in solution in benzene than in the solid state. The decomposition products were sulphur, sulphur dioxide, and *o*-toluic anhydride, which was identified by a determination of its melting point and by conversion into *o*-toluic acid:

0·3538 gave 0·5120 $BaSO_4$. S = 19·82.
0·567 in 18·17 benzene gave $\Delta t = -0·53$. M.W. = 294.
$C_{16}H_{14}O_4S_2$ requires S = 19·16 per cent. M.W. = 334.

Action of Sulphur Monochloride on Silver m-*Toluate.*—The experiment was carried out exactly as in the case of silver acetate. The compound, $(C_6H_4Me\cdot CO_2S)_2$, was a very viscous, slightly yellow, but perfectly transparent syrup, with almost no odour. It is apparently more stable than any of the foregoing compounds. When kept in a sealed tube it slowly crystallised, and the crystalline mass appeared to be largely undecomposed a week after preparation. When examined ten days after preparation, the appearance of the tube indicated that the substance had decomposed suddenly:

0·3192 gave 0·4414 $BaSO_4$. S = 18·99.

0·488 in 23·35 benzene gave $\Delta t = -0·38$. M.W. = 275.

$C_{16}H_{14}O_4S_2$ requires S = 19·16 per cent. M.W. = 334.

The decomposition products were sulphur, sulphur dioxide, and *m*-toluic anhydride. The latter was dissolved in sodium hydroxide solution, and on acidifying the solution, *m*-toluic acid was precipitated. *m*-Toluic anhydride does not seem to have previously been prepared:

0·1816 gave 0·5008 CO_2 and 0·0952 H_2O. C = 75·21; H = 5·82.

$C_{16}H_{14}O_3$ requires C = 75·59; H = 5·51 per cent.

m-*Toluic anhydride* melts at 71° and boils about 230°/17 mm. It is very soluble in ether, benzene, chloroform, or other solvents, but may readily be crystallised from light petroleum. It is not readily attacked by water or by sodium hydroxide solution. It is easily prepared by the following method. Two c.c. of sulphur chloride in 20 c.c. of dry ether were added to 12·5 grams of dry silver *m*-toluate (instead of 12·15 grams) in 50 c.c. of ether. After shaking, filtering, and removing the ether by distillation, the sulphur compound was heated on the water-bath until sudden decomposition set in, and when decomposition was complete, the anhydride was extracted with ether. A nearly theoretical yield was obtained of the crude anhydride, which may be purified by recrystallisation from light petroleum, making use of animal charcoal.

The formation and decomposition of the compound $(C_6H_4Me\cdot CO_2S)_2$ were followed quantitatively, with the following results: 12·15 grams of silver *m*-toluate gave 7·7 grams of the compound $(C_6H_4Me\cdot CO_2S)_2$ instead of the calculated yield, 8·3 grams; 7·7 grams of the compound $(C_6H_4Me\cdot CO_2S)_2$ gave 0·88 gram of sulphur dioxide,* 5·9 grams of crude anhydride (containing a little sulphur), and 0·87 gram of sulphur. According to the equation $2(C_6H_4Me\cdot CO_2S)_2 = 2(C_6H_4Me\cdot CO)_2O + SO_2 + 3S$, 7·7 grams of the substance should yield 0·74 gram of sulphur dioxide, 5·7 grams of anhydride, and 1·1 grams of sulphur.

Action of Sulphur Monochloride on Silver p-*Toluate*.—The reaction was carried out as before. The compound, $(C_6H_4\cdot Me\cdot CO_2S)_2$, begins to crystallise while the ether is being distilled off. It is a white, crystalline solid:

0·2604 gave 0·3766 $BaSO_4$. S = 19·87.

0·436 in 13·99 benzene gave $\Delta t = -0·50$. M.W. = 312.

$C_{16}H_{14}O_4S_2$ requires S = 19·16 per cent. M.W. = 334.

* Determined by the loss of weight after evolution of the sulphur dioxide.

A sample of this substance kept in a sealed tube was still almost white a week after preparation, thereafter the yellow colour slowly became more marked. On opening the tube, sulphur, sulphur dioxide, and *p*-toluic anhydride were found to be present. The anhydride was identified by a determination of its melting point and by conversion into *p*-toluic acid.

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