IV.—*On a New Reaction for the Production of Anhydrides and Ethers.*

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THE reactions which are employed for the preparation of the anhydrides of the monobasic organic acids are those originally discovered by Gerhardt, where either the chloride of an electro-negative radicle is made to act on the corresponding alkaline salt, giving rise to the production of an alkaline chloride and the anhydride; or the same decomposition is indirectly superinduced

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by allowing the pentachloride or terchloride of phosphorus to act on the alkaline salt.

These methods, therefore, essentially consist rather in an almost synthetical formation of the anhydride by a process of double decomposition, analogous in its nature to those by which the compound and double ethers are produced, than in a direct elimination of the anhydride from the salt, of which the reactions for producing nitric and carbonic anhydrides afford familiar instances.

In addition to the above methods, is that described by Gal (*Compt. rend.* lvi., 360), who, by acting on caustic lime and baryta with the chlorides of acetyl and benzoyl, obtained the corresponding anhydrides. As this method obviously necessitates the employment of the chloride of phosphorus, its principle rests mainly on the same decomposition as that discovered by Gerhardt.

It was therefore thought that a reaction by which the anhydrides of the organic acids could be more directly eliminated from salts, in the same manner as some inorganic anhydrides, would possess considerable interest, both in a practical and in a theoretical point of view.

For this purpose, several attempts were made to procure acetic and benzoic anhydrides by the action of boracic acid on the potassium-salts of these acids; but this method, as might probably have been foreseen, failed to produce the desired substances.

It then occurred to me to try the effect of bisulphide of carbon. This substance was shown by Frémy, many years ago, to be readily decomposed by heated metallic oxides, into carbonic anhydride and a metallic sulphide, and also when heated with water to a high temperature, to form sulphuretted hydrogen and carbonic anhydride (Schlagdenhauffen, *J. Pharm.* [3], xxix. 491). It was therefore thought probable that, by acting on the dry metallic salts of the organic acids with bisulphide of carbon, the metal would be converted into sulphide, and the anhydride set free. With this view the following experiments were performed:—

Crystallised acetate of lead was dried for several hours, at about 120°C ., and reduced to as fine a state of division as possible, and a small quantity was placed in a strong glass tube, which was then one-third filled with dry bisulphide of carbon, sealed, and heated in an oil-bath to about 150°C . After an hour's heating, the contents of the tube had become quite black, and after a few hours' exposure, the tube was removed from the bath, allowed to

cool, and then opened, when a violent escape of gas took place, attended with a strong, pungent, acid smell. This gas, on being allowed to pass into baryta-water, was found to be carbonic anhydride. Several strong tubes of hard glass were then charged with 20 grammes each of dry acetate of lead, and as much bisulphide of carbon added as was necessary to make, on agitation with the acetate, a mixture of a creamy consistency. The tubes being then rather more than one-third full, were sealed and heated in the oil-bath, to a temperature of 165°C . The mixture quickly assumed a black colour, and after some hours' heating, one of the tubes, by exploding with great violence, gave warning that a large amount of gas had been liberated. After this it was found advisable to open the tubes once a day, in order to let the carbonic acid escape; and with this precaution the digestion was continued, till it was found that on opening the tubes, only a slight rush of gas took place. The reaction was then judged to have practically terminated.

The liquid contents of the tubes were then poured off as far as possible, and the remainder adhering to the solid sulphide of lead was separated by distillation at a moderately high temperature, and the whole fluid product thus obtained was submitted to distillation. The first product passing over was the excess of bisulphide used, after which the temperature of the boiling liquid gradually rose, when some acetic acid, with a trace of acetone, made its appearance, till the temperature gradually rose to 137°C ., and remained constant till the whole had passed over.

The portions of distillate collected near the latter temperature had a pungent acid odour, attacking the eyes and nostrils; when mixed with water, it sank, and gradually dissolved, with rise of temperature. On mixing it with alcohol, the odour of acetic ether was produced. To decide the matter, an analysis was made of the portions which boiled at 137° .

0.3010 grm. burnt with oxide of copper and oxygen, gave 0.5170 of CO_2 , and 0.1636 of water.

		Calculated.	Found.
C_4	48	47.05	46.84
H_6	6	5.88	6.03
O_3	48	47.07	—
	<hr/> 102	<hr/> 100.00	

The liquid was therefore acetic anhydride, and its production can be expressed by the equation—

Experiments with acetate of silver gave a similar result, with even greater readiness.

The above reaction of bisulphide of carbon, it will be perceived, is susceptible of at least three important applications for the formation of organic bodies, if it prove to be in any respect a general one.

1. The production of anhydrides as above from metallic salts.
2. The formation of compound ethers, by allowing the anhydrides in the nascent state to react on an alcohol.
3. In certain cases, for the isolation of anhydrides of electro-positive radicles, or ethers.

For the second application it was proposed to produce an ether of acetic acid which had not hitherto been successfully prepared, and for this purpose acetate of phenyl was chosen. This substance Scrugham (*Chem. Soc. Qu. J.* vii., 241) attempted to procure by acting on acetate of potash with an alcoholic solution of phosphate of phenyl, but did not succeed in obtaining it pure. Berthelot had found, during his experiments on etherification, that a small percentage of acetic acid entered into combination with phenylic alcohol when heated with the latter in sealed tubes.

In order to procure this ether, acetate of lead was at first sealed up with an equivalent quantity of phenylic alcohol and an excess of bisulphide of carbon; but after some experiments it was found better to operate with only half an equivalent of phenylic alcohol, as the presence of some of the latter in an uncombined state seriously affected the eventual separation of the acetate in a state of purity. The following was therefore the method adopted:—

20 grammes of well-dried and finely-divided acetate of lead was sealed up in strong tubes, with 3 grammes of phenylic alcohol, and a considerable excess of bisulphide, and heated in an oil-bath to about 170°C. The reaction soon commenced, and proceeded with more regularity than in the preparation of the anhydride, since the lead-salt is soluble in the alcohol, so that the bisulphide is enabled to act with greater readiness. It was found necessary to open the tube daily, for it was shown by some explosions that the pressure

of the liberated gas was very high. When the action had ceased, the liquid products were separated as above described, and re-distilled. After the excess of bisulphide had distilled, acetic acid in considerable quantity passed into the receiver, then a small quantity of acetic anhydride, after which the temperature rose rapidly to 190°C. , when a liquid of a pleasant empyreumatic odour made its appearance, and when the temperature had attained 210°C. the whole had passed over.

The portions distilling above 190° were rectified, and by repeated fractioning, the greater part was obtained of a constant boiling point of 200° . This was submitted to analysis as follows, by combustion with oxide of copper and oxygen:—

I. 0.2142 grammes gave .5554 CO_2 and .1133 H_2O .

II. 0.1964 grammes gave .5098 CO_2 and .1060 H_2O .

		Calculated.	I.	II.
C_8	96	70.59	70.71	70.78
H_8	8	5.88	5.87	5.99
O_2	32	23.53	—	—
	<hr/>	<hr/>		
	136	100.00		

The vapour-density of the liquid was taken as follows, by Gay Lussac's method, using a bath of spermaceti:—

Weight of liquid employed 0.2299 grm.

Observed volume of vapour 70.28 cc.

Temperature 218°C.

Height of barometer 744.5 mm.

Difference of heights of internal and external mercury 32 mm.

Height of column of spermaceti 230 mm. at 45° .

These data give sp. gr. of vapour 4.72. The calculated density of acetate of phenyl is 4.59.

The liquid therefore was acetate of phenyl.

Acetate of phenyl is a colourless liquid, boiling at 200°C. , of a peculiar and fragrant odour, which is very persistent; its sp. gr. is 1.074, being somewhat heavier than phenylic alcohol, as acetic ether is heavier than ordinary alcohol. Though quite colourless when freshly distilled, it becomes somewhat yellow by keeping. It is slightly soluble in water, in which it sinks, and to which it imparts its peculiar odour. It is neutral to test-paper, and is not decomposed by boiling water; even when heated with water to 180°

it acquires but a very slight acid reaction. Boiling solutions of the fixed alkalis gradually dissolve acetate of phenyl, with formation of an alkaline acetate and phenate. Its index of refraction is the same as that of German fusible glass, on which account tubes of the latter become invisible when immersed in this ether.

It will appear from the above experiments that this reaction of bisulphide of carbon will most probably be found of service in isolating anhydrous acids, in cases where the ordinary methods are not convenient, and will also, it is believed, receive many applications as a general mode of preparing compound ethers, since it has the advantage of being applicable to small quantities. Phenyl alcohol, which has hitherto been found so difficult of etherification, may probably, by the above process, yield its full complement of ethers in the manner of alcohols of other series.

Experiments have been commenced to illustrate the third application of this reaction, namely, that of eliminating phenylic ether from phenate of lead.

Whether the method be applicable as a means of procuring double ethers and anhydrides, further experiment must show.

In conclusion, the following desultory qualitative experiments have been tried:—

Chloride, bromide, iodide, and fluoride of lead are not attacked by bisulphide of carbon.

Nitrate of silver is most readily acted on by bisulphide of carbon, with production, in addition to sulphide of silver, of a green liquid and a white solid substance; but on attempting to open the tubes, they have burst with a most violent explosion.

Sulphate of lead is not affected by sulphide of carbon.

Benzoate, succinate, and ferrocyanide of lead are readily acted on by the bisulphide.

Formate of lead is entirely converted into sulphide by bisulphide of carbon, with much evolution of gas; traces of a strong acid are evolved, together with a sulphur-compound of a powerful odour; all attempts to obtain formic anhydride have been unsuccessful, the latter being apparently entirely decomposed into gases.

Oxalate of lead is entirely unaffected by sulphide of carbon at a high temperature.

I take this opportunity of expressing my thanks to Professor Frankland for opportunity and leisure to make the above experiments.