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TRANSACTIONS.

I.—*The Preparation and Reactions of Benzoyl Nitrate.*

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The investigation of the action of nitrates of silver and lead on benzoyl chloride was carried out by B. Lachowicz (*Ber.*, 1884, **17**, 1281), who showed that nitrogen tetroxide and oxygen were evolved and benzoic anhydride formed. The reaction appears to be general (*Ber.*, 1885, **18**, 2990), and mono- and di-basic acid chlorides of the aliphatic and aromatic series give good yields of the corresponding anhydrides.

But if the interaction of benzoyl chloride and silver nitrate takes place at a much lower temperature, oxides of nitrogen are not evolved and benzoyl nitrate is formed; this change, which is nearly quantitative, may be expressed by the equation:

$$C_6H_5{\cdot}CO{\cdot}Cl + AgO{\cdot}NO_2 = C_6H_5{\cdot}CO{\cdot}O{\cdot}NO_2 + AgCl.$$

The greatest care has to be taken during this reaction to avoid the presence of moisture, since this at once brings about the decomposition of the nitrate into benzoic and nitric acids.

Thirty-five grams of benzoyl chloride are treated with excess of dry powdered silver nitrate in a flask provided with a phosphoric oxide drying tube, and kept at a temperature of −15° with continual shaking for two and a half hours. At the end of that time, the change of benzoyl chloride into the nitrate is usually complete, and the contents of the flask are rapidly filtered through a layer of carefully dried asbestos, and, if then not free from solid silver salts, may be again filtered through dry filter paper, but should the latter be in the slightest degree moist explosive decomposition may set in. Thirty grams of a clear yellow oil are obtained, which it is only possible to preserve for any length of time by sealing up in glass tubes.

When benzoyl nitrate is carefully and gradually heated to about 100°, oxides of nitrogen are rapidly evolved and benzoic anhydride formed in theoretical quantity, but if a small amount is heated with a free flame this decomposition sets in with explosive violence and the yield of anhydride is much diminished.

It is, therefore, clear that in the case of benzoyl chloride, and most probably with the other acid chlorides, benzoyl nitrate and corresponding derivatives are the intermediate products in the Lachowicz reaction for the preparation of anhydrides. The decomposition of the nitrate, a substance which may be regarded as the mixed anhydride of benzoic and nitric acids, is expressed by the following equation:

$$2C_6H_5{\cdot}CO{\cdot}O{\cdot}NO_2 = (C_6H_5{\cdot}CO)_2O + O + N_2O_4.$$

This reaction is similar to that undergone by the mixed anhydrides of both aliphatic and aromatic acids, which on distillation yield a mixture of the corresponding simple anhydrides.

The conditions under which benzoyl nitrate is converted into *m*-nitrobenzoic acid are at present being investigated, but it appears probable that with the pure nitrate this change only takes place with small velocity; sealed up in glass tubes and kept at a temperature of 12°, small quantities of solid only commenced to separate out after seven days. When impurities are present, however, the velocity of this change appears to be greatly increased. No other isomeric acid is formed, since, on fractionally recrystallising the barium salt, the various acids obtained showed no indication of the presence of the less fusible *p*-derivative or of the sweet *o*-nitrobenzoic acid.

An apparently similar change takes place in several inert solvents, but notably in nitrobenzene. A solution of the nitrate in this solvent left in a warm place deposited pure *m*-nitrobenzoic acid in the course of ten days. An investigation of the filtrate showed that no dinitrobenzene had been formed. Now, since benzoyl nitrate acts as a nitrating agent, as described later, it appears that the presence of a nitrogroup in the benzene nucleus prevents the entrance of a second group, and that consequently *m*-nitrobenzoyl nitrate would not show a tendency to pass into 3 : 5-dinitrobenzoic acid. For this reason, a small amount of *m*-nitrobenzoyl nitrate was prepared in a manner similar to that previously described in the case of the benzoyl derivative, but since the acid chloride melts at 35° the temperature maintained during the reaction was between 30° and 40°. An oil was obtained which sets to a hard, white, crystalline mass on cooling. It fuses between 40° and 50°, and, owing to the extreme ease with which it absorbs moisture, was not obtained quite free from *m*-nitrobenzoic acid. It fumes in the air, decomposes slowly at the ordinary temperature, and with explosive violence if rapidly heated to 100°. But so far as the investigation of this substance has been carried out, no change into 3 : 5-dinitrobenzoic acid has, as yet, been observed.

Benzoyl nitrate is a most reactive substance, and the following decompositions with perfectly dry reagents take place at temperatures between 0° and $-15°$.

Ethyl alcohol gives ethyl nitrate and benzoic acid, the former substance being readily detected by its boiling point, odour, and insolubility in water. Benzene and, less readily, toluene are converted into their nitro-derivatives with the simultaneous production of benzoic acid. If the reagent is added to an excess of well cooled phenetole, benzoic acid separates, and, after extracting the substance with aqueous caustic potash, a quantitative yield of nitrophenetole, presumably the *o*-derivative, is obtained from the residue. The nitro-derivative boils between 264° and 269° and melts below 0°, and is apparently quite free from isomeric nitrophenetoles. The reaction with phenol takes place equally readily and *o*-nitrophenol is the chief product. Methylaniline dissolved in light petroleum and well cooled is converted into phenylmethylnitramine, $C_6H_5\cdot N(CH_3)\cdot NO_2$, and benzoic acid, the former substance being recognised by its melting point and characteristic behaviour with sulphuric acid; this reaction again takes place quantitatively. Dimethylaniline in the same solvent does not react so simply, but *p*-nitrodimethylaniline is among the products. These are some of the reactions which have been but partially investigated, and a more detailed examination of the whole question is in progress. But it appears very probable that in benzoyl nitrate we have a new nitrating agent, which will enable this operation to be carried out at low temperatures and in the absence of water.

The only reaction in which benzoyl nitrate shows its analogy to the chloride is in the case of aniline, which, under light petroleum, is quantitatively converted into aniline nitrate and benzanilide.

It is hoped that mixed anhydrides of organic and other inorganic acids may be isolated, and experiments on these lines are now being carried out.

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