CLVII.—*The Iodination of* o-*Nitrophenol.*

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Hübner (*Ber.*, 1874, **7**, 461) described, but did not analyse, two iodonitrophenols, termed by him α and β, m. p. 90—91° and 66—67°, respectively, which he obtained by iodinating *o*-nitrophenol in glacial acetic acid in presence of mercuric oxide, and separated by fractionally crystallising their potassium salts from alcohol. The α-compound is stated to be only slowly volatile in steam, the β much more readily, and both were assumed to be monoiodonitrophenols.

In Beilstein's "Organische Chemie" (II, p. 700), the α- and the β-compound are recorded as 5(?)-iodo-2-nitrophenol and 6(?)-iodo-2-nitrophenol, respectively. Roberts (J., 1923, **123**, 2708) doubts whether they are pure substances, since neither is identical with his 4-iodo-2-nitrophenol (m. p. 80—81°) or with Brenans's 2-iodo-6-nitrophenol (m. p. 110°) or2-iodo-4-nitro phenol (m. p. 86—87°) (*Compt. rend.*, 1902, **134**, 357). Keimatsu (*J. Pharm. Soc. Japan*, 1924, No. 507, 319) regards the Hübner compounds as 3- and 4-iodo-2-nitrophenols. If this is so, the former would be an example of an unexpected type of iodination.

The present author, having already prepared 5-iodo-2-nitrophenol (m. p. 96°) and 3-iodo-2-nitrophenol (m. p. 73·5°) (this vol., p. 630) is in possession of the necessary standards for the solution of this problem. He has found that in all cases of direct iodination of *o*-nitrophenol with the aid of mercuric oxide, whether the quantity of iodine taken is less than, equal to, or greater than that required for mono-iodination according to the equation $2NO_2{\cdot}C_6H_4{\cdot}OH + 2I_2 + HgO = 2NO_2{\cdot}C_6H_3I{\cdot}OH + HgI_2 + H_2O$, di-iodination occurs to a considerable extent and various quantities of mercurous salts are also produced. Hübner's α- and β-compounds have proved to be 4 : 6-di-iodo-2-nitrophenol and 4-iodo-2-nitrophenol, respectively, mixed with small quantities of 6-iodo-2-nitrophenol. The mono-iodo-2-nitrophenols are all readily volatile in steam.

The considerable tendency toward di-iodination, and the formation of 4-iodo-2-nitrophenol in excess of that of the 6-iodo-isomeride, indicate that the initial mono-iodination of *o*-nitrophenol occurs preferentially in position 4. No indication of the presence of 3-iodo-2-nitrophenol has been detected.

Experimental.

For purposes of comparison, 6-iodo-2-nitrophenol (m. p. 110°) and 4-iodo-2-nitrophenol (m. p. 80—81°) were prepared by direct nitration of 2- and 4-iodophenols, respectively; 4 : 6-di-iodo-2-nitrophenol (m. p. 98°) by direct iodination of *o*-nitrophenol in glacial acetic acid in presence of yellow mercuric oxide, by iodination of 4-iodo- and 6-iodo-2-nitrophenols, and by Roberts's method (*loc. cit.*); 6-iodo-2 : 4-dinitrophenol (m. p. 106°) and 4-iodo-2 : 6-dinitrophenol (m. p. 113°) by direct iodination of 2 : 4- and 2 : 6-dinitrophenols, respectively, and also by the dinitration of 2- and 4-iodophenols by Hodgson and Moore's method for the dinitration of *m*-chlorophenol (J., 1925, **127**, 1601).

Iodination by Hübner's Method.—A solution of *o*-nitrophenol (2 mols.) and iodine (2 mols.) in glacial acetic acid, while being vigorously shaken, was treated gradually with yellow mercuric oxide until the iodine had disappeared. The mixture was then filtered, and the filtrate diluted with water to precipitate the iodonitrophenols. These were washed by decantation, and treated with warm aqueous potassium hydroxide, and the filtered solution was evaporated to dryness. The solid residue was boiled with alcohol several times, and the combined extracts were allowed to cool; long, red needles were deposited, which were continually removed (α) until more tabular and yellower crystals began to appear (β). The two batches, α and β, were each treated with sulphuric acid, and then steam-distilled until the more volatile products had passed over. In each case, the slowly volatile material was crystallised several times from dilute alcohol, the melting point being thus raised from 94° to 98° (Found: I, 65·1. Calc. for $C_6H_3O_3NI_2$: I, 64·9%). Mixed with authentic 4 : 6-di-iodo-2-nitrophenol, the substances again melted at 98°. The potassium salts of these two compounds were alike in every way and different from the potassium salt of any of the monoiodo-2-nitrophenols.

The steam-volatile product in each case was recrystallised from alcohol until the m. p. had been raised from about 63° to 78° (Found for the compounds from the α- and the β-batch, respectively: I, 48·2, 48·1. Calc. for $C_6H_4O_3NI$: I, 47·9%). Mixed with authentic 4-iodo-2-nitrophenol, each compound melted at 79—80°, and the identity was further established (*a*) by iodination to 4 : 6-di-iodo-2-nitrophenol, (*b*) by nitration to 4-iodo-2 : 6-dinitrophenol, and (*c*) by nitration to picric acid without 3-iodo-2 : 4 : 6-trinitrophenol being detected.

The residual potassium salt from the original alcoholic extract (above) was suspended in dilute sulphuric acid and submitted to steam-distillation. The volatile product, after several crystallisations from alcohol, melted at 102° (Found: I, 48·0. Calc. for $C_6H_4O_3NI$: I, 47·9%). Its identity with 6-iodo-2-nitrophenol was indicated by the like crystalline forms, and by the melting point of a mixture of the two substances, and was confirmed (*a*) by iodination to 4 : 6-di-iodo-2-nitrophenol, (*b*) by nitration to 6-iodo-2 : 4-dinitrophenol, and (*c*) by trinitration to picric acid without 3-iodo-2 : 4 : 6-trinitrophenol being detected.

A slightly volatile product obtained in the above steam-distillation was 4 : 6-di-iodo-2-nitrophenol.

The same results were obtained when the iodination of *o*-nitrophenol was carried out at 40—50° ; when iodine, dissolved in ether, was added in small portions at a time, and the mixture was shaken during the gradual addition of mercuric oxide until the iodine had disappeared; and when alcohol was employed instead of glacial acetic acid as solvent.

Modifications of Hübner's Method.—(*a*) Instead of the potassium salts being prepared, the water-precipitated iodonitrophenols were steam-distilled, and several fractions collected. The earlier ones contained a little 6-iodo-2-nitrophenol, but consisted mainly of 4-iodo-2-nitrophenol. The later fractions contained a little 4 : 6-di-iodo-2-nitrophenol, and the residue was a mixture of this compound with mercurous and mercuric salts.

(*b*) The iodination was carried out as described above (*a*), but half the quantity of iodine was used. The steam-distillate was collected in three fractions, which were filtered off and extracted with boiling alcohol. The extract of the first fraction left a residue containing mercurous iodide, and deposited, on cautious dilution, crystals of 6-iodo-2-nitrophenol followed by an oil. The latter was dissolved in aqueous sodium hydroxide, the alcohol removed, and the solution was acidified and very slowly steam-distilled. The first-runnings deposited *o*-nitrophenol on cooling. The second fraction was treated similarly and found to contain mercurous iodide and 4- and 6-iodo-2-nitrophenols. The third fraction contained these substances and also 4 : 6-di-iodo-2-nitrophenol.

The original residue consisted mainly of 4 : 6-di-iodo-2-nitrophenol mixed with mercuric iodide.

(*c*) In this experiment, twice the quantity of iodine was used. The steam-volatile product was only small in amount, had a high m. p., and contained mercury. The bulk of the reaction product was the very slightly volatile 4 : 6-di-iodo-2-nitrophenol.

Evidence of the Absence of 3-*Iodo*-2-*nitrophenol.*—The entire water-precipitated mixture of iodonitrophenols obtained in an experiment according to Hübner was washed, dried, and divided into three equal portions. One of these was mixed with *m*-iodophenol, another with 3-iodo-2-nitrophenol, and the two mixtures and the third portion were separately trinitrated, and the products were worked up, by the methods used in the trinitration of *m*-iodophenol (*loc. cit.*, p. 634). The mixture containing *m*-iodophenol and that containing 3-iodo-2-nitrophenol each gave a sublimate of 3-iodo-2 : 4 : 6-trinitrophenol, but the third portion of the Hübner product gave only picric acid. This result indicates the absence of 3-iodo-2-nitrophenol from this product.

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