ART. XVIII.—*On a New Formation of Dinitroaniline, and some Reactions of Dinitrobrombenzol*; by PETER TOWNSEND AUSTEN.

ENGAGED in an extensive research concerning the stability of the bromine atom in dinitromonobrombenzol, I was led to treat that compound with potassium cyanate in the hope of obtaining a dinitrophenylecyanic ester, according to the reaction,

Dinitrobrombenzol was mixed with about one and a half times its volume of potassium cyanate, and the mixture heated to 100° in a closed tube with very dilute alcohol for eight hours; on cooling, the tube became filled with a mass of bright yellow leaflets, and on opening gave off carbonic acid. The

* *Ann. Chem. Pharm.*, cxxxix, 107.

substance, after crystallization from boiling water, fused at 175° – 176° , and on analysis* proved to be the ordinary dinitroaniline.

The reaction by which dinitroaniline is formed admits of various explanations. Wöhler has shown that potassium cyanate by repeated distillation with water, splits according to the formula—

Hence we may suppose the formation of the dinitroaniline to be due simply to the action of the dinitrobrombenzol on the ammonium carbonate,

The bromhydric acid thus formed acts on the potassium carbonate, so that the whole reaction is—

We can, however, suppose the action to take place directly without admitting the previous formation of ammonium carbonate—

Nor is there anything very improbable in the supposition that ammonium carbonate is not formed previously, as there are so many cases in which a substance withdraws from another elements not previously directly united with each other, but with which it can form a compound (predisposing affinity).

It is, however, also not impossible that the formation of the dinitroaniline may depend upon the production and subsequent decomposition of a dinitrophenylecyanic ester according to the reaction discovered by Wurtz,

but this appears to me doubtful, since the dinitrobrombenzol is not freely soluble in the very dilute alcohol used. Hence the potassium cyanate is exposed principally to the action of the water, and much less to the action of the dinitrobrombenzol; therefore, although a partial formation of the ester might take place, the chief part of the potassium cyanate would be decomposed at the same time by the action of the water, so that if the ester were formed, it could only be in small quantities.

* Calculated.
C = 39.34
H = 2.72

Found.
39.35
3.01

Mononitrobrombenzol and Potassium Cyanate.

The substances, heated in a sealed tube to 100° with dilute alcohol for eight hours, gave no mononitroaniline, as was to be expected, since mononitrobrombenzol is not acted on by ammonia itself under 160°. The cyanate, however, was completely converted into the corresponding carbonates.

Trinitrochlorbenzol and Potassium Cyanate.

By boiling a concentrated solution of potassium cyanate with trinitrochlorbenzol, I obtained, with strong evolution of ammonia, a red oil which solidified on cooling, and contained considerable unchanged trinitrochlorbenzol. The filtrate contained chlorine (showing that a reaction had taken place), and some picric acid, while chlorhydric acid precipitated a green powder. I have not as yet had time to examine either of these substances farther than to establish the absence of trinitroaniline. By heating for five hours at 100° no picramide was obtained.

Dinitrobrombenzol and Water.

Gottlieb* has stated that trinitrochlorbenzol was decomposed in the cold by water. It was afterwards found by Clemm† that this was not the case, trinitrochlorbenzol not being acted on by water even when boiling. Later, however, Engelhardt and Latschinoff‡ found it was acted on by boiling water.

With dinitrobrombenzol I found no action on boiling with water. The substance was then heated with water in closed tubes successively at 100°, 150°, and 200°, for eight hours, in all these tubes there was no pressure or formation of bromhydric acid. At 220° a minute trace of bromhydric acid had formed, and the liquid was perceptibly reddened on addition of sodium hydrate solution. After heating at this temperature the substance remained liquid for several days, although when it had solidified, it was found to have lost none of its characteristic properties.

Dinitrobrombenzol and Potassium Nitrite.

It appeared not impossible from the ease with which the bromine atom in dinitrobrombenzol can be substituted (although this is chiefly the case in substitution by a positive radical), that by action of potassium nitrite a trinitrobenzol might be formed. The substances were heated in a closed tube six hours with dilute alcohol at 100°. The tube on cooling contained massive red needles of potassium dinitrophenylate. Much aldehyde had also formed. The reaction had probably been—

* Ann. Chem. Pharm., xcii, 326.

† Journ. fr. pr. Chem., [2], i, 145.

‡ Zeit. Chem., 1870, 235.

The resulting nitrogen oxide, or oxides, had acted on the alcohol and produced aldehyde. Sealed under the same conditions with 99 per cent alcohol, there was but an exceedingly slight reaction, only traces of the phenol having been formed, which doubtless owed their origin to the small amount of water present. The same results were obtained with sodium nitrite. I shall describe the application of this method of phenol formation to other compounds at another opportunity.

Dinitrobrombenzol, Benzol, and Zinc.

Since benzylchloride treated with benzol and zinc dust gives a benzylbenzol, it seemed not improbable that dinitrobrombenzol might give a dinitrodiphenyl, owing to the weakened attraction of the bromine atom from the presence of the nitro-group, although in this case the bromine atom is attached directly to the benzol skeleton, and not indirectly, as in the benzylchloride.

Dinitrobrombenzol, benzol, and zinc dust were heated twelve hours in a closed tube at 100°, and then again at 160°. In both cases there was no action. Toluol instead of benzol also remained unchanged. Perhaps nitro toluol, in which the hydrogen atom of the methyl-group may be weakened by the introduction of the nitro-group in the benzol kernel, may give better results.

Dinitrobrombenzol and Sodium Acetate.

Wishing to ascertain if a dinitrophenyl acetic ester could be obtained according the reaction

I heated the substances with alcohol for six hours in a closed tube at 100°. There was no pressure on opening the tube, but a strong smell of acetic ether. The tube contained orange-red crystals of sodium dinitrophenylate, and in the solution there was considerable sodium bromide. The reaction had probably gone.

So that the whole reaction would be—

The next time, to avoid the formation of acetic ether, the substances were heated with glacial acetic acid at 160° . The whole product was sodium dinitrophenylate. Hence probably,

although at the time I neglected to prove the formation of the acetic anhydride. The substances heated, under the same conditions with acetic anhydride, remained entirely unchanged.

We see hence that although the stability of the bromine atom is greatly weakened by the introduction of nitro-groups, this weakening is to a great extent only in relation to positive radicals. Thus dinitrobrombenzol reacts easily with ammonia, but with potassium nitrite or sodium acetate there is no analogous reaction. By inversion it naturally follows that in aniline the amido-group must be rendered much more stable by the introduction of nitro-groups. This is shown to be so by the fact that while aniline is most violently acted on by amyl nitrite, trinitroaniline remains, under the same treatment, utterly unaffected.