CXXXVII.—*The Action of Amines on Trinitrophenylmethylnitroamine.*By THOMAS CAMPBELL JAMES, JAMES IVOR MORGAN JONES, and
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It is a well-known property of polynitro-aromatic compounds that they form additive derivatives with various types of aromatic substances, such as hydrocarbons, phenols, amines, etc. The most recent work on these derivatives has been carried out by Sudborough and his collaborators, who have examined in detail the formation and properties of a large series of the additive compounds formed by *s*-trinitrobenzene. In a review of the compounds prepared by them, Sudborough and Beard (T., 1910, **97**, 773) were led to suggest a possible formula for the compound of trinitrobenzene with aniline, representing it as possessing a hemi-quinonoid structure:

The present investigation was undertaken with a view to ascertain whether trinitrophenylmethylnitroamine (tetryl) forms additive compounds of a similar type to *s*-trinitrobenzene. It was observed that solutions of this substance in a variety of solvents became deeply coloured on the addition of any amine, primary, secondary, or tertiary, except in such cases where the amine contains strongly negative radicles, and in a large number of cases it has been possible to isolate from these solutions definite crystalline compounds, which are, without exception, compounds of tetryl and the base, united in equimolecular proportions. Owing to the fact that the additive compounds are largely dissociated in solution, the separation of the pure product is difficult in cases where the constituents are less readily soluble than the additive product.

The general conclusions drawn by Sudborough and Beard (*loc. cit.*) regarding stability and depth of colour have been confirmed, although the stability of this series of compounds is, on the whole, less than that of the corresponding compounds of the trinitrobenzene series. Thus, additive compounds of tetryl with phenols and tertiary amines have not been isolated in a pure state, although evidence of their formation is afforded by the production of a red colour when solutions of the components are mixed, and also, in

some cases, by an investigation of the melting points of mixtures of the components. Hydrocarbons and nitrophenols do not yield additive products.

The chief point of difference between the additive compounds under consideration and those of the trinitrobenzene series is that, in many cases, like the additive compounds of picryl chloride with bases, described by Sudborough and Picton (T., 1906, **89**, 583), they readily undergo a change to a condensed compound; thus, the compound of trinitrophenylmethylnitroamine and aniline, on storing in a sealed tube or on slow crystallisation from a hot solvent, yields 2:4:6-trinitrodiphenylamine, condensation apparently occurring according to the equation

We have not succeeded in isolating the methylnitroamine, despite various attempts, and it is probably decomposed during the condensation. The products are identical with those formed by the action of picryl chloride on the amine, and in a number of cases exist in two or more modifications differing in crystalline form and colour (compare Sudborough and Picton, *loc. cit.*; Busch and Pungs, *J. pr. Chem.*, 1909, [ii], **79**, 546; Hantzsch, *Ber.*, 1910, **43**, 1678). It is of interest to note, however, that the first product is generally of a red colour, whilst yellow or orange modifications are obtained by the use of picryl chloride, this being due to the presence of hydrogen chloride, which is instrumental in converting red forms into yellow.

Molecular-weight determinations of the additive compounds indicate that, notwithstanding the development of deep colour in the solutions, dissociation into the components is almost complete in dilute solution.

EXPERIMENTAL.

The method of work consisted, in general, in allowing a cold saturated solution of tetryl in alcohol, acetone, or benzene, and treated with rather more than one molecular proportion of the amine in the same solvent or in ether, to remain until crystallisation took place. In many cases, crystals of the additive compound were deposited with ease; in others, condensation took place, and the picryl derivative was obtained as first product. When the mixed solutions were heated for some time on a water-bath or when the crystallisation was prolonged by leaving the solvent to evaporate slowly on a hot plate, the condensation compound was usually deposited.

Ammonia.—The addition of an alcoholic solution of ammonia (one and two equivalents, respectively, were used in different

experiments) to a saturated alcoholic solution of tetryl yielded a deep red solution of an additive compound, which it was not possible to isolate. The deep colour gradually disappeared on warming, and from the resulting yellow solution, picramide (m. p. 188°), in a yield corresponding with 53 per cent. of the theoretical, crystallised out. The filtrate, on evaporation, provided a further yield of crystals, which proved to be ammonium picrate.

When dry ammonia was passed into a solution of tetryl in benzene, little action took place, but on the addition of a small amount of acetone, a deep red solution was produced, from which a fluorescent, green oil separated. This solidified, on keeping, to a deep green mass, which, when freshly prepared, had a strong odour of ammonia. It is soluble in water or alcohol, giving orange-coloured solutions, but it has not been obtained in good crystalline form, and the melting point is indefinite, the substance decomposing explosively on heating above 100° . After excess of ammonia is removed, the substance contains C=34.19, H=3.61, and N=24.97 per cent., corresponding with the formula $C_{10}H_{12}O_8N_6$.

Methylamine.—When treated with an alcoholic solution of methylamine, tetryl gives a deep red-coloured solution, which, after slight warming, deposits reddish-brown needles (m. p. 112°) consisting of 2:4:6-trinitromethylaniline (Romburgh, *Rec. trav. chim.*, 1883, **2**, 105). On recrystallising from alcohol containing a small proportion of acid, pure, yellow needles melting at 114.8° are obtained (Found: N=23.45. Calc.: N=23.09 per cent.).

Benzylamine.—This yields 2:4:6-trinitrophenylbenzylamine, consisting of chocolate-coloured needles (m. p. 143.3°), which, when crystallised from alcohol containing a little acid, becomes golden-yellow and melts at 144.8° (Found: N=17.70. $C_{13}H_{10}O_6N_4$ requires N=17.61 per cent.).

Aniline.—The additive compound of tetryl with aniline was readily obtained from benzene solution, and forms orange-red plates melting at 64° (Found: N=21.35. $C_{13}H_{12}O_8N_6$ requires N=22.11 per cent.).

The substance decomposes on keeping in the air, by treatment with acids, and by treatment with many solvents, regenerating tetryl (0.5425 treated with acid gave 0.4064 tetryl, =74.91. Calc.: tetryl=75.48 per cent.).

On keeping in a sealed tube for several weeks, the substance became moist, and the product on crystallisation proved to be 2:4:6-trinitrodiphenylamine. This substance is also obtained by slow crystallisation of the original mixture from warm benzene, acetone, or alcohol solutions. It forms orange crystals melting at

178°, corresponding with the description of Bamberger and Müller (*Ber.*, 1900, **33**, 188).

o-Toluidine.—An additive compound with tetryl is readily obtained by adding a slight excess of the base to a hot solution of tetryl in benzene solution, and allowing to crystallise. It consists of brick-red crystals melting at 63° (Found: N=21.18; tetryl=72.7. $C_{14}H_{14}O_8N_6$ requires N=21.32; tetryl=72.8 per cent.).

The substance decomposes on exposure to the atmosphere and also on recrystallisation, yielding tetryl. It does not, however, yield a condensation product, and 2:4:6-trinitrophenyl-*o*-tolylamine is not formed, even when the mixture of components is boiled for forty-eight hours in a reflux apparatus using various solvents.

m-Toluidine.—The additive compound in this case has not been obtained in a pure form, as it is rapidly changed, even at the ordinary temperature, to a condensed derivative. The product obtained from a mixture of the components in benzene solution consists of deep red needles melting at about 80°, which on treatment with acid regenerate tetryl. On warming this product with benzene or with a mixture of chloroform and light petroleum and allowing to crystallise, bright scarlet needles are deposited which melt at 118.5° (Found: N=17.37. $C_{13}H_{10}O_6N_4$ requires N=17.73 per cent.).

This substance, when first prepared, could be recrystallised from alcohol without change, but on the addition of a drop of acid to a saturated solution in alcohol, orange-yellow, prismatic crystals separated. These melt at 129° and correspond with 2:4:6-trinitrophenyl-*m*-tolylamine, as described by Busch and Pungs (*J. pr. Chem.*, 1909, [ii], **79**, 550). These authors state that the substance occurs in two forms, an orange modification (m. p. 129.5°) and a pure yellow form (m. p. 130°). The forms obtained by us are readily soluble in alkali hydroxide, yielding deep red solutions, which, on acidifying, yield a pure yellow form melting at 129°. We have been unable, so far, to reconvert the stable yellow form into the labile scarlet form melting at 118.5°.

p-Toluidine.—In the case of this amine, an additive compound with trinitrophenylmethylnitroamine is readily obtained by crystallising a mixture of the components from benzene or alcohol. It consists of deep red needles melting at 54°, which are readily decomposed by acids, regenerating tetryl (Found: N=20.82; tetryl=72.1. $C_{14}H_{14}O_8N_6$ requires N=21.32; tetryl=72.8 per cent.).

The condensation compound, 2:4:6-trinitrophenyl-*p*-tolylamine, was obtained in the manner described above, and was isolated in

the two forms described by Busch and Pungs (*loc. cit.*, p. 548) as orange-yellow needles (m. p. 163—164°) and blood-red prisms (m. p. 165°).

m-Xylidine.—This base yields with tetryl a very unstable additive compound, which undergoes condensation very readily to form 2:4:6-trinitrophenyl-*m*-xylidine,

this crystallises in orange-yellow needles melting at 157° (Found: N=17.11. $\text{C}_{14}\text{H}_{12}\text{O}_6\text{N}_4$ requires N=16.86 per cent.).

o-Anisidine.—We were unable to isolate an additive compound in this case, although the colour of the solution indicated that such a compound is formed. From a warm solution in alcohol, red crystals of 2':4':6'-trinitro-2-methoxydiphenylamine separated, melting at 143° (Busch and Pungs, *loc. cit.*, p. 552, give 142°).

p-Anisidine.—In this case, again, no additive compound was isolated, for 2':4':6'-trinitro-4-methoxydiphenylamine was obtained even when cold solutions of the components were mixed. This consists of orange-red needles melting at 172.5° (Found: N=16.75. Calc.: N=16.77 per cent.).

Busch and Pungs (*loc. cit.*, p. 552) describe this compound as melting at 138°. We have repeated their preparation of the substance from picryl chloride and *p*-anisidine, and find that the product melts at 172.5°, as given above.

p-Aminophenol.—The additive compound in this case has not been obtained pure, and readily passes into the condensed derivative, 2':4':6'-trinitro-4-hydroxydiphenylamine, which consists of brick-red needles melting at 174° (Turpin, T., 1891, **59**, 718).

α-Naphthylamine.—The additive compound of this base is readily obtained by crystallising a mixture of the components in equivalent amounts from benzene. It consists of well-defined black prisms melting at 94°. The compound is of considerably greater stability than the additive compounds previously described, but is partly decomposed by crystallisation from many solvents, and completely by warming with acids (Found: N=19.73; tetryl=66.46. $\text{C}_{17}\text{H}_{14}\text{O}_8\text{N}_6$ requires N=19.53; tetryl=66.73 per cent.).

No condensation product is formed, even after prolonged boiling of the additive compound or of a mixture of the components in a variety of solvents.

β-Naphthylamine.—The additive compound is similar to the above, and is obtained in black prisms melting at 90° (Found: N=19.72. $\text{C}_{17}\text{H}_{14}\text{O}_8\text{N}_6$ requires N=19.53 per cent.).

The compound is fairly stable and does not yield a condensed derivative.

m-Phenylenediamine.—The additive compound of this base is readily obtained by crystallisation from benzene solution, and consists of silky, brown needles melting at 84° , which are moderately stable, but are partly decomposed by recrystallisation and completely by warming with acids (Found: N=24.94. $C_{13}H_{13}O_8N_7$ requires N=24.81 per cent.).

The condensation compound, 2:4:6-trinitro-*m*-aminodiphenylamine, is obtained by slow crystallisation from hot acetone, and forms a deep red, crystalline powder melting at 207° (compare Jaubert, *Ber.*, 1898, **31**, 1182).

Methylaniline.—This base yields an additive compound with trinitrophenylmethylnitroamine, which consists of deep red plates melting at 86° (Found: N=21.86. $C_{14}H_{14}O_8N_6$ requires N=21.32 per cent.).

The condensation compound has not been obtained by our general method.

Dimethylaniline, ethylaniline, and diethylaniline all yield deeply coloured solutions when mixed with solutions of tetryl, but pure additive compounds have not yet been obtained in these cases. Moreover, condensation to picryl derivatives does not occur even after prolonged boiling in alcohol or acetone solutions.

Similarly, *m*-nitroaniline and *p*-nitroaniline yield slightly coloured solutions with tetryl, but the separation of pure additive compounds has not been achieved. An investigation of the freezing-point curves of mixtures of these bases with tetryl indicates that unstable molecular compounds can exist.

Halogen-substituted amines give only feeble colorations with solutions of tetryl, and form no additive compounds; condensation is also not possible.

Summary and Conclusion.

Trinitrophenylmethylnitroamine (tetryl) readily forms equimolecular additive compounds with the simpler amines, which in many cases readily condense to form picrylamines. The presence of alkyl substituents in the ortho-position in the amine does not affect the formation of the additive compound, but inhibits the condensation. The presence of the methoxy-group in the ortho-position does not, however, prevent the condensation (compare *o*-toluidine and *o*-anisidine). On the other hand, substitution in the meta-position renders the molecular compound unstable, and it readily passes into the corresponding picrylamine. The naphthylamines and the secondary amines yield stable additive

compounds, which do not pass into condensation derivatives (compare Sudborough and Picton, *loc. cit.*, p. 589).

According to Werner, the components of molecular compounds

Freezing-point curves of tetryl-*m*-nitroaniline (I) and tetryl-*p*-nitroaniline mixtures (II).

of this type are to be represented as united by the residual or auxiliary valencies of the nitro- and amino-groups (I):

(I.)

(II.)

It may be pointed out, however, that a representation in accordance with Sudborough and Beard's suggestion (p. 1273) brings the nitroamine group into close proximity with the amino-group. If the amine be represented as possessing a hemi-quinonoid structure, the intense colour of the molecular compounds and the comparative stability of the derivatives of secondary amines may also be explained. Thus the molecular compound with methylaniline might be represented as (II).

The influence of substituents in the phenyl group of the amine on the ease with which condensation can take place is not obvious in a formula of this type, whereas in the case of the Werner formula such substituents may be represented as modifying the amount of residual valency, whereby the amine is attached to the nitro-group.

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