| Huygens Institute - Royal Netherlands Academy of Arts and Sciences (KNAW) |
|--|
| |
| Citation: |
| Romburgh, P. van, Additive compounds of m.Dinitrobenzene, in: KNAW, Proceedings, 14 I, 1911, Amsterdam, 1911, pp. 46-47 |
| |
| |
| |
| |
| |
| |
| |
| |
| |
| |
| |
| |
| |
| |
| |
| |
| This PDF was made on 24 September 2010, from the 'Digital Library' of the Dutch History of Science Web Center (www.dwc.knaw.nl) > 'Digital Library > Proceedings of the Royal Netherlands Academy of Arts and Sciences (KNAW), http://www.digitallibrary.nl' |
| |
| |
| |
| |

"amide d'un acide oxalylbiurétique" prepared by Grimaux which in the German literature is wrongly called oxalyldiureïd. The oxalyldiureïd obtained by me not only shows complete insolubility in all the ordinary solvents, but also gives no biuret reaction.

Symmetric dimethylurea whether in ether at the ordinary temperature or in boiling benzene gave the well-known cholestrophane, whereas with asymmetric dimethylurea, when boiled in benzene, carbonyl-

di-(as. dimethylurea) CO $(CH_3)_2$. $^1/_2$ H $_2$ O is obtained in parti-NH CO N $(CH_3)_2$

cularly beautifully formed prismatic crystals melting at 140° C.

Chemistry. — "Additive compounds of m. Dinitrobenzene." By Prof. P. van Romburgh.

(Communicated in the meeting of April 28, 1911).

The increased interest taken in the coloured compounds of polynitrosubstances with aromatic amines induces me to call attention again to the fact that m. dinitrobenzene is also capable of yielding with different amines beautifully coloured crystallised compounds as I mentioned casually many years ago 1).

Generally speaking, these compounds are obtained less readily, and many are less stable than those of s. trinitrobenzene. This probably explains why Noelting and Sommernoff?) have not succeeded in isolating such products. Kremann 3) has studied the equilibrium between aniline and m. dinitrobenzene and states that no data occur in the literature as to the existence of a compound between these substances although I had already mentioned having isolated the same.

If we dissolve m. dinitrobenzene in aniline the liquid turns intensely red on warming and when cold, a beautiful red compound crystallises in large crystals, which melt at 41°—42° (in a capillary tube). According to Kremann the melting point lies at 40°. The compound consists of an equal number of molecules of the components. On exposure to the air, the crystals lose the aniline.

Analysis: Found 64.1°/₀ C₀H₄(NO₂)₂. Calculated 64.3°/₀.

Dimethyl p. toluidine when heated with m. dinitrobenzene gives an intensely coloured solution from which, on cooling, crystallises a

¹⁾ R. 6, 366 (1887).

²) B. 39. 76 (1906).

³⁾ M. 25, 1298 (1904).

nearly black compound m.p. 43°, which in an open vessel is completely decomposed in a few days.

Analysis: Found $55.07^{\circ}/_{\circ}$ C₆H₁(NO₂)₂.

Theory for 1 mol. $C_0H_4(NO_2)_2 + 1$ mol. $C_7H_7N(CH_8)_2$ 55.4%.

With α -naphthylamine in alcoholic solution in dinitrobenzene forms a compound crystallising in red needles m. p. 67°. Nitrogen determination: Found $13.47^{\circ}/_{\circ}$. Calculated for equal molecules $13.5^{\circ}/_{\circ}$.

Dimethyl- β -naphtylamine in alcoholic solution also gives dark red needles of a compound consisting of equal mols. of the components and melting at 52° — 53° .

Nitrogen determination: Found: 12.62°/₀ N. Calculated: 12.39°/₀. Tetramethylmetaphenylenediamine ¹) forms with m. dinitrobenzene — but less readily so in alcoholic solution — a very dark garnet red compound melting at 58°.

Analysis: Found 50.1 $^{\circ}$ / $_{0}$ C $_{6}$ H $_{4}$ (NO $_{2}$) $_{2}$. Calculated for 1 mol. C $_{6}$ H $_{4}$ (NO $_{2}$) $_{2}$ + 1 mol. C $_{6}$ H $_{4}$ N $_{2}$ (CH $_{3}$) $_{4}$ 50.6 $^{\circ}$ / $_{0}$.

With benzidine metadinitrobenzene gives black crystals, which are fairly stable, but are decomposed by hydrochloric acid. The melting point is 128°.

Analysis: Found $47.6^{\circ}/_{0}$ C₀H₄(NO₂)₂. Calculated for equal molecules $47.73^{\circ}/_{0}$.

With tetramethylbenzidine in alcoholic solution only a small quantity of a dark coloured compound is obtained; the bulk of the components crystallise separately.

On the other hand 4.4' tetramethyldiaminodiphenylmethane ') gives a fine garnet red compound crystallising in plates or compact crystals m. p. 76° and containing 2 mols. of the amine for 1 mol. of dinitrobenzene.

Analysis: Found $25.2^{\circ}/_{\circ}$, $25^{\circ}/_{\circ}$ $C_{\circ}H_{4}(NO_{2})_{2}$. Calculated $24.85^{\circ}/_{\circ}$.

4.4'. Tetramethyldiaminobenzophenone in alcoholic solution gives very beautiful, clear red plates m. p. 91°. In this compound, however two mols. of dinitrobenzene are present for 1 mol. of the base.

Analysis: Found 55.4°/₀ C₀H₄(NO₂)₂. Calculated 55.6°/₀.

With many other liquid aromatic amines m. dinitrobenzene gives strongly coloured solutions; with numerous solid amines, in alcoholic solution, a more or less powerful coloration is obtained also. Very probably, it will appear possible to isolate a number of these additive products in the solid condition.

Utrecht.

Org. Chem. Lab. University.

¹⁾ R. 7, 3 (1888).

²) R. 7, 228 (1888).