

CCLXIV.—2 : 3 : 4-*Trinitrotoluene*.

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THE purification of crude trinitrotoluene is sometimes effected by washing with cold alcohol, and on evaporation of the solvent the "trinitrotoluene residues," constituting about 10% of the original material, are obtained. The present authors have found that if the brown, pasty mass is melted and then allowed to crystallise at 18—20° after inoculation, a mixture of 2 : 4-dinitrotoluene and β -trinitrotoluene separates first and that only after 6 or 7 days is the product contaminated with the α - or the γ -isomeride. By crystallisation from sulphuric acid, the solid product yields β -trinitrotoluene in a satisfactory state of purity. A considerable number of derivatives of the substance have been obtained, but the work was carried out in special circumstances in 1917 and 1918 and we have been anticipated in several directions.

EXPERIMENTAL.

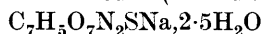
Preparation of β -Trinitrotoluene.—The residues (23,810 g., 21,718 g.) were melted and treated with about 10 g. of the mixture of 2 : 4-dinitrotoluene and β -trinitrotoluene obtained from a previous experiment. After a suitable interval (7 days, 5 days) the solid (6810 g., 7323 g.) was separated in a centrifuge and heated at 80—100° with concentrated sulphuric acid (3 parts). The crystals which separated on cooling, after being washed with sulphuric acid and with water and dried, melted at 108° (yield 12.3%, 13.5% of the original residue). On recrystallisation the highest m. p. observed was 112°.

If the mixture is stirred, the period required is much shortened. Residues (500 g.) stirred at 18° for 7.5 hours gave 87 g. of a solid which yielded 58 g. (11.6 % of the original residues) of β -trinitro-

toluene. We are informed that stirring is impracticable in large-scale work and the yield which can be regularly obtained is 6—7%.

A complete examination of the residues was made by taking advantage of the fact that in regard to solubility in sulphuric acid γ -trinitrotoluene is intermediate between the very sparingly soluble β -isomeride and the readily soluble dinitrotoluenes. The quantities actually isolated from 100 g. were : 2 : 4-dinitrotoluene, 47.7 g.; β -trinitrotoluene, 12.3 g.; γ -trinitrotoluene, 16.9 g. The 23 g. unaccounted for were shown to contain dinitrotoluenes and α -, β -, and γ -trinitrotoluenes. The content of β -trinitrotoluene in the residues cannot be less than 15%, nor that of γ -trinitrotoluene less than 20%.

Sodium m-Tolylenediamine-3-sulphonate, $C_6H_2Me(NH_2)_2 \cdot SO_3Na$.—The solution obtained by agitating 2 : 3 : 4-trinitrotoluene (50 g.), crystallised sodium sulphite (63.5 g.), and water (100 c.c.) at 75° was cooled; sodium 2 : 4-dinitrotoluene-3-sulphonate (55 g.) separated, and a further quantity (10 g.) could be salted from the solution (yield 90%). The substance crystallised from dilute brine in large, light amber-coloured rhombohedra (Found : H_2O , 13.6.



requires H_2O , 13.7%). The anhydrous salt has been described by Brady, Hewetson, and Klein (J., 1924, 125, 2402). On being gently heated, a solution of the sulphonate containing sodium hydroxide developed an intense permanganate colour and crystals having a bright beetle-green iridescence were deposited.

The hydrated sulphonate (100 g.), dissolved in water containing 25 c.c. of hydrochloric acid (d 1.16), was gradually added to a vigorously stirred mixture of boiling water with an excess of iron powder. When a drop of the liquid produced a grey spot on filter-paper (about 1 hour), the bulk was made alkaline with sodium hydroxide, filtered hot, and concentrated under diminished pressure. The *sodium m-tolylenediamine-3-sulphonate* that separated on cooling (yield 65—70%) crystallised from a little water in lustrous plates and from 80% alcohol in pearly, hexagonal leaflets (Found : S, 14.2; Na, 10.3. $C_7H_9O_3N_2SNa$ requires S, 14.3; Na, 10.3%). The substance is very readily soluble in water and sparingly soluble in absolute alcohol. It discolours at 250° and decomposes at 264°.

As a component in the preparation of azo-dyes, this salt is of some interest. All the shades are redder than those produced by the isomeric 2 : 4-diaminotoluene-5-sulphonic acid. Sulphanilic acid \rightarrow *m*-tolylenediamine-3-sulphonic acid gives an orange-red, crystalline compound which dyes wool and silk in bright reddish-orange shades from an acid bath. Benzidine \rightarrow *m*-tolylenediamine-3-sulphonic acid (2 mols.) gives a brilliant red dyestuff, which is

substantive to cotton. This substance is a sensitive indicator (blue when acid), and other members of the series resemble it in this respect.

When a solution of the *m*-tolylenediamine-3-sulphonate was shaken with acetic anhydride, a *monoacetyl* derivative was obtained. The free acid crystallised well from water in white needles. A number of dyes were prepared from it by diazotisation, coupling, hydrolysis, further diazotisation and coupling. The *monobenzoyl* derivative, obtained by shaking together an aqueous solution of sodium tolylenediaminesulphonate (1 mol.) and benzoyl chloride (1 mol.), crystallised from water in colourless needles (Found in material dried at 110°: C, 55.2; H, 4.8. $C_{14}H_{14}O_4N_2S$ requires C, 54.9; H, 4.6%).

Sodium 2 : 4-Dinitro-3-sulphobenzoate.—Sodium 2 : 4-dinitrotoluene-3-sulphonate (49 g.) dissolved in water (2000 c.c.) was oxidised for 6 hours at 98° with potassium permanganate (60 g.) in presence of sodium carbonate (5 g.). The excess of permanganate having been destroyed, the solution was filtered, concentrated to 300 c.c., acidified (Congo-red), and the product salted out (39 g.). It crystallised from dilute brine in colourless needles, changing in contact with the solvent into large prisms which, air-dried, lost 7.8% at 130° (Found in material dried at 130°: S, 10.0; Na, 7.2. $C_7H_3O_9N_2SNa, 1.5H_2O$ requires H_2O , 7.9%. $C_7H_3O_9N_2SNa$ requires S, 10.2; Na, 7.3%). On being strongly heated, the substance deflagrates.

The corresponding diaminosulphobenzoic acid was employed as a component in the preparation of azo-compounds. The dye from tetrazotised benzidine was a little less sensitive to acids than the corresponding product from *m*-tolylenediamine-3-sulphonic acid.

2 : 3 : 4-Triaminotoluene.—2 : 4-Dinitro-*m*-toluidine (30 g.) (obtained in 90% yield from 2 : 3 : 4-trinitrotoluene by heating with alcoholic ammonia) dissolved in hot alcohol containing concentrated hydrochloric acid (5 c.c.) was gradually added to a well-stirred mixture of alcohol and iron powder. When the solution became almost colourless, the alcohol was distilled under diminished pressure and the residue was taken up in water and filtered. Ferrous hydroxide was then precipitated from the hot liquid by the addition of sodium hydroxide, sufficient water being employed to dissolve the base, and charcoal also was introduced. The filtrate was acidified with hydrochloric acid, concentrated under diminished pressure, and the hydrochloride salted out (yield 12.5 g.). It crystallised in hydrated, elongated, rhombic prisms. The free base crystallised from ether in colourless prisms, m. p. 106° (Found: C, 61.5; H, 8.0; N, 30.1. $C_7H_{11}N_3$ requires C, 61.3; H, 8.0; N, 30.7%). It is very readily soluble in water, alcohol, or benzene,

and its solutions give a violet coloration with ferric chloride. It is very readily oxidisable and gave good results as a photographic developer, requiring, however, the addition of sodium hydroxide.

Janovsky (*Monatsh.*, 1889, **10**, 591) obtained a triaminotoluene, which he considered to be the vicinally substituted compound, by reduction of trinitroazotoluene. The m. p. of the base was not given, but the trihydrochloride was analysed. The reactions, especially that with ferric chloride, quoted by Janovsky are not in very good agreement with those of the substance described above.

2 : 4-Dinitro-3-methoxytoluene was obtained by the action of methyl-alcoholic potassium hydroxide on 2 : 3 : 4-trinitrotoluene and also by the methylation of 2 : 4-dinitro-*m*-cresol, m. p. 100°, which was prepared from 2 : 3 : 4-trinitrotoluene in several different ways, none of which gave such good results as that described by Brady, Hewetson, and Klein (*loc. cit.*). The cresol derivative was also obtained in poor yield from 2 : 4-dinitro-*m*-toluidine, which in its turn yielded 2 : 4-dinitrotoluene on deamination. These relations establish the constitution of the dinitromethoxytoluene. The substance (see the following communication) crystallises from alcohol in leaflets, m. p. 86° (Found : C, 45.2; H, 3.8; N, 13.4. $C_8H_8O_5N_2$ requires C, 45.3; H, 3.8; N, 13.2%).

Condensation of β -Trinitrotoluene with Amines.—This subject has been investigated by Ryan and O'Riordan (*Proc. Roy. Irish Acad.*, 1918, **34**, 175) and by Brady, Hewetson, and Klein (*loc. cit.*). 2 : 6-Dinitro-3 : 4'-dimethyldiphenylamine, obtained from *p*-toluidine, softens at 147° and melts at 152° (Ryan and O'Riordan give m. p. 131°). 2 : 4-Dinitro-3-benzylaminotoluene, from β -trinitrotoluene and benzylamine, crystallised from ethyl acetate in yellow, rhombic tablets, m. p. 115—116° (Found : N, 14.5. $C_{14}H_{13}O_4N_3$ requires N, 14.6%). A similar compound obtained from dibenzylamine crystallised from alcohol in yellow, tetrahedral rods, m. p. 87—88°. 2 : 4-Dinitro-*m*-tolylpiperidine was obtained from β -trinitrotoluene and an excess of piperidine. In the case of strong secondary bases alcoholic solutions should not be employed, since there is a tendency to produce the alkyloxy-compounds. The substance separates from alcohol in yellow laminae, m. p. 101° (Found : N, 15.9. $C_{12}H_{15}O_4N_3$ requires N, 15.8%). 2 : 4-Dinitro-*m*-tolyl- α -naphthylamine crystallises from alcohol-ethyl acetate in rosettes of needles, m. p. 169—170° (decomp.) (Found : N, 13.1. $C_{17}H_{13}O_4N_3$ requires N, 13.0%). This substance gives an intense blue solution in sulphuric acid.