254. *Derivatives of 2 : 4 : 6-Trinitrotoluene : Monoreduction of Polynitro-compounds.*

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The reduction of 2 : 4 : 6-trinitrotoluene derivatives has been studied, and a method for monoreduction at the 4-position has been worked out. In this and other ways routes to new derivatives of this compound have been made available.

One of the commonest reduction products of 2 : 4 : 6-trinitrotoluene (T.N.T.) is 2 : 6-dinitro-*p*-toluidine (see Tiemann, *Ber.*, 1870, **3**, 218; Beilstein, *Ber.*, 1880, **13**, 243; Holleman and Boeseken, *Rec. Trav. chim.*, 1897, **16**, 425; Brand and Eisenmenger, *J. pr. Chem.*, 1913, **87**, 487; Körner and Contardi, *Gazzetta*, 1917, **47**, i, 228; Brady, Day, and Reynolds, *J.*, 1929, 2264; McGookin, Swift, and Tittenson, *J. Soc. Chem. Ind.*, 1940, **59**, 92). All these methods involve the use of ammonium hydrogen sulphide. The presence of a large amount of alkali has an adverse effect by producing coloured complexes with T.N.T. and by interfering with intermediate reduction products. Further, poly-component systems of molecular compounds may be formed which, along with the impurities normally resulting from organic reactions, make isolation of products difficult. Also, most of the methods given involve heterogeneous mixtures.

The function of the base may be catalytic and, if so, only a trace should be necessary. As

T.N.T. is extremely soluble in dioxan the use of this solvent was tried along with only a trace of ammonia, and it was then found that reduction with comparatively crude hydrogen sulphide took place smoothly with deposition of sulphur and a good yield of 2 : 6-dinitro-*p*-toluidine was obtained.

By this means 2 : 6-dinitrotoluene is made much more readily accessible, and many other derivatives can be obtained by diazotisation; *e.g.*, 4-iodo-2 : 6-dinitrotoluene was prepared in quantitative yield. The method has been found to be adequate for 2 : 4 : 6-trinitrophenyl compounds and it can also be applied to such substances as 2 : 4-dinitrotoluene and 2 : 4-dinitrostilbene. A mixture of 2 : 4- and 2 : 6-dinitrotoluene (Gibson, Duckham, and Fairbairn, *J.*, 1922, **121**, 270) gave 2-nitro-*p*-toluidine, the 2 : 6-isomer being unaffected. This provides another route to 2 : 6-dinitrotoluene.

6-Nitro-2 : 4-diaminotoluene (Tiemann, *loc. cit.*; Ruggli and Zaeslin, *Helv. Chim. Acta*, 1936, **19**, 434; Brady, Day, and Reynolds, *loc. cit.*) has been monoacetylated in good yield by means of acetic anhydride in acetone, diazotisation and deamination giving 2-nitro-*p*-toluidine. A series of nitro-amines may thus be obtained from T.N.T.

EXPERIMENTAL.

2 : 6-*Dinitro*-p-*toluidine*.—T.N.T. (100 g.) was dissolved in dioxan (250 c.c.) and three drops of ammonia (*d* 0·88) were added with shaking. Hydrogen sulphide (from dilute hydrochloric acid and ferrous sulphide, washed with aqueous sodium hydrogen sulphide and dried over calcium chloride), was passed in at a moderate rate. Reaction set in after 3—5 mins. (with gentle warming, if necessary), the temperature being kept below 40°. Monoclinic sulphur was precipitated and the hydrogen sulphide stream was continued until the temperature fell. A further three drops of ammonia were added, and the procedure repeated. Sulphur (39 g.) was filtered off and washed with dioxan and ether; 3 drops of concentrated hydrochloric acid were added to filtrate and washings, and the solvent was removed by distillation under reduced pressure from a water-bath. The residual solid was powdered and dried (90 g., 100%). It contained a trace of T.N.T. as shown by Janovsky's test. This was used for diazotisation without purification. Isolation could also be achieved as hydrochloride by passing dry hydrogen chloride into the dioxan solution, 50—60% of almost pure hydrochloride being obtained; m. p. 172° (acetyl derivative, m. p. 221·5°) (Found: C, 45·2; H, 3·65. Calc. for $C_9H_9O_5N_3$: C, 45·2; H, 3·76%).

4-*Chloro- and* 4-*Iodo*-2 : 6-*dinitrotoluene*.—2 : 6-Dinitro-*p*-toluidine hydrochloride (47 g.; 0·2 mol.) was finely powdered and suspended in concentrated hydrochloric acid (500 c.c.). A saturated aqueous solution of sodium nitrite (16 g.) was added at 0°. After one hour a cloudy solution was formed. Three-fourths of this solution was added with stirring to a cold solution of cuprous chloride (10 g.) in concentrated hydrochloric acid (100 c.c.) and one-fourth to a cold solution of potassium iodide (20 g.) in water (100 c.c.). The respective halides floated to the top of the solution and were filtered off, washed, and dried; yields were 15 g. (0·05 mol.) of 4-iodo-2 : 6-dinitrotoluene and 33 g. (0·15 mol.) of chloro-compound. The latter, crystallised from alcohol, had m. p. 76° (Cohen and McCandlish, *J.*, 1905, **87**, 1265).

6-*Nitro*-2 : 4-*diaminotoluene*.—Ruggli and Zaeslin's method (*loc. cit.*) was found satisfactory: yield, 78%, m. p. 129° after distillation in a vacuum and repeated recrystallisation from water (Ruggli and Zaeslin give 135°).

2-*Nitro*-6-*acetamido*-p-*toluidine*.—(*a*) 6-Nitro-2 : 4-diaminotoluene (5 g.) was finely ground and cooled in ice–salt. Acetic anhydride (3·05 g., 1 mol.) was added dropwise with stirring. A viscous mass was formed which then solidified. It was finely ground and extracted once with toluene (charcoal). From the toluene the *acetyl* compound was obtained as an orange solid, m. p. 155°, after several recrystallisations (Found: C, 51·7; H, 5·25. $C_9H_{11}O_3N_3$ requires C, 51·7; H, 5·20%). The portion soluble in toluene was extracted with alcohol to yield white fluffy needles of the *diacetamido*-compound, m. p. 265° (Found: C, 50·6; H, 5·2. $C_{11}H_{13}O_3N_3$ requires C, 50·6; H, 5·4%). A small amount of starting material was obtained from the mother-liquor.

(*b*) 6-Nitro-2 : 4-diaminotoluene (5 g.) was vigorously shaken with 2N-sodium hydroxide (20 c.c.) and ice (20 g.). Acetic anhydride (3·05 g.) was added slowly with shaking. The product was repeatedly recrystallised from toluene and from 80% alcohol to give poor yields of the monoacetyl derivative.

(*c*) 6-Nitro-2 : 4-diaminotoluene (5 g.) was dissolved in dried and distilled acetone. Acetic anhydride (3·05 g.) in similar acetone (10 c.c.) was slowly added with stirring. After 30 mins. at room temperature the solvent was removed on the water-bath, yielding the monoacetyl compound as a solid (5·3 g.). This was pure after one crystallisation from 80% alcohol or toluene (4·9 g., 92%).

(*d*) 6-Nitro-2 : 4-diaminotoluene (5 g.) was heated on a water-bath in 25 c.c. of acetic acid for 60 mins. The acetic acid was removed at room temperature over sodium hydroxide. An intractable gum was obtained.

6-*Nitro*-o-*toluidine*.—2-Nitro-6-acetamido-*p*-toluidine (2 g.) was shaken with concentrated hydrochloric acid (15 c.c.) and ethyl acetate (1 c.c.). The suspension was cooled to 0° and the theoretical amount of saturated aqueous sodium nitrite added gradually with stirring. After 30 mins. the solution was slowly poured into alcohol (20 c.c.) boiling on a water-bath. When evolution of nitrogen and acetaldehyde ceased the solution was evaporated in a vacuum over sodium hydroxide. The tar produced was extracted with hot 2N-hydrochloric acid (charcoal) and precipitated with ammonia. Yellow-orange 6-nitro-*o*-toluidine was filtered off (0·8 g., 54%) and crystallised from 30% acetic acid; m. p. 90°. It was identical with an authentic specimen (Bernthsen, *Ber.*, 1882, **15**, 3017; Green and Lawson, *J.*, 1891, **59**, 1013). Its acetyl derivative had m. p. 156° after crystallisation from aqueous alcohol.

2 : 6-*Dinitro*-4-*aminostilbene*.—2 : 4 : 6-Trinitrostilbene (7 g.) (Bishop and Brady, *loc. cit.*) in dioxan (50 c.c.) plus one drop of aqueous ammonia (*d* 0·880) was treated with hydrogen sulphide as in the reduction of 2 : 6-dinitro-*p*-toluidine. Sulphur (1·8 g.) was filtered off. Removal of solvent at 50° in a vacuum gave a hard red gum which resisted purification. The product was isolated as hydrochloride by precipitation with dry hydrogen chloride. The yellow precipitate was filtered off after standing overnight and washed with dioxan and dry ether; m. p. 173° (decomp.) (2·6 g.). More hydrochloride was obtained by leaving the filtrate in a vacuum over concentrated sulphuric acid for 36 hours. The hydrochloride was shaken with ether–dilute aqueous ammonia until it had dissolved. The ethereal layer was dried, and solvent removed to give orange needles (4·5 g., 70%) of the 4-*amino*-compound, which were recrystallised from 80% alcohol; m. p. 157° (Found : C, 58·7; H, 4·05. $C_{14}H_{11}O_4N_3$ requires C, 58·9; H, 3·86%). The *acetyl* derivative formed pale yellow needles, m. p. 208·5°, from 80% alcohol (Found : C, 58·5; H, 4·1. $C_{16}H_{13}O_5N_3$ requires C, 58·6; H, 4·0%).

2 : 6-*Dinitrostilbene*.—2 : 6-Dinitro-4-aminostilbene (1 g.) was dissolved in hot acetic acid (10 c.c.) and added to concentrated sulphuric acid (10 c.c.) cooled in ice–salt. Dry, finely powdered sodium nitrite (0·3 g.) was added slowly at 0° with stirring. After two hours the deep orange solution was slowly added to alcohol (60 c.c.) boiling on a water-bath. When no more acetaldehyde came off the mixture was added to 400 c.c. of cold water. After standing overnight, the precipitate was filtered off and taken up in hot alcohol (5 c.c.), charcoal was added, and then water slowly. A tar came down, followed by yellow-orange needles. More charcoal was added, and the solution boiled and filtered. The yellow-orange needles obtained, recrystallised from aqueous alcohol (charcoal), had m. p. 111° (0·1 g., 12%) (Found : C, 62·0; H, 3·9; N, 10·7. Calc. for $C_{14}H_{10}O_4N_2$: C, 62·2; H, 3·7; N, 10·4%). Janovsky's test gave a delicate green colour as for 2 : 6-dinitrostilbene (Pfeiffer, *Ber.*, 1906, **39**, 1304; *Annalen*, 1916, **411**, 72).

Reduction of 2 : 4 : 6 : 3′-Tetranitrostilbene (5 g.) (Brady and Bishop, *loc. cit.*) by the method used for 2 : 4 : 6-trinitrostilbene gave sulphur (1 g. Calc. : 1·3 g.). Attempts to work up the mixture failed and no crystalline product was obtained.

Reduction of 2 : 4 : 6-*Trinitrobenzoic Acid* (*Org. Synth.*, **2**, 95).—2 : 4 : 6-Trinitrobenzoic acid (2 g.) was powdered, suspended in water (20 c.c.), and ammonia (*d* 0·880) added slowly with stirring until a permanent red colour formed and all acid dissolved. Hydrogen sulphide was passed in for one hour and the solution left overnight. Very finely divided sulphur was filtered off, and the filtrate shaken with ether. Concentrated hydrochloric acid was slowly added until the ethereal layer was a much deeper orange than the aqueous layer. The former layer gave an orange solid (1·4 g., m. p. 176—180°), and the latter gave ammonium chloride and a trace of red solid. The product was extremely soluble in water, alcohol, acetone, ethyl acetate, or dioxan, very slightly soluble in hot benzene, toluene, or chloroform, and insoluble in light petroleum (b. p. 80—100°). It could not be distilled or sublimed. After six precipitations from hot benzene (95%) and alcohol (5%) by light petroleum (b. p. 80—100°), a constant m. p. of 218° (decomp.) was obtained (Found : C, 35·5; H, 2·3. Calc. for $C_7H_5O_6N_3$: C, 37·0; H, 2·2%). An acetyl derivative of similar solubility properties was made; white plates, m. p. 220° (decomp.). On diazotisation and reaction with hot alcohol a white acidic solid, m. p. 203°, was obtained.

Reduction of 2-(2′ : 4′ : 6′-*Trinitrophenyl*)*ethanol by Hydrogen Sulphide*.—The ethanol (Vender, *Gazzetta*, 1915, **45**, ii, 97) (5 g.) in dioxan (25 c.c.) and one drop of aqueous ammonia (*d* 0·880) was reduced with hydrogen sulphide as was T.N.T. Sulphur (1·7 g.) was filtered off, and a white solid, m. p. 161—165° (3·7 g.), precipitated by dry hydrogen chloride. The white solid was treated with ether–dilute ammonia, and a yellow solid (3·2 g.) isolated from the ether. It was recrystallised from acetic acid and then from toluene, forming yellow fluffy needles of 2-(2′ : 6′-*dinitro*-4′-*aminophenyl*)*ethanol* (Found : C, 42·6; H, 4·1. $C_8H_9O_5N_3$ requires C, 42·5; H, 4·0%). The *diacetyl* derivative formed white plates, m. p. 139°, from aqueous alcohol (Found : C, 46·2; H, 4·3. $C_{12}H_{13}O_7N_3$ requires C, 46·3; H, 4·2%).

Reduction of 2-(2′ : 4′ : 6′-*Trinitrophenyl*)*ethyl Acetate by Hydrogen Sulphide*.—The acetate (2 g.) (Vender, *loc. cit.*) in dioxan (10 c.c.) and one drop of aqueous ammonia (*d* 0·880) was reduced with hydrogen sulphide as was T.N.T. The product was isolated as described for trinitrophenylethanol to give an orange solid (1·7 g., 94%), which crystallised from aqueous alcohol and then benzene as yellow needles, m. p. 116·5° (Found : C, 44·5; H, 4·0. $C_{10}H_{11}O_6N_3$ requires C, 44·4; H, 4·1%). Attempts to acetylate this 4′-*amino*-compound gave intractable gums.

2 : 4 : 6 : 2′ : 4′ : 6′-*Hexanitrodibenzyl*.—T.N.T. (5 g.) and sodium carbonate (5 g.) in water (150 c.c.) were heated on the water-bath and air was passed through the mixture for 5 hours. It was then cooled and centrifuged, and the solid (6 g.) was dried in a vacuum over concentrated sulphuric acid and extracted with benzene (Soxhlet). The residue, 2·4 g. of finely divided black solid, could not be purified and exploded on heating. The benzene extract was evaporated to 40 c.c. and then left in a vacuum over concentrated sulphuric acid. White needles were formed at the bottom of the solution and then T.N.T. on the walls of the dish. The white needles were separated (0·2 g., 4%) and recrystallised from toluene; m. p. 216—217° (decomp.). The residual benzene gave only T.N.T. on total evaporation.

Reduction of 2-(2′ : 4′ : 6′-*Trinitrostyryl*)*furan by Hydrogen Sulphide*.—The furan (Pastak, *Bull. Soc. chim.*, 1926, **39**, 72, 77) (5 g.) in dioxan (20 c.c.) was treated with hydrogen sulphide in the presence of a trace of ammonia; only slight reaction took place after 6 hours, yielding a trace of sulphur (0·1 g.). The experiment was repeated with a drop of 2N-sodium hydroxide instead of ammonia. No reaction took place, so a drop of aqueous ammonia (*d* 0·880) was added. The temperature immediately rose and was kept below 40° with cooling. When the temperature fell, sulphur was filtered off (1·5 g.). The filtrate was dissolved in ether (200 c.c.) and repeatedly shaken with water. The ether was removed, leaving a red gum, from which, by recrystallisation from aqueous alcohol, very unstable red needles were isolated, m. p. 133°, not identical with the starting material. The m. p. was found to have fallen substantially after the substance had been kept for an hour in a vacuum. Immediately after recrystallisation the red needles gave an olive-green colour with concentrated sulphuric acid. The substance could not be acetylated.

Colour reactions with alkali of derivatives of T.N.T. (*Janovsky's test*).

Colours observed when 10—20 mg. of the compound were dissolved in about 5 c.c. of solvent and one drop of alkali added. The colour was formed more quickly and was more intense with sodium hydroxide instead of aqueous ammonia.

	EtOH and NaOH.		COMe$_2$ and NaOH.	
Compound.	Cold.	Hot.	Cold.	Hot.
2 : 4-Dinitrotoluene	Blue	Deep red	Blue	Deep red
2 : 4-Dinitrostilbene	Green	Red-brown	Deep blue	Purple
T.N.T.	Red	Red	Red	Red
4-Chloro-2 : 6-dinitrotoluene	Red; blue fluorescence	Deep red	Pink	Magenta
4-Iodo-2 : 6-dinitrotoluene	Blue-violet	Black	—	—
2 : 4 : 6-Trinitrostilbene	Bright crimson	Deep red	Bright crimson	Deep red
2 : 4 : 6 : 3′-Tetranitrostilbene	Bright red	Deep red	Bright red	Deep red
Dinitroaminostilbene	Orange red	Deep red-brown	—	—
Acetyl derivative	Yellow	Yellow	Yellow	Orange-yellow
2 : 6-Dinitro-4-acetamidotoluene	Yellow	Yellow	Yellow	Orange-yellow
Dinitroaminophenylethanol	Green	Grey-green	Olive-green	Dark olive-green
Diacetyl derivative	Green	Green-yellow	Yellow	Yellow
Trinitrophenylethanol	Bright red	Deep red	Bright red	Deep red
Trinitrophenylethyl acetate	Bright red	Deep red	Bright red	Deep red
Dinitroaminophenylethyl acetate	Red	Deep red	—	—
Ammonium or sodium trinitrobenzoate	Red	Deep red	Red	Deep red
2 : 4 : 6-Trinitrobenzaldehyde	Red	Deep red	Red	Deep red
Anil of above	Red	Deep red	Red	Deep red
2-Furylidene-T.N.T.	Red	Deep red	Red	Deep red

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