326. *Derivatives of* 2 : 4 : 6-*Trinitrotoluene:* (a) *the Nitration of Polynitrostilbenes,* (b) 2-(2 : 4 : 6-*Trinitrophenyl*)*ethyl Alkyl* (*Aryl*) *Sulphides.*

By Frederick Challenger and Peter H. Clapham.

The nitration of 2 : 4 : 6-tri- and 2 : 4 : 6 : 2′-tetranitrostilbene gives 2 : 4 : 6 : 2′ : 4′-pentanitrobenzil. In the case of the 2 : 4 : 6-derivative, 2 : 4-dinitro- and 2 : 4 : 6-trinitro-benzoic acid are also formed. The pentanitrobenzil is also obtained from 2 : 4 : 6 : 2′ : 4′-pentanitrostilbene under similar conditions. 2-(2 : 4 : 6-Trinitrophenyl)ethanol yields the chloride, and this with the sodium derivative of the appropriate thiol gives methyl and *p*-tolyl 2-(2 : 4 : 6-trinitrophenyl)ethyl sulphide and thence the sulphones. The chloride forms quaternary salts with pyridine and quinoline.

When 2 : 4 : 6-trinitrostilbene (Bishop and Brady, *J.*, 1922, **121**, 2367) is heated with sulphuric acid and nitric acid (*d* 1·41), 2 : 4 : 6 : 2′ : 4′-*pentanitrostilbene* is formed. An attempt to synthesise this compound from 2 : 4 : 6-trinitrotoluene and 2 : 4-dinitrobenzaldehyde failed. When this or the 2 : 4 : 6-trinitro- or the 2 : 4 : 6 : 2′-tetranitro-derivative (Bishop and Brady, *loc. cit.*) is heated with sulphuric acid and nitric acid (*d* 1·5) at 100°, oxidation occurs and a compound (*D*, see p. 1613) is obtained which appears to be 2 : 4 : 6 : 2′ : 4′-*pentanitrobenzil* because oxidation with hydrogen peroxide in glacial acetic acid gives 2 : 4-dinitrobenzoic acid and 1 : 3 : 5-trinitrobenzene. The last-named compound arises by decarboxylation of 2 : 4 : 6-trinitrobenzoic acid. Pentanitrobenzil also gives 2 : 4-dinitrobenzoic acid on oxidation with alkaline potassium permanganate. After the formation of pentanitrobenzil from 2 : 4 : 6-trinitrostilbene, 2 : 4-dinitro- and 2 : 4 : 6-trinitro-benzoic acid can be isolated from the spent acids. These probably arise from oxidation at an intermediate stage in the formation of *D*, as this can be recovered quantitatively from a hot mixture of sulphuric and fuming nitric acid.

2 : 4 : 6 : 2′ : 4′-Pentanitrobenzil (*D*) is colourless, whereas mono- and di-nitrobenzil are yellow. It turns orange-brown in light. Some dinitrobenzils change from pale yellow to green under similar conditions (see p. 1614).

Attempts to prepare pentanitrobenzil by the nitration of 2 : 2′-dinitrobenzil (Kliegl and Haas, *Ber.*, 1911, **44**, 1213; Chattaway and Coulson, *J.*, 1928, 1363) or 4 : 4′-dinitrobenzil (Chattaway and Coulson, *loc. cit.*) failed. When the 4 : 4′-derivative was heated with sulphuric and fuming nitric acid under conditions which converted trinitrostilbene to pentanitrobenzil, only 2 : 4-dinitrobenzoic acid was obtained. With sulphuric and nitric acid (*d* 1·41) the dinitrobenzil was unchanged. The 2 : 2′-dinitro-derivative with sulphuric and fuming nitric acid under similar conditions was mostly unaltered.

The pentanitro-derivatives of diphenylacetylene, deoxybenzoin, hydrobenzoin, and benzoin possess the same carbon skeleton as pentanitrobenzil, and could be oxidised to the corresponding di- and tri-nitrobenzoic acids. It would appear improbable, however, that *D* can be identical with one of these compounds, as they would all probably be oxidised to the benzil derivative with hot nitrating mixture.

During the purification of the pentanitrobenzil a nitro-compound, m. p. 260°, which gives a deep purple colouration with acetone and sodium hydroxide, was isolated. This has been detected by other workers during the nitration of various aromatic hydrocarbons and will be described later.

2-(2 : 4 : 6-Trinitrophenyl)ethanol yields the *chloride* with phosphorus pentachloride. This with methylthiol and *p*-tolylthiol in presence of sodium ethoxide gives *methyl* 2-(2 : 4 : 6-*trinitrophenyl*)*ethyl sulphide* (*A*) and p-*tolyl* 2-(2 : 4 : 6-*trinitrophenyl*)*ethyl sulphide* (*B*). From *A* the corresponding *sulphone* and from *B* the *sulphoxide* and *sulphone* were prepared by oxidation with hydrogen peroxide in glacial acetic acid. *p*-Tolyl 2-(2 : 4 : 6-trinitrophenyl)ethyl sulphone was also obtained from the nitrated chloride and sodium toluene-*p*-sulphinate.

The chloride forms quaternary salts with pyridine and quinoline; 2-(2 : 4 : 6-*trinitrophenyl*) *ethylpyridinium chloride, picrate,* and *benzenesulphonate* were prepared and also the *quinolinium chloride.*

EXPERIMENTAL.

Nitration of 2 : 4 : 6-*Trinitrostilbene.*—The nitro-compound (7·5 g.) was gradually added to a mixture of sulphuric acid (50 c.c.) and nitric acid (*d* 1·5; 50 c.c.) and heated for 8 hours at 100°. The experiment was repeated at 120—130° for 3 hours. In each case effervescence occurred and a crystalline solid (*A*) separated after 10 minutes but was not removed. The nitration mixtures were poured on ice giving identical buff-coloured solids (*B*) of m. p. 240—250° (decomp.). Other nitrations at 100°, during 4 and 8 hours respectively, gave similar results. The spent acids (*S*) were retained.

Products *B* were united and washed with aqueous sodium carbonate which became dark red. The insoluble matter (*C*, 4·2 g.) was separated; m. p. 220—240° (decomp.). Extraction with acetone left a sparingly soluble product (*D*), m. p. 260° (decomp.). The acetone extract (*E*) was reserved. Substance *D* (2 : 4 : 6 : 2′ : 4′-*pentanitrobenzil*) was crystallised from acetone (m. p. 261°), and then successively from glacial acetic acid, acetone–light petroleum, and benzene–light petroleum (m. p. 260° each time) Another specimen was crystallised 7 times from various similar mixtures of solvents, and the m. p. 260° (decomp.) confirmed. Further nitration under the same conditions as before did not alter the m. p. (Found: C, 39·2, 39·4; H, 1·5, 1·4; N, 15·9, 16·1; *M*, 453. $C_{14}H_5O_{12}N_5$ requires C, 38·6; H, 1·2; N, 16·1%; *M*, 435).

The solid *A* when removed after 15 minutes melted at 260° (decomp.) on recrystallisation and was identical with *D*. Long heating is, therefore, probably unnecessary.

The spent acids *S* gave a deep red colour with sodium hydroxide. On concentration a solid was deposited. This was washed with nitric acid and dried; m. p. 170—220°. On recrystallisation from benzene it was identified as 2 : 4 : 6-trinitrobenzoic acid by the blood-red colouration with sodium carbonate and by m. p. (*a*) 210°, (*b*) 212°, and mixed m. p. (*a*) 213° and (*b*) 212° with an authentic specimen of m. p. 210°. The m. p. depends on the rate of heating. The benzene mother liquor with light petroleum yielded a solid which after three crystallisations had m. p. 162—166°. Trinitrobenzoic acid was removed from this as the insoluble barium salt. The soluble portion, on acidification, gave an acid, m. p. 166°, which on crystallisation had m. p. and mixed m. p. 179—180° with authentic 2 : 4-dinitrobenzoic acid. The *p*-nitrobenzyl ester had m. p. and mixed m. p. 137° with an authentic specimen m. p. 139°.

In order to check the purity of the pentanitrobenzil, attempts were made to prepare addition products with naphthalene and anthracene. Yellow and red solutions in acetone were obtained respectively, but only pentanitrobenzil separated on concentration.

More definite evidence of compound formation was obtained with solid thiophthen [thiopheno (2′ : 3′ : 3 : 2)thiophen] (Challenger and Harrison, *J. Inst. Pet. Tech.*, 1935, **21**, 135; Challenger and Gibson, *J.*, 1940, 305). When pentanitrobenzil (1 mol.) and thiophthen, m. p. 54° (4—5 mols.), were dissolved in acetone and the solution completely evaporated, an impure yellow solid separated which, after being washed with a little acetone, could be recrystallised with only partial decomposition from acetone containing thiophthen. This operation was repeated thrice, the m. p. of the impure addition product being 200—220°, 220—230°, and 220—224°. Treatment in acetone solution with ligroin regenerated pentanitrobenzil, the m. p. of which could not be raised above 259° (Found: C, 39·1, 39·1; H, 1·2, 1·2; N, 15·8, 15·9%). By heating the yellow addition product for 10 minutes at 110° the thiophthen volatilised and the residue melted at 258—259°.

Pentanitrobenzil was recovered largely unchanged after being boiled with hydroxylamine hydrochloride in glacial acetic acid or added to *o*-phenylenediamine in hot glacial acetic acid.

Nitration of 2 : 4 : 6 : 2′-*Tetranitrostilbene.*—The tetranitro-compound was prepared by Bishop and Brady's method (*J.*, 1922, **121**, 2367); m. p. 181°. 0·5 G. was nitrated under the conditions employed for the trinitro-derivative. A crystalline deposit separated after 10 minutes but was not removed. After 3 hours the mixture was filtered through glass wool and the solid washed with nitric acid, water, sodium carbonate, and water, and dried; m. p. 256° (decomp.). On recrystallisation from acetone–light petroleum, the m. p. and mixed m. p. was 258° with pentanitrobenzil of m. p. 259°. The spent acids contained some trinitrobenzoic acid and yielded a small amount of a compound, m. p. 260°, which gave a purple colour with acetone and sodium hydroxide. This was also obtained on acidification of the sodium carbonate washings of *B*—see the nitration of trinitrostilbene, p. 1613.

Nitration of 2 : 4 : 6-*Trinitrostilbene under Milder Conditions.*—The nitro-compound (5 g.) was gradually added to a mixture of sulphuric acid (10 c.c.) and nitric acid (*d* 1·41; 10 c.c.). An orange solid separated. The mixture was heated for 2 hours at 100° and poured on ice. The crude solid (4·5 g.) on recrystallisation from benzene or from acetone–light petroleum and finally from benzene–acetone, formed greenish-yellow needles of 2 : 4 : 6 : 2′ : 4′-*pentanitrostilbene*, m. p. 198—199° (Found: C, 41·6, 41·6; H, 1·8, 1·85; N, 16·8, 17·0. $C_{14}H_7O_{10}N_5$ requires C, 41·5; H, 1·74; N, 17·3%). A later preparation gave 21 g. of crude product from 18 g. of trinitrostilbene.

Oxidation of 2 : 4 : 6 : 2′ : 4′-*pentanitrostilbene to* 2 : 4 : 6 : 2′ : 4′-*pentanitrobenzil.*—The pentanitrostilbene (2 g.) was heated with the nitration mixture as in the case of the tetranitro-compound. A solid separated after 10 minutes. Pentanitrobenzil (1 g.), m. p. and mixed m. p. 259°, was isolated as before. The spent acids in this and the two preceding nitrations gave a deep red colour with sodium hydroxide.

Orientation of the Nitro-groups in Pentanitrobenzil.—(*a*) The nitro-compound (2 g.) was dissolved in boiling glacial acetic acid, and hydrogen peroxide (20 vols.) added at intervals until a test-portion, on dilution with water, showed only a faint turbidity. The solution was then diluted with water, filtered, and evaporated to dryness. The yellow residue was extracted with hot benzene, which deposited a solid. This, on recrystallisation from benzene, had m. p. and mixed m. p. 180° with authentic 2 : 4-dinitrobenzoic acid. Yield, 0·66 g.

The mother liquors yielded 1 : 3 : 5-trinitrobenzene which, after being washed with sodium hydrogen carbonate and recrystallised from alcohol, had m. p. 119° and 120° in admixture with an authentic specimen, m. p. 122°. The naphthalene and anthracene compounds melted at 153—154° and 162—163° respectively (lit. gives 152·5° and 164°). Trinitrobenzoic acid was not isolated, although the crude oxidation product gave a red colour with sodium hydroxide. Oxidation of 2 : 4 : 6-trinitrobenzoic acid under these conditions gave trinitrobenzene.

(*b*) The pentanitrobenzil (0·5 g.) was boiled with excess of alkaline 3% aqueous potassium permanganate till oxidation ceased. Addition of a few drops of alcohol and filtration gave a pale yellow solution (absence of trinitrobenzoic acid) which, on acidification and extraction with ether, yielded 2 : 4-dinitrobenzoic acid, m. p. 177—178°, mixed m. p. 179° with a specimen of m. p. 180°. The *p*-nitrobenzyl ester had m. p. and mixed m. p. 140°.

Properties of Pentanitrobenzil.—The colourless compound gives no colour with aqueous sodium carbonate, in which it is insoluble. With aqueous sodium hydroxide it gives slowly a faint orange colour which becomes brown on standing or on boiling, and the solution then contains nitrite or nitrate. Ammonia is evolved on boiling. On exposure to light the colourless compound becomes orange red, and the m. p. falls slightly (to 257—258°). 2 : 2′- and 2 : 3′-Dinitrobenzil are phototropic (Chattaway and Coulson, *J.*, 1926, 1073).

The compound was recovered unchanged after treatment with a chloroform solution of bromine at the b. p. and evaporation of the solvent. With aqueous sodium dichromate and sulphuric acid at 150° some oxidation occurred, but even after several hours the reaction was incomplete, and unchanged 2 : 4 : 6 : 2′ : 4′-pentanitrobenzil was recovered. Chattaway and Coulson found that 2 : 2′-dinitrobenzil does not form a quinoxaline, and is the only one of the mono- and di-nitrobenzils which is not readily oxidised by chromic acid (*J.*, 1928, 1081). On being heated with nitric acid (*d* 1·5) at 100° or with this acid and sulphuric acid at 130—135°, pentanitrobenzil was recovered almost quantitatively. The evaporated nitric acid contained no trinitrobenzoic acid.

2-(2 : 4 : 6-*Trinitrophenyl*)*ethyl chloride.*—2-(2 : 4 : 6-Trinitrophenyl)ethanol (Vender, *Gazzetta*, 1915, **45**, II, 97; Bruson and Butler, *J. Amer. Chem. Soc.*, 1946, **68**, 2348) was largely recovered unchanged after (*a*) treatment with excess of thionyl chloride at room temperature for 10 days, (*b*) being boiled with excess of thionyl chloride under reflux for several hours, or (*c*) treatment with anhydrous hydrogen chloride in glacial acetic acid. In each case the mixture was poured into water or on ice and the product crystallised from benzene or aqueous alcohol.

The finely ground trinitrophenylethanol (5 g.) was covered with light petroleum (b. p. 40—60°) and treated with finely ground phosphorus pentachloride (7 g.) under a reflux condenser and calcium chloride tube. Reaction began on slightly warming; when it slackened a further 0·5 g. of the pentachloride was added. The mixture was finally poured on ice, the solvent volatilised, and the residue crystallised 3 or 4 times from benzene–light petroleum or carbon tetrachloride, giving colourless needles, m. p. 76°, which became opaque when dry. Yield 2·4 g. of m. p. 72°. Later experiments gave 8 g. from 10 g. of the ethanol. The optimum quantity of ethanol appears to be 10—20 g. With phosphorus oxychloride as solvent instead of light petroleum the yield was 1·7 g. of *chloride*, m. p. 67°, from 5 g. of ethanol (Found: C, 35·2; H, 2·2; Cl, 13·4. $C_8H_6O_6N_3Cl$ requires C, 34·8; H, 2·2; Cl, 12·9%).

Attempts to convert the chloride into the thiocyanate or selenocyanate by reaction with the corresponding sodium or potassium salts in acetone were unsuccessful. No reaction occurred with silver cyanide or thiocyanate in cold or boiling benzene. 2-(2 : 4 : 6-*Trinitrophenyl*)*ethyl pyridinium chloride* was prepared from the chloride in pyridine. A solid separated after a few hours. After being washed with acetone and crystallised from aqueous acetone or alcohol–ether this melted at 132—134° (Found: Cl, 9·8, 10·0. $C_{13}H_{11}O_6N_4Cl$ requires Cl, 10·0%). The corresponding *picrate* on crystallisation from aqueous acetone had m. p. 115—116° depending slightly on the rate of heating (Found, by Nitron method: $-O\cdot C_6H_2(NO_2)_3$, 39·1, 39·7. $C_{19}H_{13}O_{13}N_7$ requires 41·6%). A slight trace of some halogen compound could not be removed on crystallisation. The *benzenesulphonate* formed a white precipitate,

m. p. 181—182° after crystallisation from alcohol–ether, 183° after crystallisation from water (Found : C, 48·2; H, 3·5; N, 11·7. $C_{19}H_{16}O_9N_4S$ requires C, 47·8; H, 3·4; N, 11·8%).

2-(2 : 4 : 6-*Trinitrophenyl*)*ethylquinolinium chloride* was prepared by using the minimum quantity of quinoline; with more than this the quaternary chloride did not separate. 1 G. of the chloride gave 0·4 g. of the quinolinium compound which melted at 159—160° (decomp.) after recrystallisation from alcohol-ether or aqueous acetone (Found : Cl, 8·9, 8·9. $C_{17}H_{13}O_6N_4Cl$ requires Cl, 8·75%). Addition of sodium picrate to an aqueous solution gave a precipitate, m. p. 160—180°, m. p. 200° after recrystallisation from alcohol. The mixed m. p. with quinoline picrate was 201°, the arylquinolinium complex having apparently decomposed.

p-*Tolyl* 2-(2 : 4 : 6-*Trinitrophenyl*)*ethyl Sulphide*.—The chloride (1 g.) and *p*-tolylthiol (0·5 g.; slight excess) were dissolved in alcohol, and a solution of sodium (0·07 g., slightly less than 1 atom) in alcohol slowly added. The solution was only faintly red at the conclusion of the addition, and was gently boiled (1 hour) till no more sodium chloride separated. Excess of sodium ethoxide gives rise to red tar. Filtration and concentration gave an oil which solidified and was recrystallised twice from alcohol. The *sulphide* formed orange-yellow needles, m. p. 91° (Found : C, 49·6; H, 3·65; N, 11·3; S, 8·7. $C_{15}H_{13}O_6N_3S$ requires C, 49·6; H, 3·6; N, 11·6; S, 8·8%).

With methyl iodide at room temperature, or on boiling the mixture with nitromethane, no methiodide was formed.

p-*Tolyl* 2-(2 : 4 : 6-*Trinitrophenyl*)*ethyl Sulphoxide*.—The sulphide in glacial acetic acid at 100° was treated with excess of hydrogen peroxide. After 15 minutes, dilution with water gave pale yellow needles of the *sulphoxide*, m. p. 132° raised to 137—138° on recrystallisation from alcohol (Found : C, 47·8; H, 3·25; N, 10·6; S, 8·25. $C_{15}H_{13}O_7N_3S$ requires C, 47·5; H, 3·4; N, 11·1; S, 8·4%).

p-*Tolyl* 2-(2 : 4 : 6-*Trinitrophenyl*)*ethyl Sulphone*.—The sulphide (0·8 g.) was heated at 100° with excess of hydrogen peroxide in glacial acetic acid for 1 hour; a white solid separated (0·7 g.), m. p. 190°. The m. p. rose to 197—198° after 2 crystallisations from acetone and 1 from acetone-light petroleum (Found : C, 45·8; H, 3·6; N, 10·5; S, 8·0. $C_{15}H_{13}O_8N_3S$ requires C, 45·6; H, 3·3; N, 10·6; S, 8·1%). The same *sulphone* was obtained when the chloride (2 g.) and toluene-*p*-sulphinic acid (1 g.) were boiled with alcohol (100 c.c.) and sodium (0·1 g.) in alcohol, slowly added. After 1 hour, sodium chloride and brown crystals separated. These were treated with water, and the insoluble matter (1·1 g.) recrystallised from acetone–alcohol; m. p. and mixed m. p. with the sulphone, 197—198°. A further quantity (0·5 g.) was obtained from the filtered reaction mixture.

Methyl 2-(2 : 4 : 6-*Trinitrophenyl*)*ethyl Sulphide*.—The nitrated chloride (2 g.) in hot alcohol was gradually treated with a solution of methylthiol (0·5 c.c.) and sodium (0·14 g.) in alcohol. After 1 hour's boiling, the filtered solution was concentrated, depositing a brownish-yellow solid, m. p. 85—86° after recrystallisation from alcohol (Found : C, 37·9; H, 3·1; N, 14·6; S, 11·2. $C_9H_9O_6N_3S$ requires C, 37·6; H, 3·1; N, 15·4; S, 10·6%).

Dimethyl-2-(2 : 4 : 6-*trinitrophenyl*)*ethylsulphonium Iodide*.—When the *sulphide* was left for several days with methyl iodide and nitromethane, or when the mixture was boiled for 30 minutes, red needles separated on cooling, m. p. 148° (decomp.). These contained ionic iodine and were recrystallised from warm water; the *iodide* then had m. p. 150° unchanged on further crystallisation, although a slight odour of dimethyl sulphide was apparent. This was much increased by the action of cold, and still more by that of warm, sodium hydroxide (cf. Crane and Rydon, *J.*, 1947, 766) (Found : I, 29·2. $C_{10}H_{12}O_6N_3IS$ requires I, 29·6%).

Methyl 2-(2 : 4 : 6-*Trinitrophenyl*)*ethyl Sulphone*.—The sulphide was heated at 100° in glacial acetic acid with excess of hydrogen peroxide. The white solid *sulphone* which separated was recrystallised from acetone–light petroleum; m. p. 187° constant (Found : C, 33·6; H, 3·0; N, 13·2; S, 10·0; $C_9H_9O_8N_3S$ requires C, 33·9; H, 2·8; N, 13·2; S, 10·0%).

This work is published with the consent of the Ministry of Supply. The authors thank Imperial Chemical Industries Ltd. for a grant, and the Trustees of the Broterton Scholarship for an award to P. H. C.

THE UNIVERSITY, LEEDS.

[*Received, October 4th,* 1947.]