215. *Some New Di- and Tri-nitro*-p-*terphenyls.*

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Preparations and, where necessary, proofs of structure are described for five new dinitro- and three new trinitro-*p*-terphenyls—2,2′-, 2,3′-, 2,2″-, 2,4″-, and 4,2′-dinitro-*p*-terphenyl, and 2,2′,2″-, 2,2′,4″-, and 2,3′,4″-trinitro-*p*-terphenyl. Account being taken of the known 4,3′- and 4,4″-dinitro- and 4,2′,4″-trinitro-*p*-terphenyl, all the di- and tri-nitro-isomers likely to be formed in significant amount by direct nitration of the hydrocarbon in organic solvents have now been characterised.

Methods for preparing 2-, 2′-, and 4-nitro-, 4,4″-dinitro-, and 4,2′,4″-trinitro-*p*-terphenyl by nitration of the hydrocarbon have been discussed recently,[1] and it was decided to undertake quantitative work on the ratios of the nitro-isomers which are produced under various conditions for the mono-, di-, and tri-nitration of *p*-terphenyl. Apart from the work of France, Heilbron, and Hey [2] who proved the constitutions of 4,3′- and 4,4″-dinitro- and 4,2′,4″-trinitro-*p*-terphenyl, nothing was however known about other di- and tri-nitro-*p*-terphenyls which may be formed in significant amount by direct substitution of the hydrocarbon in organic solvents. Such products were required as reference compounds for the quantitative studies, and the syntheses and, where necessary, the proofs of structure of five new dinitro- and three new trinitro-*p*-terphenyls are now described. In selecting the particular compounds for study, it was assumed that the deactivating effect of a nitro-group would retard the entry of a second nitro-group into a ring until the other two rings in the *p*-terphenyl molecule had themselves been mononitrated. Compounds containing two or more nitro-groups in a given ring were not therefore studied. Moreover, substitution in the 3- and the 3″-position was considered unlikely, since a biphenylyl or nitrobiphenylyl group is *ortho* : *para*-directing. The exclusion of 3- and 3″-nitro-derivatives has been vindicated by quantitative data [3] for the mononitration of *p*-terphenyl, no 3-nitro-*p*-terphenyl being detected in the products.

The eight new nitro-*p*-terphenyls, together with 4,3′- and 4,4″-dinitro-, and 4,2′,4″-trinitro-*p*-terphenyl, and the hitherto unknown 3,4″-dinitro-*p*-terphenyl (isolated from an isomeric mixture) are shown in the chart, which also summarises the preparative routes employed.

Condensation of 4-nitro-4′-*N*-nitrosoacetamidobiphenyl with nitrobenzene yielded the three possible isomers, of which (III) had already been characterised by France, Heilbron, and Hey.[2] The constitution of isomer (VI) was confirmed when no m. p. depression was obtained on admixture with the product obtained by condensing 2-nitro-4′-*N*-nitrosoacetamidobiphenyl and nitrobenzene and when the infrared spectra of the two compounds were found to be identical. The identity of the isomer (V) followed by elimination, but was also proved when the same compound was prepared by deaminating 4-amino-3,4″-dinitro-*p*-terphenyl.

The dinitro-isomer (VII) was identified by its further nitration, in good yield, to the trinitro-isomer (VIII). The syntheses of isomers (XI) (a known compound [2]) and (XII) were unambiguous.

Preparation of the 2,2′-dinitro-isomer (IX) was particularly difficult, and attempts to obtain it by condensation of 3-nitro-4-*N*-nitrosoacetamidobiphenyl and nitrobenzene or by the Gomberg reaction between the corresponding amine and nitrobenzene failed. Yet, from both reactions, the isomeric 4,2′-dinitro-*p*-terphenyl (I) was obtained. The preparation of 4-amino-2,2′-dinitrobiphenyl (XIII) was then undertaken, to make possible the preparation of the dinitroterphenyl (IX) by the Gomberg reaction with benzene. Attempts to prepare this amine by selective reduction of 2,4,2′-trinitrobiphenyl and by

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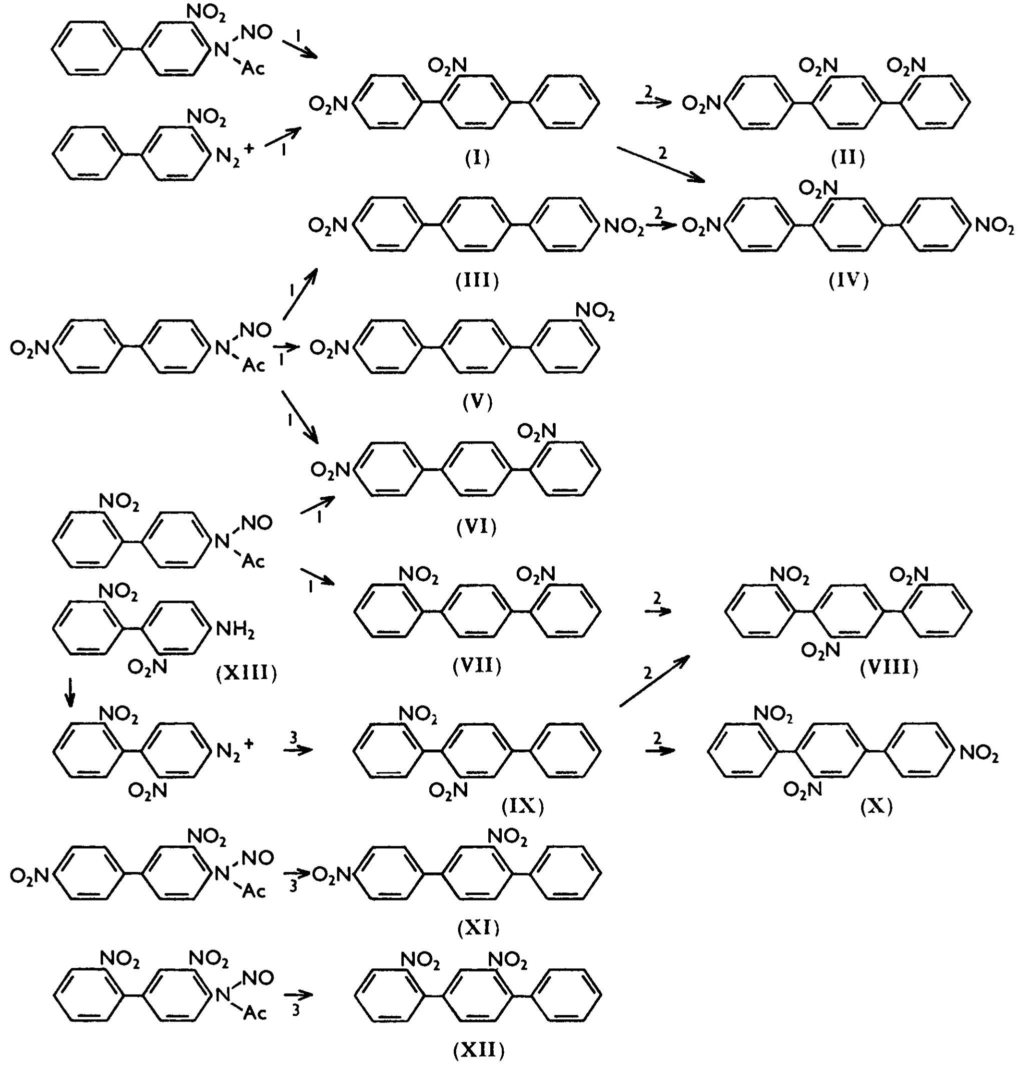
[1] Culling, Gray, and Lewis, *J.*, 1960, 1547.

[2] France, Heilbron, and Hey, *J.*, 1938, 1364.

[3] Gray and Lewis, unpublished work.

dinitration of 4-aminobiphenyl in concentrated sulphuric acid were unsuccessful. The latter failure is surprising, since 2-aminobiphenyl is readily nitrated under similar conditions.[4] The dinitro-amine (XIII) was finally obtained by nitrating 4-amino-2′-nitrobiphenyl in concentrated sulphuric acid, according to the method of Finzi and Bellavita,[5] who quoted no yields, but " estimated " the ratio of nitration at the 2- and 4′-position as 40 : 60. We have actually isolated 41% of the amine (XIII), but could obtain no more than 25% of 4-amino-2′,4′-dinitrobiphenyl. It should be noted that since this work was carried out, Arcos, Arcos, and Miller [6] have isolated from this reaction 55% of the amine (XIII) and 25% of 4-amino-2′,4′-dinitrobiphenyl. From both pieces of work it is clear that more nitration occurs at the 2-position than was estimated by Finzi and Bellavita.[5] It is of interest that we could detect none of the expected, but as yet uncharacterised, 4-amino-2′,6′-dinitrobiphenyl in the product.



Reagents: 1, Ph·NO_2. 2, HNO_3. 3, C_6H_6.

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[4] Smith and Brown, *J. Amer. Chem. Soc.*, 1951, **73**, 2439.

[5] Finzi and Bellavita, *Gazzetta*, 1938, **68**, 77.

[6] Arcos, Arcos, and Miller, *J. Org. Chem.*, 1956, **21**, 651.

Preparations of the unknown trinitro-isomers (II, VIII, and X) were not attempted by Gomberg reactions between the appropriate 4-aminodinitrobiphenyls and nitrobenzene, as it was foreseen that the separation of the isomeric mixtures would be difficult. Indeed, such syntheses are not necessary, for the mononitration of compound (VII) will give almost exclusively compound (VIII), which is therefore characterised by this reaction. Moreover, this compound (VIII) will also be formed, with its isomer (X), by the nitration of 2,2′-dinitro-*p*-terphenyl (IX). And the mononitration of 4,2′-dinitro-*p*-terphenyl (I) gives only the trinitroterphenyl (II) and the known compound (IV). The two binary mixtures of the trinitro-isomers were readily separated into their components, and isomers (VIII) and (IV) having been characterised, the identities of (II) and (X) followed by elimination. The two samples of compound (VIII), obtained by different routes, were shown to be identical by comparison of their infrared spectra, and by the absence of any m. p. depression on admixture of the two specimens.

EXPERIMENTAL

General Procedure for the Nitrosation of Acetylamines.—Acetylamines were nitrosated with nitrosyl chloride in acetic acid–acetic anhydride and condensed with benzene or nitrobenzene as described by Gray and Worrall [7] for the nitrosation of 3-fluoro- and 3-iodo-4-octyloxyacetanilide and the condensation with methyl benzoate.

*4,2′-Dinitro-*p*-terphenyl.*—4-Acetamido-3-nitrobiphenyl, m. p. 131—132°, was obtained in 76% yield by the method of Campbell, Anderson, and Gilmore [8] for the nitration of 4-acetamidobiphenyl. Their yield of 92% was not realised, partly because some dinitration occurred, as shown by the isolation of some 4-acetamido-3,4′-dinitrobiphenyl, m. p. 237—240°, from the liquors of the crystallisation of the 3-nitro-isomer.

(a) *N-Nitrosoacetylamine reaction.* 3-Nitro-4-*N*-nitrosoacetamidobiphenyl was obtained as a brown viscous oil by carrying out the general nitrosation procedure on the acetylamine (23 g.). Condensation with nitrobenzene (500 ml.) was allowed to proceed at room temperature for 4 days. The residue (24·5 g.), on removal of the nitrobenzene, was dissolved in benzene and adsorbed on a column (41 × 4·9 cm.) of alumina (750 g.). The first volume of eluate (350 ml.) yielded a red glass, and the next three fractions (total volume, 800 ml.) an orange-yellow solid (3·6 g.), m. p. up to 138°. Attempts to crystallise a product from the glass were unsuccessful, and further chromatography was employed to separate more of the orange-yellow solid (0·75 g.) from the gummy components. The combined fractions of the orange-yellow solid (4·35 g.) were dissolved in benzene (10 ml.), and light petroleum (b. p. 40—60°; 8 ml.) was added to the hot solution, which was then cooled. The thick supernatant liquid was decanted from the crystals which were crystallised from benzene and then from acetic acid. The yield of *4,2′-dinitro-*p*-terphenyl*, m. p. 158—159°, was 6% (Found: C, 67·7; H, 3·8; N, 8·9. $C_{18}H_{12}N_2O_4$ requires C, 67·5; H, 3·75; N, 8·75%). The dinitro-isomer was characterised by further nitration, one of the two trinitro-isomers isolated being the known 4,2′,4″-trinitro-*p*-terphenyl.[1]

Solid products were also obtained from other fractions from the various chromatograms. These solids melted between 82° and 144° and analysed as dinitro-*p*-terphenyls, but no pure 2,2′- or 3,2′-dinitro-*p*-terphenyl could be isolated from these materials.

(b) *Gomberg reaction.* 4-Amino-3-nitrobiphenyl [8] was diazotised and condensed with nitrobenzene essentially as described for the preparation of 2′-nitro-*p*-terphenyl.[1] To minimise acetylation of the nitro-amine, the nitrosylsulphuric acid (90 ml.) was added all at once to the amine sulphate, prepared by mixing the amine (21·4 g.) and concentrated sulphuric acid (21·4 ml.) at room temperature. The acetic acid (107 ml.) was then added slowly to the cooled, stirred mixture, which was poured on ice 1 hr. after completion of the addition. The Gomberg reaction mixture was worked up after 40 hr., but the emulsified organic layer was difficult to separate and dry. The nitrobenzene was removed under reduced pressure (2 mm.), and part (19·7 g.) of the residue was digested with boiling benzene (100 ml.). The filtrate from the cooled extraction was adsorbed on alumina (130 g.), and the first fraction (50 ml.) to be eluted contained a red glass (2·11 g.). This material was dissolved in benzene (32 ml.) and readsorbed on alumina (47 g.), and from the first volume (110 ml.) of red eluate was again obtained a

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[7] Gray and Worrall, *J.*, 1959, 1545.

[8] Campbell, Anderson, and Gilmore, *J.*, 1940, 449.

glass (1·26 g.) which could now be crystallised, first from benzene–light petroleum (b. p. 40—60°) and then from benzene. The pale yellow spherulites of 4,2′-dinitro-*p*-terphenyl (1%), m. p. 158—159°, gave no m. p. depression on admixture with the same product obtained by method (a).

All other products from the first chromatogram decomposed on heating, and although an extremely small amount of a red crystalline compound, m. p. 234—236·5°, was obtained from the last fraction of the second chromatogram, no 2,2′- or 3,2′-dinitro-*p*-terphenyl was isolated from this preparation.

*2,4″-, 3,4″-, and 4,4″-Dinitro-*p*-terphenyls.*—4-Acetamido-4′-nitrobiphenyl [1] (14·6 g.) was nitrosated in the usual way [7] and condensed with nitrobenzene (700 ml.) by stirring for 19 hr. After removal of the nitrobenzene under reduced pressure, part (15 g.) of the residue was distilled at 0·06 mm. Two oily fractions which set to yellow solids, (8·2 g.) b. p. 250—260°, and (0·95 g.) b. p. 260—300°, were collected before the residue suddenly carbonised at a bath temperature of 330°. Part (5·9 g.) of the lower-boiling fraction, m. p. 151—177°, was dissolved in benzene and the solution concentrated to 100 ml. The suspension was cooled, and the yellow solid (1·86 g.), m. p. 209—228°, was thrice crystallised from acetic acid to yield 4,4″-dinitro-*p*-terphenyl (0·65 g.), m. p. 272—274·5°. This m. p. was undepressed on admixture of the product with the 4,4″-dinitro-isomer obtained by nitration of the hydrocarbon. The acetic acid liquors from the first crystallisation contained mainly 4-acetamido-4′-nitrobiphenyl (4—8%).

The benzene solution from the extraction of the low-boiling fraction was passed through a column (34 × 1·7 cm.) of alumina, and the broad, pale yellow region was eluted with benzene. The products obtained on evaporation of the first three fractions (50, 50, and 75 ml.; m. p. limits respectively 130—133°, 124—130°, and 109—128°) were dissolved separately in benzene and adsorbed on alumina (column dimensions, 63 × 1 cm.). The first of the above products was not improved, but the other two were separated from an impurity (A) (0·22 g.), and the m. p.s rose to 130—133°. The combined material (2·52 g.), m. p. 130—133°, was crystallised from ethanol and yielded large yellow blades of *2,4″-dinitro-*p*-terphenyl* (2·29 g.), m. p. 132—133° (Found: C, 67·45; H, 4·1; N, 8·6. $C_{18}H_{12}N_2O_4$ requires C, 67·5; H, 3·75; N, 8·75%). Crystallisation from benzene raised the m. p. to 133°. This isomer was identified when the same product was isolated after condensation of 2-nitro-4′-*N*-nitrosoacetamidobiphenyl and nitrobenzene.

The material A was added to the product (0·09 g.), m. p. 117—187°, obtained from the fourth fraction (100 ml. of eluate) from the original chromatogram, and dissolved in benzene. Further chromatography on alumina gave various fractions of which the first and the last from the column (66 × 1 cm.) were respectively 2,4″-dinitro-*p*-terphenyl (0·08 g.) and 4,4″-dinitro-*p*-terphenyl (0·01 g.). The intermediate fractions yielded a product (0·1 g.), m. p. 147—157°, which was crystallised four times, alternately from benzene and ethanol. The m. p. of the *3,4″-dinitro-*p*-terphenyl* remained constant at 160° from the last three of these crystallisations, although the melt was slightly turbid until 161°. This isomer (Found: C, 67·3; H, 4·2; N, 8·8%) was also obtained by deamination of 4-amino-3,4″-dinitro-*p*-terphenyl. The overall yields of the 2,4″-, 3,4″-, and 4,4″-dinitro-*p*-terphenyl were 17%, 0·4%, and 6% respectively.

*3,4″-Dinitro-*p*-terphenyl.*—Nitrosylsulphuric acid (5·7 ml., *ca.* 1·55 equiv.) [from a solution prepared in the usual way from powdered sodium nitrite (2·07 g.) and concentrated sulphuric acid (16·6 ml.)] was added during 18 min. to a stirred suspension of powdered 4-amino-3,4″-dinitro-*p*-terphenyl [9] (2·23 g.) in acetic acid (10 ml.). The temperature was maintained at 20° during the addition and for 30 min. after its completion. Diazotisation was only partly successful because of the low solubility of the amine sulphate, but 31% w/w aqueous hypophosphorous acid (12·7 ml., 10 equiv.) was then added, the temperature being kept about 20°. After the reaction mixture had been held at 4° for 36 hr., a positive coupling reaction was given, and it was necessary to heat the suspension for 24 hr. at 50° to complete deamination. The solid was filtered off, washed with water, 5N-ammonia, and again water, and dried. A portion (1 g.) of this purple-brown solid (2·02 g.) was refluxed with benzene (50 ml.), and, after cooling, the insoluble matter was filtered off. The filtrate was passed through a column (22 × 2·2 cm.) of alumina, and the chromatogram was developed with benzene. The broad yellow zone, lying under a red band (unchanged dinitro-amine), was eluted in 50—100 ml. fractions. The

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[9] Culling, Gray, and Lewis, *J.*, 1960, 2699.

solids (0·08 g.) from the first two volumes of eluate melted rather higher, 169—170° and 162—166°, than the products (total weight, 0·25 g.), m. p. limits 159—160·5°, obtained from fractions 3—10. Fraction 11 (400 ml. of eluate) gave material (0·02 g.) of m. p. 156—158°. Fractions 3—10 were combined and crystallised twice from benzene and twice from s-butyl alcohol, giving pale yellow crystals, m. p. 161—162° (Found: C, 67·3; H, 3·6; N, 9·0%). The total yield of 3,4″-dinitro-*p*-terphenyl, after one crystallisation, was 20%, and this product gave no depression of the m. p. on admixture with the same isomer, m. p. 160—161°, obtained by the *N*-nitrosoacetylamine reaction.

2,4″- *and* 2,2″-*Dinitro*-p-*terphenyl*.—2-Nitro-4′-*N*-nitrosoacetamidobiphenyl was prepared by the general nitrosation procedure from the acetylamine [1] (20 g.), and condensed in the usual way with nitrobenzene (500 ml.), the mixture being stirred for 2 days. The solvent-free residue (22·3 g.) was adsorbed from benzene (600 ml.) on a column of alumina (600 g.; 33 × 4·9 cm.). Development of the chromatogram with benzene gave three regions, which were, from the top of the column, brown (7 cm. thick), orange (5 cm.), and yellow (11 cm.). The material in the yellow band was eluted with benzene (3·5 l.) in fifteen fractions of approximately equal volume. Separation was poor, the m. p.s of the products ranging from 194—218° (first fraction) to 155—180° (last fraction). The fractions were combined (total wt., 10·4 g.) and crystallised four times from benzene. The mother-liquors were evaporated and the residue crystallised again. In this way a total yield of 2·5 g. (10%) of 2,2″-*dinitro*-p-*terphenyl*, m. p. 228—230·5°, was obtained (Found: C, 67·7; H, 3·6; N, 9·1. $C_{18}H_{12}N_2O_4$ requires C, 67·5; H, 3·75; N, 8·75%). The orientation of the nitro-groups was proved by further nitration to 2,2′,2″-trinitro-*p*-terphenyl, also obtained by nitration of 2,2′-dinitro-*p*-terphenyl.

The mother-liquors from the last crystallisation were adsorbed on alumina in an attempt to obtain the 2,3″- and the 2,4″-dinitro-isomer, but little separation was achieved (recovery from column, 96%). Adsorption on active carbon, with benzene, chloroform, or alcohol as solvents, gave a low recovery (20—35%), and only a little 2,2″-dinitro-isomer was isolated pure. The remaining material (4 g.) was sublimed at 10^{-3}—10^{-4} mm. Material of m. p. 110—176° (bath-temperature up to 162°) was discarded, and the second fraction (1·3 g.), m. p. 110—166° (bath-temperature 170°) was resublimed at 10^{-4}—10^{-5} mm.:

Bath-temp.	up to 130°	140°	154°	160°
Wt. of sublimate (g.)	0·1	0·3	0·7	0·15
M. p.	up to 179°	128—171°	114—162°	112—120°

The last fraction was crystallised twice from ethanol, yielding 2,4″-dinitro-*p*-terphenyl (0·07 g., equiv. to a yield of 0·6%), m. p. 132—133°. A third crystallisation raised the m. p. to 133° and gave bright yellow blades of 2,4″-dinitro-*p*-terphenyl (Found: C, 67·4; H, 4·0; N, 8·7%). A mixture with the same product (m. p. 133°) prepared by the *N*-nitrosoacetylamine reaction gave no depression of the m. p., and the infrared spectra of the solids were identical ($C-NO_2$ absorption bands occurred at 1353 and 1515 $cm.^{-1}$).

2,2′-*Dinitro*-p-*terphenyl*.—Powdered 4-amino-2′-nitrobiphenyl [1] (10 g.) was dissolved in 96% w/v sulphuric acid (100 ml.), kept at 15—20° by cooling. The stirred solution was maintained at −4° to −6° during the addition of ethyl nitrate (4 ml., 1·04 equiv.) and for 10 min. after the addition. The reactants were poured on ice (400 g.), and, the temperature being kept below 50°, the suspension was basified with aqueous ammonia (250 ml.; *d* 0·88). An attempt was made to crystallise the red precipitate (12 g.; m. p. 110—113°) according to the brief description given by Finzi and Bellavita.[5] This rather unsatisfactory process gave only 3% of orange-yellow 4-amino-2,2′-dinitrobiphenyl, m. p. 141—141·5°, and 3% of the red 4-amino-2′,4′-dinitrobiphenyl, m. p. 137·5—138·5°. A better procedure for the isolation of the 2,2′-dinitro-isomer is to crystallise the crude nitration product from a large volume (1·8 l.) of carbon tetrachloride, carrying out a hot filtration; a 41% yield is obtained on cooling to 31°. The material contained in the mother-liquors (the 2,2′- and 2′,4′-dinitro-isomers) was dissolved in benzene and chromatographed (alumina). In this way a 25% yield of the 2′,4′-dinitro-isomer was obtained. Finzi and Bellavita [5] record both isomers as melting at 138—139°.

Normal methods of acetylation gave 4-*acetamido*-2,2′-*dinitrobiphenyl* (97%), m. p. 124—130°, which is difficult to crystallise. From chloroform–light petroleum (b. p. 60—80°) (5 : 2) are obtained almost colourless crystals (60%), m. p. 134—135° (Found: C, 55·5; H, 3·7; N, 14·1. $C_{14}H_{11}N_3O_5$ requires C, 55·8; H, 3·7; N, 13·95%). The derivative is extremely light-sensitive.

4-Amino-2,2′-dinitrobiphenyl (10·36 g.), 32% w/w hydrochloric acid (26 ml., 6·6 equiv.), and water (40 ml.) were warmed, and the suspension of the hydrochloride was cooled rapidly and diazotised at 0° to −5° with aqueous sodium nitrite (3·26 mol.) (addition time 2·5 hr.). Excess of nitrous acid was destroyed by sulphamic acid, benzene (500 ml.) was added, and the mixture was stirred and carefully basified with 40% aqueous sodium hydroxide (25 ml.) at 5—10°. Stirring was continued at room temperature for 48 hr., then the organic layer was separated, tar adhering to the walls of the flask being rejected. The washed and dried extract was concentrated to 45 ml. and passed over alumina (200 g.; 23 × 3·4 cm.). The nitro-compound (pale yellow band) was eluted in seven fractions with benzene (1·25 l.). The last fraction contained material (0·06 g.) of m. p. 80—104° and this was rejected. The remaining fractions were combined (4·43 g.; m. p. 100—109°) and crystallised from ethanol. The quality of the almost colourless *2,2′-dinitro-*p*-terphenyl* (4 g., 31%), m. p. 109—110° (Found: C, 67·4; H, 3·5; N, 9·2. $C_{18}H_{12}N_2O_4$ requires C, 67·5; H, 3·75; N, 8·75%) was not improved by further crystallisation.

*4,3′-Dinitro-*p*-terphenyl.*—4-Acetamidobiphenyl (10·5 g.) was dinitrated [10] and the product crystallised from acetic acid (300 ml.) to give 4-acetamido-3,4′-dinitrobiphenyl (8·5—9·0 g.; m. p. 238—240°). 3,4′-Dinitro-4-*N*-nitrosoacetamidobiphenyl, prepared by the usual procedure from the acetylamine (10 g.), was filtered off after the nitrosation mixture had been poured into iced water. The nitroso-compound was pressed dry, and condensed in the usual manner with benzene (500 ml.) by stirring them for 5·5 days. A solution of the solvent-free residue in benzene was passed down a column of alumina (300 g.). The nitro-compound, eluted with benzene (2 l.), crystallised from benzene and then from acetic acid to yield slightly yellow 4,3′-dinitro-*p*-terphenyl (Found: C, 67·25; H, 4·0; N, 8·9%) (6%), m. p. 177—177·5°. France, Heilbron, and Hey [2] record the m. p. 174—175°.

*2,3′-Dinitro-*p*-terphenyl.*—The acetic acid liquors from the crystallisation of 4-acetamido-3,4′-dinitrobiphenyl were poured into water (1 l.), and the precipitate filtered off. Attempts to isolate pure 4-acetamido-3,2′-dinitrobiphenyl from this material, by crystallisation, were unsuccessful. The filtrate from a hot suspension of 15·5 g. of the product in benzene (260 ml.) was passed through a column of alumina (350 g.). Almost pure dinitroacetylamine (3—4 g.) was contained in the first 1·2 l. of eluate (benzene). Further elution (1 l.) gave impure material (1—2 g.) which was added to the chromatogram on the next batch of material. Crystallisation of the nearly pure material from alcohol and pyridine (3 : 1) gave bright yellow needles, m. p. 162—162·5°, in an overall yield of 11% (Found: C, 56·2; H, 3·5; N, 14·4. Calc. for $C_{14}H_{11}N_3O_5$: C, 55·8; H, 3·7; N, 13·95%). Finzi and Bellavita [5] record the m. p. 160—161°. 4-Acetamido-3,2′-dinitrobiphenyl was also obtained by nitrating 4-acetamido-2′-nitrobiphenyl according to the method [10] for the dinitration of 4-acetamidobiphenyl. The crude nitration product (94%) melted at 158·5—159°.

The acetyl derivative was readily hydrolysed by refluxing it for 15 min. with 70% w/w sulphuric acid, though Finzi and Bellavita [5] reported no deacetylation under such conditions. Alkaline hydrolysis of the acetylamine is, however, preferable: the acetylamine (0·54 g.) in ethanol (19 ml.) was treated according to the method [8] for hydrolysing 4-acetamido-3-nitrobiphenyl; the yield of *4-amino-3,2′-dinitrobiphenyl* (orange-yellow needles), m. p. 170—170·5°, was 0·41 g. (88%), (Found: C, 55·8; H, 3·6; N, 16·0. $C_{12}H_9N_3O_4$ requires C, 55·6; H, 3·5; N, 16·2%).

2,3′-Dinitro-4′-*N*-nitrosoacetamidobiphenyl, prepared by the general nitrosation procedure from the acetylamine (15 g.), and isolated as described for 3,4′-dinitro-4-*N*-nitrosoacetamidobiphenyl, was condensed with benzene (500 ml.) by stirring them for 4 days. The solvent-free residue, dissolved in benzene, was adsorbed on a column of alumina (250 g.). The eluted nitro-compound was contaminated with an orange impurity, which was readily removed by further chromatography on alumina. The product crystallised from alcohol, yielding slightly yellow *2,3′-dinitro-*p*-terphenyl* (6%), m. p. 118—119°. Further crystallisation raised the m. p. to 119·5—120·5° (Found: C, 67·2; H, 3·9; N, 8·8. $C_{18}H_{12}N_2O_4$ requires C, 67·5; H, 3·75; N, 8·75%).

*Nitration of Dinitro- to Trinitro-*p*-terphenyls.*—Fuming nitric acid (13 ml.; *d* 1·51) was added during 1—1·5 min. to a solution or suspension of the dinitro-compound (0·5 g.) in acetic acid (21·5 ml.), initially at 111° (bath-temperature 114°). The mixture was shaken occasionally and, after a total reaction time of 15 min., the solution was poured into water (70 ml.). After

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[10] Le Fèvre and Turner, *J.*, 1928, 253.

cooling, the precipitate (pale yellow or colourless) was filtered off, washed with water, 5N-aqueous ammonia, and again with water. The average yield of crude product was 98%.

4,2′,4″-*Trinitro*-p-*terphenyl.* The crude product, m. p. 189—191°, from the nitration of 4,4″-dinitro-*p*-terphenyl was crystallised from xylene (10 ml.), and washed with benzene. The yield of 4,2′,4″-trinitro-*p*-terphenyl,[1] m. p. 194—195°, was 0·46 g. (81%).

2,3′,4″- *and* 4,2′,4″-*Trinitro*-p-*terphenyl.* The crude product, m. p. 154°, from the nitration of 4,2′-dinitro-*p*-terphenyl (1 g.) was crystallised twice from benzene, yielding 4,2′,4″-trinitro-*p*-terphenyl (41%), m. p. 193·5—194° undepressed on admixture with the product obtained from 4,4″-dinitro-*p*-terphenyl. The infrared spectra of the two solids were identical (C–NO_2 absorption bands occurred at 1347 and 1520 cm.$^{-1}$).

The mother-liquors and the benzene washings from the first crystallisation were adsorbed on alumina (60 g., 26 × 1·7 cm.), and the chromatogram developed with benzene. The pale yellow colour of the adsorbed nitro-compounds was only just visible. The 2,3′,4″-trinitro-isomer was eluted first, and the best material, m. p. 178—180°, was contained in the fifth to tenth of the 50-ml. volumes of eluate collected. Crystallisation from benzene gave 2,3′,4″-*trinitro*-p-*terphenyl*, m. p. 179·5—180° (Found: C, 59·3; H, 2·9; N, 11·3. $C_{18}H_{11}N_3O_6$ requires C, 59·2; H, 3·0; N, 11·5%), in 23% yield.

2,2′,2″-*Trinitro*-p-*terphenyl.* The crude product, m. p. 158—159°, from the nitration of 2,2″-dinitro-*p*-terphenyl crystallised from benzene–light petroleum (b. p. 60—80°), to give the pale yellow, poorly crystalline 2,2′,2″-*trinitro*-p-*terphenyl*, m. p. 159—159·5° (Found: C, 59·3; H, 3·1; N, 11·7%), in 61% yield. This isomer is light sensitive.

2,2′,2″- *and* 2,2′,4″-*Trinitro*-p-*terphenyl.* Nitration of 2,2′-dinitro-*p*-terphenyl (1 g.) gave a low-melting product which crystallised from benzene. These crystals melted sharply at 148°, but the melt effervesced and this behaviour persisted after two further crystallisations from benzene. When this material was kept for one month, the m. p. gradually rose to 151—153°, and if it was melted on a microscope slide for a short time, the m. p. of the solidified melt was 164·5°, and the melt was clear. The occlusion of benzene in the crystals appeared to explain the melting behaviour, and the analytical figures (Found: C, 61·6; H, 3·3; N, 10·8. Calc. for $C_{18}H_{11}N_3O_6$: C, 59·2; H, 3·0; N, 11·5%) correspond to an approximate molar ratio of trinitro-compound to benzene of 3 : 1. When this material was crystallised from alcohol–acetone, or was dissolved in benzene or alcohol and recovered by rapid evaporation, the product melted from 150°. The upper m. p. was indefinite (>180°) owing to the dark colour and mistiness of the melt.

The crude product from a second nitration was crystallised four times from acetic acid. The m. p.s from the last three crystallisations were constant at 164°, but the melts were cloudy. Solvent occlusion may again be responsible for this behaviour, although the liquors from the second and third crystallisations slowly deposited pale yellow needles, m. p. 164—165°, giving a clear melt. The m. p. of 2,2′,4″-*trinitro*-p-*terphenyl* appears to be 164—165°, and a mixture of this product with 2,2′,2″-trinitro-*p*-terphenyl, m. p. 160—161°, also present in the crude nitration product, gave a large m. p. depression. The 2,2′,4″-trinitro-isomer (Found: C, 59·2; H, 3·4; N, 11·6. $C_{18}H_{11}N_3O_6$ requires C, 59·2; H, 3·0; N, 11·5%) is also very light-sensitive, and no accurate assessment of the yield can be given, because of the preparative difficulties encountered.

The liquors from the first crystallisation of the product from the first nitration were adsorbed on alumina (60 g., 26 × 1·7 cm.); elution was carried out with benzene, and 50 ml. fractions were collected. In view of the light-sensitivity of the material, it is imperative that the column should be covered with thick paper throughout the separation. The 2,2′,2″-trinitro-isomer was eluted first, and these fractions containing material of m. p. 158—159·5° were combined and evaporated to dryness, and the residue was crystallised from benzene. The 2,2′,2″-trinitro-*p*-terphenyl, m. p. 160—161° (Found: C, 59·3; H, 3·0; N, 11·5%), was obtained in 17% yield and was identical with the product, m. p. 159—159·5°, obtained by nitration of 2,2″-dinitro-*p*-terphenyl, as shown by a mixed m. p. and a comparison of the infrared spectra (C–NO_2 absorption at 1347 and 1515 cm.$^{-1}$).

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