## **311.** *The Nitration of* p-*Terphenyl in Glacial Acetic Acid.*

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The nitration of *p*-terphenyl in glacial acetic acid with fuming nitric acid has been studied, and reproducible reaction conditions are given for the preparation of 4-nitro-, 4,4''-dinitro-, and 4,2',4''-trinitro-*p*-terphenyl. Methods previously reported in the literature for the preparation of these compounds are discussed, and, for the first time, 2- and 2'-nitro-*p*-terphenyl have been isolated by chromatography from the liquors of the mononitrations. The constitutions of the mononitro-isomers have been verified by unambiguous syntheses.

France, Heilbron, and Hey[1] have described the preparation of 2- and 4-nitro-, 4,3'- and 4,4''-dinitro-, and 4,2',4''-trinitro-*p*-terphenyl by unambiguous routes. With these reference compounds available, they then studied the nitration of *p*-terphenyl in different media. For example, the hydrocarbon was nitrated at 100° with fuming nitric acid (*d* 1·5) in glacial acetic acid to yield 4,4''-dinitro-*p*-terphenyl (43%), m. p. 272—273°, together with 4,2',4''-trinitro-*p*-terphenyl (28%), m. p. 193—194°, which was obtained by dilution of the nitration mixture after separation of the dinitro-derivative. On the other hand, nitration with fuming nitric acid (*d* 1·5) in acetic anhydride at 45—50° gave 4,4''-dinitro-*p*-terphenyl (68%), m. p. 272—273°. The authors comment that neither in these reactions nor in any other nitration experiments which they carried out was any mononitro-*p*-terphenyl isolated, even under nitration conditions which would have been suitable for the mononitration of biphenyl.

In our hands, neither the nitration in glacial acetic acid nor that in acetic anhydride gave pure 4,4''-dinitro-*p*-terphenyl, and the liquors from the acetic acid nitration did not contain the trinitro-isomer.

The nitration in acetic acid seemed the more promising, and a large number of nitrations were carried out in this medium in order to ascertain the influence of several variables upon the nature, yield, and melting point of the nitration product. A standard procedure, described in the Experimental section, was adopted in all cases, so that the results would be as comparable as possible.

With these standard conditions and an addition time within the limits 60—90 sec., the effect of increasing the volume of nitric acid over the range 0—70 ml. was first studied. The results are summarised in the Figure where the m. p.s and yields of the crude and crystallised products are plotted against the volumes of fuming nitric acid employed.

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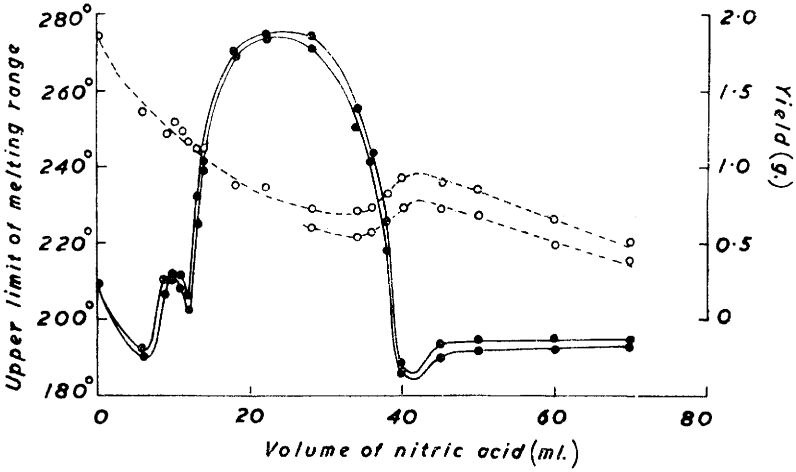
[1] France, Heilbron, and Hey, *J.*, 1938, 1364.

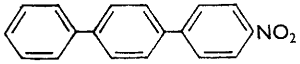
The full curves for the m. p.s * of the crystallised (upper curve) and crude (lower curve) products each show two well-defined maxima. The first, occurring between 10 and 11 ml. of nitric acid, corresponds to the m. p. of 210—211·5° of 4-nitro-*p*-terphenyl (I). The volume of nitric acid required for mononitration is therefore critical. The second, broader maximum corresponds to the m. p. of 272—274·5° of 4,4''-dinitro-*p*-terphenyl (II), which is obtained in a pure state over a much wider range of nitric acid volumes (22—28 ml.). The product obtained with about 50 ml. of nitric acid is 4,2',4''-trinitro-*p*-terphenyl (III), m. p. 194—194·5°. The same product is obtained with 70 ml., and the volume of fuming nitric acid required for its formation is not at all critical. This is to be expected, since each ring in the *p*-terphenyl molecule then contains one nitro-group, and the whole molecule will be deactivated to further substitution under these conditions.

*Plots of the upper limits of the melting ranges (full lines) and the yields (broken lines) of the nitration products against the volumes of fuming nitric acid. (For the meaning of the duplicate lines see the text).*

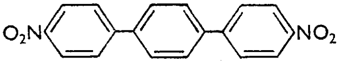


The minima in the m. p. curves, on either side of the maxima for mono- and di-nitration, correspond, in order of their appearance with increasing volumes of nitric acid, to mixtures of (*a*) *p*-terphenyl and (I), (*b*) (I) and (II), and (*c*) (II) and (III). The interpretation of these m. p. curves has been fully substantiated by obtaining the m. p.s of each of these binary mixtures over a range of composition, and plotting these m. p.s against the percentage composition for each mixture.

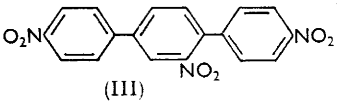
At this stage, it is convenient to mention that, while maintaining the volume of nitric acid constant at 24 ml., the following points were established: (*a*) When the internal reaction temperature was raised from 99° to 116·5°, the composition of the product passed from (II) + 20% of (I) to (II) + large quantities of (III). (*b*) When the volume of glacial acetic acid was reduced from 190 to 80 ml., the composition of the product changed from (II) + 40% of (I) to (II) + considerable quantities of (III). (*c*) Decreasing the total reaction time and increasing the rate of addition of the nitric acid were not at all critical. For example, an increase in addition time from 7 sec. to 7 min. was necessary in order to give a noticeable effect on the m. p. of the product.



(I)



(II)



(III)

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* Mixed products melted over a range of temperature, and in these cases the m. p.s plotted represent the upper limits of the melting ranges.

The conditions employed by France, Heilbron, and Hey,[1] by which they obtained a 43% yield of the dinitro-compound (II) from the hydrocarbon, appear at first sight to be equivalent to ours using acetic acid (120 ml.) and fuming nitric acid (14·5 ml.), conditions which yield mainly the mononitro-compound (I). Moreover, their lower reaction temperature of 100° would further favour the formation of mononitro-isomers. An experiment using their conditions did give mainly mononitration. Since France, Heilbron, and Hey obtained no mononitro-isomers, and isolated the trinitro-compound (III) from the liquors of such nitrations, their fuming nitric acid must have been a much more powerful nitrating agent than ours, although we both record a density of 1·5 for the acid. The fuming nitric acid used in the present experiments had $d_4^{15}$ 1·5 and contained 94 ± 0·5% of $HNO_3$. This acid did contain 0·5% of nitrous acid (estimated volumetrically), which would retard our nitrations relative to those of France, Heilbron, and Hey if their acid contained a lower concentration of nitrous acid.

It is clearly demonstrated by our experiments that *p*-terphenyl can be successfully nitrated in glacial acetic acid to give 4-nitro-*p*-terphenyl. Moreover, the liquors from such mononitrations have yielded 2-nitro-*p*-terphenyl (5—9%) and 2′-nitro-*p*-terphenyl (0·5%). The 2-nitro-isomer had already been prepared by France, Heilbron, and Hey[1] from 2-nitro-4′-*N*-nitrosoacetamidobiphenyl and benzene, and the 2′-nitro-isomer by Basford[2] by dehydrogenation of 2-nitro-4-cyclohexylbiphenyl. The 2-, 2′-, and 4-nitro-*p*-terphenyls were, however, again synthesised by unambiguous routes in order to verify that these products had been obtained, in the case of the 2- and 2′-nitro-derivatives for the first time, by direct nitration of the hydrocarbon. The low yields of the 2- and the 2′-isomer arise from the poor separation which is achieved on an alumina chromatogram, and quantitative work now being undertaken on the ratio of the mononitro-isomers shows that much larger quantities of these *ortho*-isomers are in fact produced.

The critical dependence of mononitration upon the volume of nitric acid means that the method of nitration in glacial acetic acid is of limited value for the preparation of 4-nitro-*p*-terphenyl (I). However, details have been included in the Experimental section for the mononitration of the hydrocarbon (12 g.). The yield of (I) was 52—54%. Allen and Burness[3] have reported that the 4-nitro-isomer is obtained in good yield (72%) by nitrating a suspension of the hydrocarbon in acetic acid with a mixture of red and yellow fuming nitric acid, and this method will be referred to below.

The broken curves in the Figure indicate the change in yield of nitration product (crude material, upper curve; crystallised material, lower curve) with increasing volume of nitric acid. The lower curve is not shown for volumes of acid less than 30 ml., since in these experiments the products supersaturated on crystallisation, and the yields were variable. As nitration proceeds to an increasing extent up to 10·5 ml. of acid, the yield curve falls.

Quantitative data to be published will show that the nitration of *p*-terphenyl in glacial acetic acid gives 60% of the 4-nitro-isomer. This figure agrees with our practical yield of 52—54% of (I), and if the nitration of *p*-terphenyl is assumed to give the same ratio of *ortho*- to *para*-isomers as biphenyl,[4,5] the yield of (I) would indeed be expected to be about 60%. The yield of 72% reported by Allen and Burness[3] seems high, though their conditions may give a different isomer ratio. Commercial red fuming nitric acid could not be purchased in order to reproduce their procedure, but using yellow fuming nitric acid, through which nitrous fumes had been passed, a yield of 57—60% of (I) was obtained, agreeing with the yield by our method and with that predicted on the basis of biphenyl.

As the volume of fuming nitric acid is increased from 10 to 28 ml., only pure (I) or (II) or a mixture of the two compounds is isolated, other mono- and di-nitro-isomers remaining

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[2] Basford, *J.*, 1937, 1440.

[3] Allen and Burness, *J. Org. Chem.*, 1949, **14**, 175.

[4] Bell, Kenyon, and Robinson, *J.*, 1926, 1239.

[5] Jenkins, McCullough, and Booth, *J. Ind. Eng. Chem.*, 1930, **22**, 31.

dissolved in the cold nitrating medium. Since the dinitroterphenyl (II) must arise from the 4-nitro-*p*-terphenyl, and if the latter gives the same ratio of *ortho*- to *para*-isomers as does 4-nitrobiphenyl,[6] the optimum yield of 4,4''-dinitro-*p*-terphenyl would be about 30%, agreeing with our practical yields for the dinitration. The 43% yield obtained by France, Heilbron, and Hey [1] for the dinitration in acetic acid is somewhat greater than this, and their yield in acetic anhydride is considerably greater. The latter is surprising, and does not agree with our preliminary quantitative data which indicate a higher percentage of *ortho*-substitution in acetic anhydride than in acetic acid.

Since this work was undertaken, an excellent method for preparing 4,4''-dinitro-*p*-terphenyl has been published by VanAllan.[7] Nitration in nitrobenzene gives a 59% yield, although our yields by this process again lay between 30 and 32·5%.

The shapes of the yield curves for volumes of nitric acid in excess of 35 ml. are difficult to explain satisfactorily, particularly in the range 35—45 ml. of acid, where an increase in yield is observed. In this range, the product is a mixture of di- and tri-nitro-compounds, and gives marked supersaturation. The fall in yield with volumes greater than 45 ml. of acid is probably due to the fact that, although the trinitro-compound is produced in all cases, its solubility increases with increasing concentration of the fuming nitric acid.

It has also been found that the fuming nitric acid used in the present work did not give the results obtained by France, Heilbron, and Hey [1] for the following nitrations: (*a*) nitration in fuming nitric acid at 100° of (I) to (II) (1 hr.), of (II) to (III) (15 min.), and of 4,3'-dinitro-*p*-terphenyl (a synthetic product) to (III) (2 hr.); (*b*) nitration of the hydrocarbon in fuming nitric acid alone (initially at room temperature, but rising to 75°), reported to give a 100% yield of (III); (*c*) nitration of the hydrocarbon in concentrated nitric acid–sulphuric acid–water medium at 45—50°, quoted as giving a 50% yield of (III).

In all cases, our acid gave less extensive nitration, suggesting again that the acid used by France, Heilbron, and Hey was a stronger nitrating agent. The 100% yield of (III) reported in (*b*) is interesting, and requires that no nitration occurs, under these conditions, at the 2-position, which is shown by our quantitative data to be appreciably reactive.

## EXPERIMENTAL

*Standard Nitration Procedure.*—A three-necked flask (500 ml.) fitted with a stirrer, condenser, and thermometer, and containing powdered *p*-terphenyl (2 g.) in glacial acetic acid (120 ml.) was heated in an oil-bath, also equipped with a stirrer and thermometer, until the hydrocarbon dissolved. The temperature of the solution was adjusted to 111°, and a given volume of fuming nitric acid (*d* 1·5) was delivered through a filter-funnel plugged with asbestos and glass wool previously moistened with fuming nitric acid. The compactness of the plug was adjusted in accordance with the required addition time. After a total time of 15 min., the reaction mixture was cooled rapidly to 0°, and the precipitate collected in a sintered-glass funnel. The product was washed with glacial acetic acid (2 × 10 ml.), water (4 × 10 ml.), and 96% ethanol (2 × 5 ml.). The moist solid was dissolved in nitrobenzene (24 ml.), and the solution cooled to 25—26°. The crystals were washed with 96% ethanol (2 × 5 ml.), and dried, and the yield and m. p. were recorded. With volumes of fuming nitric acid greater than 40 ml., it was necessary to cool the reaction mixture to −8°, and reproducible results were obtained only if the vessel walls were scratched continuously for 15 min. to minimise supersaturation of the product. The solvent for crystallisation was changed to xylene (20 ml.), and benzene was used for washing the crystals.

4-*Nitro*-p-*terphenyl: Nitration in Glacial Acetic Acid.*—Fuming nitric acid (60 ml.; *d* 1·5) was added in 1—1·5 min. to a stirred solution of *p*-terphenyl (12 g.) in glacial acetic acid (720 ml.) at 111° (bath-temperature 115°). After a total time of 15 min., the precipitate was filtered off and washed (see standard procedure). The crude product (7·4—7·8 g., 52—54%), m. p. 206—210°, crystallised from nitrobenzene, giving very pale yellow, poorly crystalline 4-nitro-*p*-terphenyl, m. p. 210—211·5°. The conditions for the nitration are critical. Under-nitration

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[6] Gull and Turner, *J.*, 1929, 491.

[7] VanAllan, *J. Org. Chem.*, 1956, **21**, 1154.

of the hydrocarbon gives a crude product which is difficult to filter off, whilst the liquors from the filtration of an over-nitrated product give a small amount of gum, together with solid product, when diluted with water.

4-*Nitro*-p-*terphenyl: Nitration by Red Fuming Nitric Acid.*—The method is based on that of Allen and Burness.[3] Nitrous fumes, prepared by warming a mixture of concentrated nitric acid and starch, were dried ($CaCl_2$) and bubbled into fuming nitric acid (*d* 1·505) maintained at about 10°. Eventually, two layers formed, and a portion of the lower layer (5 ml.) was added to fuming nitric acid (2·5 ml.; *d* 1·505). This mixture was added in 3 min. to a stirred suspension of powdered *p*-terphenyl (11·5 g.) in glacial acetic acid (35 ml.) at 95°. Nitrous fumes were evolved copiously. After 30 min. at 95—98°, the reactants were cooled to 30°, and the product was filtered off and washed with acetic acid, water, and ethanol. The crude product (7·8—8·2 g., 57—60%), m. p. 199—207°, crystallised from nitrobenzene to give 4-nitro-*p*-terphenyl, m. p. 204—208°.

4-*Nitro*-p-*terphenyl: From 4′-Nitro*-4-N-*nitrosoacetamidobiphenyl.*—Crude 4,4′-dinitrobiphenyl[6] was reduced to 4-amino-4′-nitrobiphenyl,[8] which was obtained in a yield of 48%, with m. p. 195—198·5° after crystallisation from ethanol. The acetyl derivative, m. p. 236—239° (from acetic acid), was obtained in 93% yield. The 4-acetamido-4′-nitrobiphenyl (9 g.) and sodium acetate (9 g. of the fused salt) were dissolved in hot glacial acetic acid (135 ml.) and acetic anhydride (67·5 ml.), and nitrosated with nitrosyl chloride; the procedure used was that described for 3-fluoro- and 3-iodo-4-octyloxyacetanilides.[9] The solid *N*-nitroso-compound was extracted with benzene (500 ml.), a fair amount of undissolved, unused acetyl-amine being discarded. After the reaction and removal of the benzene, the residue was distilled at 0·06 mm. Part of the 4-nitro-*p*-terphenyl (1 g.; m. p. 188—200°) sublimed at about 100°, and the remainder (2·7 g.) distilled at an indefinite temperature (about 200°). Crystallisation of the combined fractions from nitrobenzene gave 4-nitro-*p*-terphenyl (2·1 g., 22%), m. p. 209—210°, undepressed on admixture with the same compound obtained by nitration.

4,4″-*Dinitro*-p-*terphenyl: Nitration in Glacial Acetic Acid.*—Fuming nitric acid (60 ml.; *d* 1·5) was added all at once to a stirred solution of *p*-terphenyl (8 g.) in glacial acetic acid (300 ml.) at 115°. After the initial heat of reaction had subsided, the temperature was maintained at 113—114° for a total reaction time of 7 min., after which the reactants were cooled to 0°, and the product was filtered off and washed with acetic acid, water, and ethanol. The crude product (3·58 g., 32%), m. p. 270·5—274°, crystallised from nitrobenzene to give bright yellow needles of 4,4″-dinitro-*p*-terphenyl, m. p. 272—274·5°. France, Heilbron, and Hey record the m. p. 272—273°.

4,4″-*Dinitro*-p-*terphenyl: Nitration in Nitrobenzene.*—The method of VanAllan[7] gave the 4,4″-dinitro-*p*-terphenyl, m. p. 272—274·5°, in 30—32·5% yield after crystallisation.

2- *and* 2′-*Nitro*-p-*terphenyls: From Mononitration Liquors.*—The liquors from the preparation of 4-nitro-*p*-terphenyl by nitration in glacial acetic acid, together with the washings of the crude product, were diluted with water (1·5 l.). The dried product (20 g.) was dissolved in benzene and adsorbed on a column of alumina (800 g.). Elution was carried out with benzene, and fractions (each of 50 ml.) were collected from the chromatogram. The first fraction (0·7—1·2 g.), m. p. 106—118°, gave colourless prisms of 2′-nitro-*p*-terphenyl (0·2 g., 0·5%), m. p. 129·5—130°, after three crystallisations from benzene. The second fraction consisted of a mixture of 2- and 2′-nitro-*p*-terphenyl (3 g.), m. p. 105—107°. The next eleven fractions were combined to give material (10 g.) of upper m. p. limits 113—124°. This was crystallised from benzene and then from benzene–ethanol (1 : 5), to give bright yellow blades of 2-nitro-*p*-terphenyl (2—4 g., 5—9%), m. p. 127·5—128°. Further elution of the column gave crude 4-nitro-*p*-terphenyl, followed by yellow gums or solids, probably mixed dinitro-*p*-terphenyls.

2-*Nitro*-p-*terphenyl: From 2-Nitro-4′*-N-*nitrosoacetamidobiphenyl.*—(a) *2,4′-Dinitrobiphenyl.* 2-Nitrobiphenyl (25 g.) was added all at once to stirred concentrated nitric acid (340 ml.; *d* 1·42). Fuming nitric acid (225 ml.; *d* 1·50) was then added in about 10 min., and the solution stirred for a further 15 min., the temperature being maintained throughout at about 35°. Water (195 ml.) was then added with cooling. The 2,4′-dinitro-isomer was allowed to crystallise, and was filtered off when the temperature reached 17—18°, or at a somewhat higher temperature if very small spherulites (presumably the 2,2′-isomer) appeared among the pale yellow needles

[8] Marler and Turner, *J.*, 1931, 1361.
[9] Gray and Worrall, *J.*, 1959, 1545.

of the desired product. After washing with concentrated nitric acid and then with water, the yield was 8—10 g., m. p. 78—93°. Crystallisation from a mixture of fuming nitric acid (10 ml./g.) and water (7 ml./g.) gave 2,4′-dinitrobiphenyl (6—8 g., 20—26%), m. p. 93·5—94·5° Gull and Turner [6] give m. p. 92·5—93·5°.

(b) 4-Amino-2′-nitrobiphenyl was prepared from 2,4′-dinitrobiphenyl by the method employed [8] for the selective reduction of 4,4′-dinitrobiphenyl. After crystallisation from methanol, the crude product, m. p. 94—96°, was obtained in 39—53% yield. Recrystallisation raised the m. p. to 97—97·5°, in agreement with the m. p. of 100° reported by Walls.[10] When the residue from the hydrochloric acid extractions of the nitro-amine was extracted with benzene and the solution was concentrated, orange-yellow needles (1·3%), m. p. 207—208°, were obtained. This product did not undergo the benzidine rearrangement with concentrated hydrochloric acid, and a solution in acetic acid was not oxidised by hydrogen peroxide, even in several days. It is likely that the product is 4-*azoxy-2′-nitrobiphenyl,* and not the corresponding azo- or hydrazo-compound. Further evidence is given by the combustion analyses [Found: C, 66·0; H, 3·5; N, 13·0%; *M* (Rast), 419. $C_{24}H_{16}O_5N_4$ requires C, 65·4; H, 3·7; N, 12·7%; *M*, 440. $C_{24}H_{16}O_4N_4$ requires C, 67·9; H, 3·8; N, 13·2%; *M*, 424. $C_{24}H_{18}O_4N_4$ requires C, 67·6; H, 4·2; N, 13·1%; *M*, 426].

(c) 4-Acetamido-2′-nitrobiphenyl was obtained by normal methods of acetylation. The product was crystallised from 50% aqueous alcohol, the yield being 94%, and the m. p. 153—154°. France, Heilbron, and Hey [1] record m. p. 152—153°.

(d) 2-*Nitro*-p-*terphenyl.* 4-Acetamido-2′-nitrobiphenyl (14·85 g.) was nitrosated and condensed with benzene in the manner described above for 4-acetamido-4′-nitrobiphenyl. One-third of the residue obtained on removal of the solvent from the reaction mixture was dissolved in benzene and run down a column of alumina (70 g.). Elution with benzene gave crude 2-nitro-*p*-terphenyl (3·3 g.), m. p. up to 125·5°. One crystallisation from benzene–methanol gave bright yellow blades (2·5 g., 47%), m. p. 126·5—127·5°. Further crystallisation raised the m. p. to 127·5—128° (Found: C, 78·6; H, 5·1; N, 5·0. Calc. for $C_{18}H_{13}O_2N$: C, 78·5; H, 4·8; N, 5·1%), undepressed on admixture with 2-nitro-*p*-terphenyl obtained by nitration of the hydrocarbon. France, Heilbron, and Hey [1] record the m. p. 127—128° for 2-nitro-*p*-terphenyl.

2′-*Nitro*-p-*terphenyl.*—4-Acetamido-3-nitrobiphenyl, m. p. 132—133°, was prepared [11] from 4-acetamidobiphenyl, m. p. 167—169°. An attempt to prepare 2′-nitro-*p*-terphenyl from 3-nitro-4-*N*-nitrosoacetamidobiphenyl and benzene was however unsuccessful. 4-Acetamido-3-nitrobiphenyl was therefore deacetylated [11] and the 2′-nitro-*p*-terphenyl obtained from the 4-amino-3-nitrobiphenyl by the Gomberg reaction.

Concentrated sulphuric acid (8·3 ml.) was slowly added to a boiling solution of 4-amino-3-nitrobiphenyl (21·4 g.) in glacial acetic acid (107 ml.). A vigorous reaction occurred. The reactants were cooled, and the yellow suspension of the amine sulphate was stirred at 18—22° during gradual addition of nitrosylsulphuric acid [75 ml., 1·3 equivalents of a solution prepared by dissolving sodium nitrite (20·7 g.) in concentrated sulphuric acid (166 ml.)]. After the addition, the reactants were stirred for 1 hr., then a further quantity of nitrosylsulphuric acid (15 ml.) was added. After a few minutes, the viscous mixture was poured on ice (250 g.), and the vigorously stirred mixture, maintained at 6—10°, was neutralised with 10N-aqueous sodium hydroxide. Much solid was deposited, and water (400 ml.) was added to prevent the formation of a thick slurry. When the end-point had been reached, an excess of sodium hydroxide solution was added, the flask was loosely corked, and stirring was continued for 80 hr., the reaction being allowed to proceed at room temperature (18—21°) after the first 1·5 hr. The mixture was filtered, and the residual salts were washed with benzene (200 ml.), the washings being added to the filtrate. The benzene layer was separated from the filtrate, washed twice with water, and dried, and the solvent removed by distillation. Decomposition occurred throughout the distillation of the residue, b. p. 200—220°/0·05—0·2 mm., and the distillate (10·2 g.) melted indefinitely in the range 100—115°. The 2′-nitro-*p*-terphenyl may be obtained by crystallisation of the distillate from ethanol, or preferably by chromatography on alumina, with benzene as solvent. The 2′-nitro-isomer is contained in the lowest, pale yellow region on the column, and two crystallisations from ethanol afforded the pure product (Found: C, 78·4; H, 5·1; N, 4·7. Calc. for $C_{18}H_{13}O_2N$: C, 78·5; H, 4·8; N, 5·1%), m. p.

[10] Walls, *J.*, 1947, 72.

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

129·5—130°, undepressed when mixed with the same product prepared by direct nitration. The m. p. reported by Basford [2] was 125°. The yield of 2′-nitro-*p*-terphenyl was 4·73 g. (17%). The above chromatogram also yielded 4-acetamido-3-nitrobiphenyl (7%), contained in a broad yellow zone, and 4-amino-3-nitrobiphenyl (1—2%), in a red band at the top of the column.

*4,2′,4″-Trinitro-*p*-terphenyl.*—Powdered *p*-terphenyl (6 g.) was suspended in boiling glacial acetic acid (72 ml.), the source of heat was removed, and fuming nitric acid (60 ml., *d* 1·505) was added in 2—3 min. The hydrocarbon dissolved during the vigorous reaction, and 2—3 min. after completing the addition, the solution was cooled and maintained at 0° for 15—30 min. The product (3·08 g., m. p. 189·5—192·5°) was filtered off, washed with acetic acid, water, and ethanol, and was crystallised from xylene, yielding pale-yellow needles of *4,2′,4″-trinitro-*p*-terphenyl*, 2·77 g. (29%), m. p. 194—194·5° (Found: C, 59·4; H, 3·0; N, 11·6. Calc. for $C_{18}H_{11}N_3O_6$: C, 59·2; H, 3·0; N, 11·5%). France, Heilbron, and Hey [1] record the m. p. 193—194°.

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