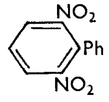
118. *The Ullmann Biaryl Synthesis. Part II.*[1] *The Effect of* m-*Dinitrated Diluents on the Self-condensation of Iodobenzene.*

By James Forrest.

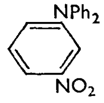
Compounds containing a *m*-dinitro-grouping are partly converted into derivatives of 2,6-dinitrobiphenyl (I) and 3-nitrotriphenylamine (II) on addition to the Ullmann reaction of an iodo-compound such as iodobenzene. The rate and course of the normal Ullmann reaction is further influenced by additional substituents in the nitrated material.

The formation of abnormal products, derivatives of 2,6-dinitrobiphenyl (I) and 3-nitrotriphenylamine (II), from Ullmann reactions between 1-chloro-2,4-dinitrobenzene, or one of its simple analogues, and iodo-compounds has been described in Part I of this series.[1] The present communication reports the Ullmann reaction of iodobenzene in the presence of non-halogenated materials containing *m*-dinitro- and allied groups in the molecule.

It has apparently been considered since the discovery of the Ullmann reaction that iodobenzene was unattacked by copper unless under pressure at temperatures above its boiling point.[2] Several instances, however, of the use of iodobenzene in unsymmetrical Ullmann syntheses at atmospheric pressure have been recorded.[3] Rule and Smith,[2] in reporting the synthesis of 2,4,6-trinitrobiphenyl (V; R = H) by the condensation of picryl chloride with iodobenzene at 160°, suggested that some form of special activation enabled the iodo-compound to partake in this type of reaction. This concept appeared inappropriate when applied to the reactions described in Part I, the nature of the abnormal products indicating, at least in part, independent reaction of the iodo-compound. Reinvestigation of the synthesis of biphenyl from iodobenzene by this means has shown, contrary to previous reports, that a slow but smooth conversion of iodobenzene was effected at its boiling point. The biaryl formed under these conditions was obtained free from secondary or resinous reaction products.



(I)



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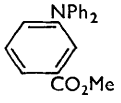
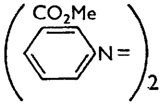


(III)



(IV)

(V)

Biphenyl formation, however, was considerably impeded by the addition of sufficient *m*-dinitrobenzene to the reactant to approximate to the conditions under which the unsymmetrical biaryls described in Part I were produced. Further, the formation of 2,6-dinitrobiphenyl (I) and 3-nitrotriphenylamine (II) in this reaction supported the theory that independent reaction of the iodo-compound was responsible for the analogous atypical products formed in these condensations. Comparable product patterns were obtained from a series of similar reactions, illustrated in Table 1, of iodobenzene in non-halogenated derivatives of *m*-dinitrobenzene. Isomers of the analogues of 2,6-dinitrobiphenyl produced in this way could not be characterised from any condensation. In the same way *p*-iodotoluene and *p*-iodoanisole respectively furnished similar unsymmetrical biaryls as by-products by interaction with *m*-dinitrobenzene. The corresponding triphenylamine derivative, however, could not be isolated from the reaction with the iodo-ether.

Replacement of one or both of the nitro-groups by a methoxycarbonyl substituent eliminated unsymmetrical biaryl formation. Thus methyl *m*-nitrobenzoate was converted into reduction products alone, 3-methoxycarbonyltriphenylamine (III), together with

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[1] Part I, preceding paper.

[2] Ullmann, *Annalen*, 1904, **332**, 38; Rule and Smith, *J.*, 1937, 1096; Mascarelli, Longo, and Ravera, *Gazzetta*, 1938, **68**, 33.

[3] For some examples see Fanta, *Chem. Rev.*, 1946, **38**, 139.

traces of 3,3′-dimethoxycarbonylazobenzene (IV). No product derived from methyl isophthalate could be detected.

TABLE 1.

No.	Aryl halide	Diluent	Copper (g.-equiv.)	Normal sym. biaryl (%) *	Abnormal unsym. biaryl (%) *	Deriv. of 2,6-dinitrobiphenyl	Reductive arylation (%) *	Deriv. of triphenylamine	Halide reacted (%) †
1	C_6H_5I	*m*-$C_6H_4(NO_2)_2$	1·3	22	8	Unsubst.	8	3-NO_2	56
2	,,	,,	1·9	25	7	,,	9	,,	65
3	,,	,,	2·3	23	8	,,	11	,,	76
4	,,	1,2,4-$C_6H_3Me(NO_2)_2$	1·3	9	3	3-Me	5	4-Me-3-NO_2	37
5	,,	1,3,5-$C_6H_3Me(NO_2)_2$	,,	0	4	4-Me	12	3-Me-5-NO_2	52
6	,,	1,3,4,6-$C_6H_2(Me)_2(NO_2)_2$	,,	0	1	3,5-Me_2	1	2,4-Me_2-5-NO_2	37
7	,,	1,2,4-$C_6H_3OMe(NO_2)_2$	,,	20	1	3-OMe	3	2-OMe-5-NO_2	71
8	,,	1,3,4,6-$C_6H_2(OMe)_2(NO_2)_2$	,,	27	1	3,5-$(OMe)_2$	5	2,4-$(OMe)_2$-5-NO_2	76
9	,,	1,3,5-$C_6H_3(NO_2)_3$	,,	0	12	4-NO_2	12	3,5-$(NO_2)_2$	78
10	,,	,,	,,	0	10	,,	3	,,	58 ‡
11	,,	*m*-$C_6H_4(CO_2Me)(NO_2)$	,,	0	0	—	7	3-CO_2Me	34
12	,,	*m*-$C_6H_4(CO_2Me)_2$	,,	0	0	—	0	—	33
13	*p*-C_6H_4IMe	*m*-$C_6H_4(NO_2)_2$	,,	32	2	4′-Me	8	4′,4″-Me_2-3-NO_2	70
14	*p*-$C_6H_4I{\cdot}OMe$	,,	,,	29	4	4′-OMe	0	—	87

* Based on halide reacted. † Calc. from recovered halide. ‡ Reaction for 2·5 hr. only.

With the exception of 1,3,5-trinitrobenzene, which is not comparable since the molecule contains more than one potential point of attack, conversion of the nitro-compound into unsymmetrical biaryl was maximal when there was no further substitution of the *m*-dinitrobenzene. A methyl or methoxyl group in position 4- or 6- of the dinitro-compound strongly suppressed this reaction. The marked drop in the yield of substituted 2,6-dinitrobiphenyl encountered on the introduction of a methoxyl group into the nitro-compound is also shown in Part I by comparison of the product patterns of the reactions between iodobenzene and 3-chloro-4,6-dinitroanisole or 1-chloro-2,4-dinitrobenzene severally. The introduction of methyl groups into the nitrated material, in particular *o*/*p* to the nitro-groups, as exemplified by 2,4-dinitrotoluene and 4,6-dinitro-*m*-xylene, markedly impeded the reaction of iodobenzene with copper, as well as unsymmetrical biaryl formation. The ester diluents, methyl isophthalate and methyl *m*-nitrobenzoate, also acted as powerful reaction suppressors. The Ullmann reaction of iodobenzene in 1,3,5-trinitrobenzene afforded, in addition to the expected product, 2,4,6-trinitrobiphenyl (V; R = H), a small quantity of the further substituted material, 2′,4′,6′-trinitro-*m*-terphenyl (V; R = Ph). Moreover, the product of reductive arylation, 3,5-dinitrotriphenylamine, was mixed with minor quantities of the partly *N*-arylated 3,5-dinitrodiphenylamine.

Self-condensation of the aryl iodide in this series was influenced in a regular pattern according to the nature of the additional substituents in the dinitrated diluent. Highest yields of the symmetrical biaryl were obtained from reactions in unsubstituted *m*-dinitrobenzene, and its 4-methoxy- and 4,6-dimethoxy-derivatives. The insertion of a methyl group into the diluent molecule suppressed the normal Ullmann reaction strongly. Thus only a small proportion of iodobenzene was converted into biphenyl in the presence of 2,4-dinitrotoluene, and the hydrocarbon could not be isolated at all after similar reactions in 3,5-dinitrotoluene or 4,6-dinitro-*m*-xylene. Methyl isophthalate and methyl *m*-nitrobenzoate also suppressed biphenyl formation completely.

The structures of 4′-methoxy- and 4′- and 4-methyl-2,6-dinitrobiphenyl were confirmed by comparison with the products of the Ullmann condensations of 1-chloro-2,6-dinitrobenzene with *p*-iodoanisole and *p*-iodotoluene, and of 4-chloro-3,5-dinitrotoluene with iodobenzene respectively. 3-Methoxy- and 3,5-dimethoxy-2,6-dinitrobiphenyl were identical with the methyl ethers obtained from 3-chloro- and 3,5-dichloro-2,6-dinitrobiphenyl by treatment with sodium methoxide. 3,5-Dinitro-di- and -tri-phenylamine were synthesised by *N*-arylation of 3,5-dinitroaniline by a modification of Goldberg's technique[4] for the synthesis of 3-nitrodiphenylamine.

Small quantities of certain substituted triphenylamines, however, required for comparison with some of the ambiguous products of reductive arylation of the nitro-group obtained in the present series of reactions, were conveniently prepared by the addition of the primary amine to the Ullmann self-condensation of the appropriate aryl iodide. Thus 2-methoxy-5-nitro- and 4-methyl-3-nitro-aniline, added to the reacting mixture of iodobenzene with copper, afforded the corresponding triphenylamine derivatives. Similarly, *m*-nitroaniline, added in reaction of *p*-iodotoluene, was fully arylated to 4,4′-dimethyl-3-nitrotriphenylamine. In some cases this reaction could even be extended to nitro-amines containing an activated halogen atom in the nucleus. For example, addition of 4-chloro-3-nitroaniline in the Ullmann self-condensations of iodobenzene and *p*-iodoanisole furnished, respectively, 4-chloro-3-nitrotriphenylamine and its 4′,4″-dimethoxy-derivative. A similar reaction with *p*-iodotoluene, however, failed to yield the required tertiary base.

EXPERIMENTAL

Iodobenzene was washed with dilute mineral acid and redistilled before use. Other general remarks apply as in Part I.[1]

General Procedure.—In the following series of reactions the condensing agent was added to the reactants in one portion, otherwise the procedure described in Part I was unchanged. Except where otherwise stated, reactions were carried out at 195° for 6 hr.

Reaction of Iodobenzene with Copper.—(a) *Undiluted.* The reaction of iodobenzene (76 g.) with copper (32 g.) gave inorganic material (66 g.), unchanged iodobenzene (19 g.), b. p. 40—50°/0·5 mm., and biphenyl (17·5 g.), b. p. 70—75°/0·5 mm. There was no distillation residue. Crystallisation of the crude biphenyl fraction from aqueous methanol gave the pure hydrocarbon (16·8 g.; 78%) in plates, m. p. 70°.

After only 1·5 hours' reaction the proportion of iodobenzene which reacted fell from 75% to *ca.* 40%. The yield of biphenyl from the converted material was unaffected.

(b) *In* m-*dinitrobenzene.* The organic product from iodobenzene (75 g.) and copper (32 g.) in *m*-dinitrobenzene (41·3 g.) yielded, after separation of copper salts, etc. (58 g.), iodobenzene (33 g.), biphenyl (3·4 g.), *m*-dinitrobenzene (35 g.), b. p. 105—115°/0·1 mm., and a red viscous oil containing suspended crystals (8·5 g.), of boiling range 155—200°/0·1 mm. A dark undistillable residue (2 g.) was discarded. The semi-crystalline product was dissolved in warm benzene (50 ml.), then light petroleum (50 ml.) was added with stirring. The pale yellow crystalline precipitate was filtered off when cool. Recrystallisation of the solid from ethyl acetate or acetone furnished almost colourless needles of 2,6-dinitrobiphenyl (3·5 g.), m. p. and mixed m. p. 189—190° (Found: N, 11·5. Calc. for $C_{12}H_8O_4N_2$: N, 11·5%). The original mother-liquors were chromatographed in benzene–light petroleum (1 : 1) and gave primarily an orange oil which crystallised from methanol in orange-yellow needles of 3-nitrotriphenylamine (2·5 g.), m. p. and mixed m. p. 78—79° (Found: C, 74·4; H, 4·8; N, 9·7. Calc. for

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[4] Goldberg, *Zentr.*, 1907, *II*, 1465.

$C_{18}H_{14}O_2N_2$: C, 74·5; H, 4·8; N, 9·7%). Final elution of the chromatogram with ethyl acetate gave 2,6-dinitrobiphenyl (0·3 g.).

A similar reaction in which 56 g. of copper were used yielded copper salts, etc. (91 g.), unchanged iodobenzene (18 g.), biphenyl (5 g.), the unsymmetrical biaryl (5·5 g.), and the triphenylamine derivative (4·5 g.). When 45 g. of copper were used under the same conditions the products were inorganic material (75·5 g.), iodobenzene (26 g.), biphenyl (4·5 g.), 2,6-dinitro biphenyl (4 g.), and 3-nitrotriphenylamine (3 g.).

(c) *In* 2,4-*dinitrotoluene.* Iodobenzene (76 g.) and copper (32 g.), in 2,4-dinitrotoluene (45·5 g.), yielded inorganic material (48 g.), unchanged iodobenzene (48 g.), biphenyl (1 g.), recovered diluent (38 g.), b. p. 115—125°/0·3 mm., then a viscous red oil (5·5 g.), of boiling range 150—200°/0·3 mm. A black undistillable residue (3 g.) was discarded. The red oil was chromatographed in benzene–light petroleum (3 : 2), yielding initially an oil (2·5 g.) which crystallised slowly from methanol in orange prisms of 4-*methyl*-3-*nitrotriphenylamine* (1·1 g.), m. p. 143—144° (Found: C, 75·3; H, 5·4; N, 9·5. $C_{19}H_{16}O_2N_2$ requires C, 75·0; H, 5·3; N, 9·2%). Further elution of the column gave a pale yellow oil (1·1 g.) which furnished stout colourless needles (from benzene–light petroleum) of 3-*methyl*-2,6-*dinitrobiphenyl* (1 g.), m. p. 112—113° (Found: C, 60·3; H, 4·0; N, 10·6. $C_{13}H_{10}O_4N_2$ requires C, 60·5; H, 3·9; N, 10·9%). Final elution of the chromatogram with ethyl acetate gave an uncrystallisable oil (1 g.).

(d) *In* 3,5-*dinitrotoluene.* Iodobenzene (28 g.) in 3,5-dinitrotoluene (17 g.) was treated with copper (12 g.) in the same way, yielding copper salts, etc. (20·5 g.), unchanged iodobenzene (13·5 g.), nitro-compound (13 g.), b. p. 110—120°/0·4 mm., and a red viscous oil (4 g.), b. p. 160—200°/0·4 mm. A dark residue (1 g.) was discarded. Treatment of the red oil with methanol–ethyl acetate gave crystals which furnished stout orange needles of 5-*methyl*-3-*nitrotriphenylamine* (1·25 g.), m. p. 167—168°, after a further crystallisation from ethyl acetate (Found: C, 74·8; H, 5·4; N, 9·4. $C_{19}H_{16}O_2N_2$ requires C, 75·0; H, 5·3; N, 9·2%). The original ethyl acetate–methanol mother-liquors were stripped of solvent, and the residue crystallised twice from benzene–light petroleum to give colourless needles of 4-*methyl*-2,6-*dinitrobiphenyl* (0·75 g.), m. p. 130—131° (Found: C, 60·4; H, 4·0; N, 10·6. $C_{13}H_{10}O_4N_2$ requires C, 60·5; H, 3·9; N, 10·9%). Chromatography of the mother-liquors in benzene–light petroleum (1 : 2) afforded successively further small quantities of the substituted triphenylamine (0·2 g.) and the nitro-biaryl (0·15 g.).

The structure of 4-*methyl*-2,6-*dinitrobiphenyl* was confirmed by comparison with the material, m. p. 130° (Found: N, 10·6%), obtained in 45% yield from the Ullmann condensation of 4-chloro-3,5-dinitrotoluene with iodobenzene at 185° for 2·5 hr.

(e) *In* 4,6-*dinitro*-m-*xylene.* Iodobenzene (76 g.), diluted with the dinitro-hydrocarbon (49 g.), on reaction with copper (32 g.), gave inorganic material (48 g.), unchanged aryl halide (48 g.), dinitroxylene (43 g.), b. p. 128—135°/0·5 mm., and a viscous red oil (4 g.), b. p. 170—190°/0·5 mm. A dark residue (3 g.) was discarded. Treatment of the red oil with methanol (15 ml.) deposited 3,5-*dimethyl*-2,6-*dinitrobiphenyl* (0·3 g.) in long colourless needles, m. p. 227° after a further crystallisation from ethyl acetate (Found: C, 61·9; H, 4·4; N, 10·1. $C_{14}H_{12}O_4N_2$ requires C, 61·8; H, 4·4; N, 10·3%). The methanolic mother-liquors were stripped of solvent and chromatographed in benzene–light petroleum (1 : 1), to give initially a yellow oil (2·2 g.) which deposited solid material in 2—3 days at 0° from methanolic solution. Recrystallisation of the crude solid from methanol–ethyl acetate gave small lemon-yellow needles of 4-6-*dimethyl*-3-*nitrotriphenylamine* (0·2 g.), m. p. 116—118° (Found: C, 75·2; H, 5·6; N, 9·1. $C_{20}H_{18}O_2N_2$ requires C, 75·5; H, 5·7; N, 8·8%). Further elution of the column gave an uncrystallisable red oil (1·2 g.).

(f) *In* 2,4-*dinitroanisole.* The product from iodobenzene (76 g.), in 2,4-dinitroanisole (50 g.), and copper (32 g.) yielded inorganic material (63 g.), iodobenzene (22 g.), biphenyl (4 g.), 2,4-dinitroanisole (40 g.), b. p. 150—160°/0·4 mm, and a viscous red oil (10·5 g.), b. p. 190—235°/0·4 mm. An undistillable dark resin (4 g.) was discarded. The viscous oil was chromatographed in benzene–light petroleum (1 : 1), affording primarily a red oil (5 g.) which during 3 days at 0° in methanol deposited a hard crystal mass. Recrystallisation of the latter from methanol–ethyl acetate (twice) gave bright yellow needles of 2-*methoxy*-5-*nitrotriphenylamine* (1·2 g.), m. p. 156—157° (Found: C, 71·0; H, 5·1; N, 8·5. $C_{19}H_{16}O_3N_2$ requires C, 71·3; H, 5·0; N, 8·8%). Continued elution of the column with the same solvent yielded a further quantity of the tertiary base (0·5 g.). Final elution of the partly exhausted chromatogram with benzene–ethyl acetate (4 : 1) gave a crude solid (1·9 g.) which, after 3 crystallisations from benzene–light petroleum, yielded almost colourless needles of 3-*methoxy*-2,6-*dinitrobiphenyl* (0·6 g.), m. p. 129—130° (Found: C, 56·6; H, 3·7; N, 10·2. $C_{13}H_{10}O_5N_2$ requires C, 56·9; H, 3·7; N, 10·2%).

The structure of 3-methoxy-2,6-dinitrobiphenyl was confirmed by comparison with an authentic sample prepared (yield, 70%) by refluxing 3-chloro-2,6-dinitrobiphenyl in methanolic sodium hydroxide for 2 hr. (Found: N, 10·2%).

4-*Methoxy*-3-*nitrotriphenylamine*, lemon-yellow plates, m. p. 107—108° (from methanol) (Found: C, 71·5; H, 5·0; N, 9·1%), which was prepared (yield 20%) by the action of methanolic sodium hydroxide on 4-chloro-3-nitrotriphenylamine (4 hr. at 100° in a sealed tube, followed by chromatography of the product in benzene–light petroleum), indicated that the methoxy-nitrotriphenylamine, m. p. 156—157°, was the 2-methoxy-5-nitro-isomer. This was confirmed by comparison with an authentic specimen, prepared as described later in this paper.

(g) *In* 1,3-*dimethoxy*-4,6-*dinitrobenzene.* The powdered product from iodobenzene (76 g.) and copper (32 g.) in the dinitro-ether (57·5 g.) yielded an insoluble residue (68 g.) after successive extractions with boiling chloroform (3 × 150 ml.) and acetone (2 × 100 ml.). The solvent was distilled from the combined chloroform extracts. The dark brown residual oil, when kept for 4—5 days, deposited mixed crystals which, after filtration from the viscous oily liquor and washing with methanol, were manually separated into large crystals of the dinitro-ether (12 g.) and small shining needles (4 g.), m. p. 150—180°. Recrystallisation of the latter (twice) from ethyl acetate afforded pale yellow prisms of 3,5-*dimethoxy*-2,6-*dinitrodiphenyl* (1·1 g.), m. p. 260—261° (Found: C, 55·1; H, 4·0; N, 9·5. $C_{14}H_{12}O_6N_2$ requires C, 55·3; H, 3·9; N, 9·2%). The original oily mother-liquor, on fractional distillation *in vacuo,* furnished iodobenzene (18 g.) and biphenyl (6 g.) successively. The distillation residue (10 g.) was stirred with warm methanol (75 ml.) and, when cool, the yellow precipitate was filtered off from the dark liquor. Recrystallisation of the solid from ethyl acetate (twice) gave yellow feathery needles which were transformed in some hours in the solvent into yellow prisms of 4,6-*dimethoxy*-3-*nitrotriphenylamine* (2·3 g.), m. p. 180—181° (Found: C, 68·4; H, 4·8; N, 8·3. $C_{20}H_{18}O_4N_2$ requires C, 68·6; H, 5·1; N, 8·0%).

The combined acetone extracts, after removal of solvent, gave a yellow heterogeneous solid residue (27 g.). Unchanged dinitro-ether (20 g.) was extracted from the latter by repeated treatment with boiling chloroform. The final insoluble residue (6·5 g.), a bright yellow powder, decomposed explosively at 250° and when shaken with dilute sulphuric acid gave a colourless solid which crystallised from aqueous methanol in needles of 3-methoxy-4,6-dinitrophenol (4 g.), m. p. and mixed m. p. 110—111° (Found: N, 12·9. Calc. for $C_7H_6O_6N_2$: N, 13·1%). The aqueous mother-liquors gave a positive test for copper.

The structure of 3,5-dimethoxy-2,6-dinitrobiphenyl was confirmed by comparison with identical material prepared (yield, 60%) from 3,5-dichloro-2,6-dinitrobiphenyl by refluxing with sodium methoxide (4 mols.) for 3 hr. in dioxan–methanol (1 : 1) (Found: N, 9·2%).

(h) *In methyl* m-*nitrobenzoate.* Reaction of the iodo-compound as in section (b), but with the substitution of the nitro-ester (45 g.) as diluent, afforded, after separation of inorganic material (47 g.), unchanged iodobenzene (50 g.) and nitro-ester (41 g.) (b. p. 130—140°/0·5 mm.), and a red viscous oil (4 g.), b. p. 170—210°/0·5 mm. The pale yellow oil, obtained on chromatography of the least volatile fraction in benzene–light petroleum (1 : 2), was saponified by refluxing 5% ethanolic potassium hydroxide (50 ml.) for 2 hr. The liquors were then diluted with water (250 ml.), and traces of unsaponifiable material extracted with chloroform. The aqueous fraction was acidified with dilute mineral acid, yielding an oil which solidified on trituration with light petroleum and crystallised (charcoal) from aqueous acetic acid (1 : 1) in straw-coloured needles of *triphenylamine*-3-*carboxylic acid* (1·6 g.), m. p. 187—188° (Found: C, 78·6; H, 5·3; N, 5·0. $C_{19}H_{15}O_2N$ requires C, 78·9; H, 5·2; N, 4·8%). Further elution of the original chromatogram with ethyl acetate yielded an oily solid which crystallised from methanol in orange feathery plates of 3,3′-dimethoxycarbonylazobenzene (0·1 g.), m. p. 156—157° [lit., 163° (corr.)] (Found: C, 64·4; H, 4·7; N, 9·1. Calc. for $C_{16}H_{14}O_4N_2$: C, 64·4; H, 4·7; N, 9·4%).

(j) *In methyl isophthalate.* In a similar reaction to (h), but with methyl isophthalate (48·5 g.) as diluent, only inorganic material (48 g.), unchanged iodobenzene (51 g.), and ester (46 g.) (b. p. 125—130°/0·5 mm.) were isolated. Higher-boiling condensates were not formed.

(k) *In* 1,3,5-*trinitrobenzene.* Copper (14 g.) was added portionwise during 15 min. to a mixture of iodobenzene (34·5 g.) and 1,3,5-trinitrobenzene (22·5 g.) at 195°; the reaction conditions were maintained for a further 6 hr. Vacuum-distillation of the organic material (inorganic residue, 28·5 g.) yielded iodobenzene (7·5 g.) and a small fraction (0·5 g.), b. p. 60—90°/0·5 mm., which partly solidified but was not further investigated. The distillation residue (27 g.), b. p. >90°/0·5 mm., crystallised from benzene–light petroleum to give unchanged trinitrobenzene (10·5 g.), m. p. 122° (after efflorescence of solvent of crystallisation). The residue obtained on removal of solvent from the mother-liquors was chromatographed in benzene–light petroleum (1 : 2), yielding primarily a red oil (4·5 g.) which crystallised readily from methanol in orange needles of 3,5-*dinitrotriphenylamine* (3 g.), m. p. 130° (Found: C, 64·3; H, 4·0; N, 12·3. $C_{18}H_{13}O_4N_3$ requires C, 64·5; H, 3·9; N, 12·5%). Further elution of the column with the same solvent gave a yellow oil (5 g.). This was combined with the residues obtained on evaporation of the methanolic mother-liquors from the first fraction, and was treated with warm methanol (40 ml.). The supernatant liquors were decanted from a small quantity of highly insoluble yellow powder before crystallisation of the main fraction commenced. Recrystallisation of the insoluble solid from glacial acetic acid furnished very pale yellow prisms of 2′,4′,6′-*trinitro*-m-*terphenyl* (0·3 g.), m. p. 228—229° (Found: C, 59·0; H, 3·0; N, 11·5. $C_{18}H_{11}O_6N_3$ requires C, 59·2; H, 3·0; N, 11·5%). The methanolic mother-liquors were stripped of solvent; the residue crystallised from benzene–light petroleum to give pale yellow needles of 2,4,6-trinitrobiphenyl (3·5 g.), m. p. and mixed m. p. 129° (Found: C, 49·6; H, 2·3; N, 14·7. Calc. for $C_{12}H_7O_6N_3$: C, 49·8; H, 2·4; N, 14·5%). Further elution of the chromatogram with benzene alone gave small quantities of the trinitrated biphenyl (1 g.) and the terphenyl (0·1 g.). Final elution of the column with ethyl acetate afforded a black resin (3 g.) which deposited rosettes of black needles from 90% methanol solution at 0° in 3—4 days (after decantation from resin originally deposited). Recrystallisation from methanol (charcoal) furnished crimson needles of 3,5-*dinitrodiphenylamine* (0·25 g.), m. p. 148—149° (after changing colour to orange at 124—126°) (Found: C, 55·8; H, 3·5; N, 16·2. $C_{12}H_9O_4N_3$ requires C, 55·6; H, 3·5; N, 16·2%).

A similar reaction for only 2·5 hr. gave copper salts, etc. (23 g.), unchanged iodobenzene (14·5 g.), the unsymmetrical biaryl (2·8 g.), the terphenyl derivative (0·4 g.), the substituted triphenylamine (0·5 g.), and 3,5-dinitrodiphenylamine (0·3 g.). Isolation of the products under these milder conditions was facilitated by a marked reduction of the relative proportion of resin formed.

Reaction of p-*Iodotoluene with Copper in* m-*Dinitrobenzene.*—The iodo-compound (28 g.), *m*-dinitrobenzene (14 g.), and copper (19 g.) afforded inorganic material (29·5 g.), *p*-iodotoluene (8·5 g.), b. p. 60—65°/1 mm., a mixture of *p*-bitolyl and *m*-dinitrobenzene (12 g.), and a viscous red oil (5 g.), b. p. 170—210°/1 mm. A dark distillation residue (1 g.) was discarded. The red oil was chromatographed in benzene–light petroleum (1 : 1), giving primarily an oil which crystallised from methanol–ethyl acetate in orange prisms of 4′,4″-*dimethyl*-3-*nitrotriphenylamine* (1·1 g.), m. p. 160—161° (Found: C, 75·3; H, 5·4; N, 9·0. $C_{20}H_{18}O_2N_2$ requires C, 75·5; H, 5·7; N, 8·8%). Further elution of the column with the same mixed solvent gave uncrystallisable oils (1·1 g.). Final elution with ethyl acetate yielded small yellowish-green prisms (from methanol) of 4′-*methyl*-2,6-*dinitrobiphenyl* (0·4 g.), m. p. 121—122° (Found: C, 60·3; H, 3·9; N, 10·8. $C_{13}H_{10}O_4N_2$ requires C, 60·5; H, 3·9; N, 10·9%). Reduction of the mixture of *m*-dinitrobenzene and *p*-bitolyl with granulated zinc in aqueous-ethanolic hydrochloric acid furnished the hydrocarbon (2·6 g.), m. p. 121°, as the neutral product.

The structure of 4′-methyl-2,6-dinitrobiphenyl was confirmed by comparison with authentic material, m. p. 121—122°, obtained (yield, 60%) on condensation of 1-chloro-2,6-dinitrobenzene with *p*-iodotoluene at 190° for 2·5 hr. (Found: N, 10·7%).

Reaction of p-*Iodoanisole with Copper in* m-*Dinitrobenzene.*—The iodo-ether (30 g.), *m*-dinitrobenzene (14 g.), and copper (19 g.) afforded inorganic material (33 g.), unchanged iodo-ether (4 g.), b. p. 60—65°/0·4 mm., *m*-dinitrobenzene (11 g.), and a pale yellow solid (6·5 g.), b. p. 160—190°/1 mm. A higher-boiling residue (3 g.) was not further investigated. The solid crystallised from methanol (50 ml.), giving a mixture (5·2 g.) of pale yellow prisms and colourless plates. Treatment with warm methanol, in which the latter were insoluble, afforded 4,4′-dimethoxybiphenyl (3·5 g.), m. p. 172°. The mother-liquors were concentrated to *ca.* 15 ml., filtered from traces of the previous product when cool, then stored at 0° overnight, giving pale yellow prisms of 4′-*methoxy*-2,6-*dinitrobiphenyl* (1·3 g.), m. p. 119—120° (Found: C, 57·2; H, 3·5; N, 10·4. $C_{13}H_{10}O_4N_2$ requires C, 56·9; H, 3·7; N, 10·2%).

An authentic specimen of 4′-methoxy-2,6-dinitrobiphenyl, m. p. 119—120°, prepared (yield, 75%) by the Ullmann reaction between 1-chloro-2,6-dinitrobenzene and *p*-iodoanisole at 190° for 2·5 hr., was identical with the compound obtained above (Found: N, 10·1%).

3,5-*Dinitro-di- and -tri-phenylamines.*—Iodobenzene (9 g., 1·5 mol.) and 3,5-dinitroaniline (5·5 g.) were dissolved in nitrobenzene (35 ml.) containing suspended anhydrous potassium carbonate (4 g.) and copper powder (0·2 g.), and refluxed for 7 hr. Chloroform was added to the cooled black liquor, then the extract was washed with water to remove inorganic salts, filtered from a little suspended material, and the mixed solvent distilled *in vacuo*. The residue was dissolved in dry ether (100 ml.). Treatment of the solution with dry hydrogen chloride gave a yellow crystalline precipitate of primary base hydrochloride which was discarded. The ethereal mother-liquors were washed with 2% aqueous sodium hydrogen carbonate, after which the solvent was removed. The oily residue crystallised (charcoal) from benzene–light petroleum (1 : 1) in crimson needles of 3,5-dinitrodiphenylamine (1·7 g.), m. p. 147° undepressed on admixture with material obtained from the Ullmann reaction of iodobenzene in 1,3,5-trinitrobenzene (Found: N, 16·0. Calc. for $C_{12}H_9O_4N_3$: N, 16·2%).

The mother-liquors from the above experiment were chromatographed in the same solvent, yielding initially an oil (0·2 g.) which crystallised slowly from methanol in golden needles of 3,5-dinitrotriphenylamine (0·05 g.), m. p. 130°, undepressed on admixture with a sample of the tertiary amine obtained as described from 1,3,5-trinitrobenzene (Found: N, 12·2. Calc. for $C_{18}H_{13}O_4N_3$: N, 12·5%).

N-*Arylation of Nitro-amines.*—*General procedure.* The iodo-compound, containing *ca.* 5% of the nitro-amine to be arylated, was treated with copper at 195—200° for 5—6 hr. The organic products were extracted with chloroform and fractionally distilled *in vacuo*. The crude amine was generally obtained as a pale red viscous oil which was either crystallised directly from methanol or methanol–ethyl acetate (method A) or chromatographically fractionated in benzene–light petroleum (1 : 1) before crystallisation (method B). Individual examples are listed in Table 2. Comparison of the triphenylamine derivatives obtained in this way with the appropriate materials formed as described earlier in this communication, established the structures of the latter. No variation from the recorded m. p. or crystal forms was encountered.

TABLE 2.

Iodo-compound	Added deriv. of *m*-nitro-aniline	Product: deriv. of 3-nitrotri-phenylamine	B. p. of crude product (mm.)	Method of purifn.	Yield (%)	N (%)	
						Found	Calc.
C_6H_5I	6-Me	6-Me	175—200°/0·3	B	25	*	*
,,	4-Me	4-Me	180—200°/0·3	A	65	9·2	9·2
,,	6-MeO	6-MeO	210—220°/0·5	A	45	8·5	8·8
p-C_6H_4IMe	Unsubst.	4′,4″-Me_2	180—200°/0·5	A	30	8·6	8·8
C_6H_5I	4-Cl	4-Cl	175—190°/0·3	B	15 ‡	8·9	8·6
p-C_6H_4IMe	,,	—	—	B	0	—	—
p-$C_6H_4I{\cdot}OMe$	,,	4-Cl-4′,4″-$(OMe)_2$	†	A	10 ‡	7·0	7·3

* Bright orange plates, m. p. 100° (from methanol–ethyl acetate) (Found: C, 74·7; H, 5·1; N, 9·3. $C_{13}H_{10}O_4N_2$ requires C, 75·0; H, 3·9; N, 9·2%).

† The crude product crystallised directly from methanol–ethyl acetate overnight at 5°, to give a mixture of shining white plates (4,4′-dimethoxybiphenyl) and small hard brown mushrooms of the crude tertiary amine. Recrystallisation of the latter (after manual separation) from the same solvent gave the pure material.

‡ Mixed m. p.s with specimens of the same substances obtained by other means, as described in Part I of this series, were undepressed.

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