

Preparation of 2,6-Dinitrobiphenyls from *m*-Dinitrobenzene and Iodoarenes with Copper(I) Oxide in Quinoline

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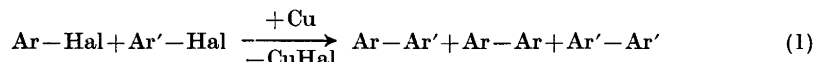
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m-Dinitrobenzene on heating with iodobenzene derivatives and copper(I) oxide in quinoline gives 2,6-dinitrobiphenyls in yields up to 80 %. Reactions using 2,6-dimethoxyiodobenzene also give 2,4-dinitrobiphenyls.

With metallic copper 2,6-dinitrobiphenyls can also be obtained but they are then accompanied by symmetrical biaryls.

The experimental variables are discussed, the reactions are compared with other copper-promoted reactions and the mechanism is discussed.

Unsymmetrical biaryls can be prepared by the Ullmann reaction¹ using two different halogenoarenes:



Such "mixed" Ullmann couplings generally give mixtures of symmetrical and unsymmetrical biaryls. However, when one of the reactants is an "activated" halogenoarene like *o*-bromonitrobenzene and the other an "unactivated" iodoarene the unsymmetrical biaryl is often the dominating product.¹

There are also other possibilities for obtaining unsymmetrical nitrobiphenyls in Ullmann-like reactions. When studying the effect of *m*-dinitrobenzene as a diluent in the reaction of iodobenzene with copper, Forrest found that small amounts of 2,6-dinitrobiphenyl (*ca.* 8 %) were formed in addition to the biphenyl.² We have briefly reported³ that 2,6-dinitrobiphenyls are formed in good yields when *m*-dinitrobenzene, an iodobenzene derivative and copper(I) oxide are heated in quinoline (Eqn. 2).

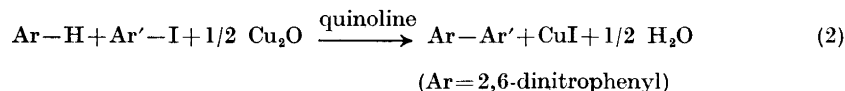
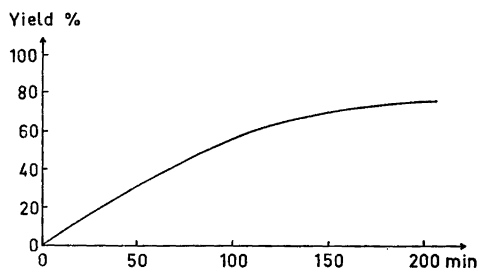
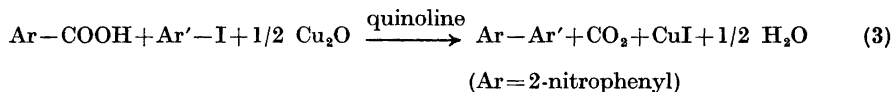


Fig. 1. Formation of 4-methoxy-2',6'-dinitrobiphenyl from equivalent amounts (0.03 mole scale) of *p*-iodoanisole, *m*-dinitrobenzene, and copper(I) oxide in quinoline at $221 \pm 2^\circ$.



This reaction seems to be related to the decarboxylative coupling of 2-nitrobenzoic acids with iodobenzene derivatives to give 2-nitrobiphenyls in the presence of copper(I) oxide in quinoline solution (Eqn. 3).⁴



The present communication gives a more detailed account of the couplings of *m*-dinitrobenzene with iodoarenes for the preparation of 2,6-dinitrobiphenyls, including reaction conditions and the influence of substituents on the reaction.

The practical application of the coupling reaction is very simple. Equivalent amounts of *m*-dinitrobenzene, iodoarene, and copper(I) oxide are suspended in quinoline and the mixture heated to about 220° for some hours with stirring. The copper oxide dissolves and water is given off. When the reaction is complete, the mixture is left to cool and a complex between quinoline and copper iodide, which is sparingly soluble in ether, precipitates and can easily be filtered off. The lowest practical reaction temperature is about 180° . At temperatures near the boiling point of quinoline (238°) side reactions leading to triarylaminines gain in importance.⁵ In prolonged reactions there is also some further coupling to give terphenyls and perhaps even higher polyphenyls (cf. also Refs. 3 and 6).⁵ Thus in general there are certain optimal conditions of temperature and time for the preparation of a biphenyl. The influence of time is illustrated in Fig. 1.

The use of quinoline as a solvent stems from its successful use in the decarboxylative coupling of *o*-nitrobenzoic acids.⁴ Attempts to use other solvents have so far given inferior results. Thus for the reaction between *m*-dinitrobenzene, *p*-iodomethoxybenzene and copper(I) oxide in an autoclave at 230° for 2 h, different solvents gave the following yields: quinoline 67 %, pyridine 43 %, isoquinoline 5 %, dimethylformamide 0 % (decomp.), triphenylphosphine 0 % (decomp.) and sulpholan 0 %. Without any solvent the reaction (230° , 3.7 h) gave an 8 % yield. The reaction in pyridine proceeded very cleanly; the reaction mixture showed little discoloration and apparently only small amounts of triarylaminines had been formed (TLC).

Substituents in the iodoarene have some effect on the reaction. A *para* nitro group slows down the reaction and an *ortho* nitro group can even hinder the reaction and favour instead dehalogenation.

Table 1. Typical results of reactions between *m*-dinitrobenzene (Ar-H) with various iodobenzene (Ar'I) derivatives. Yields denote isolated and purified 2,6-dinitrobiphenyls, the figure within brackets denotes a 2,4-dinitrobiphenyl.

Substituents in the iodobenzene	Temp.°	Time, h	Yield, %
None	220	2	15
None	238	2	41
4-Methoxy	238	0.5	28
4-Methoxy	238	2	55
4-Methoxy	220	5	81
4-Methoxy	150	30	1
2-Methoxy	220	2	10
2-Methoxy	225	3	27
2,4-Dimethoxy	238	2.2	59
3,4-Dimethoxy	238	2	58
2,6-Dimethoxy	238	0.5	46 (5)
4-Methyl	230	2	40
4-Nitro	235	6	42
2-Nitro	220	2	0

The effect of two *o*-methoxy groups is perhaps the most remarkable. In spite of the expected steric hindrance the reaction is rapid and gives good yield. In addition to the "normal" product — 2,6-dimethoxy-2',6'-dinitrobiphenyl — some 2,6-dimethoxy-2',4'-dinitrophenyl was also isolated.

Attempts to use bromoarenes instead of iodoarenes have so far given inferior results and generally the bromoarenes cannot be considered useful in the present reactions.

In some experiments the influence of substituents in the *m*-dinitrobenzene has been investigated. 1-Methoxy-2,4-dinitrobenzene and 3,5-dinitrotoluene gave only dark tars and no biphenyls could be detected. 1-Methoxy-3,5-dinitrobenzene with *p*-methoxyiodobenzene gave a low yield (5 %) of 4,4'-dimethoxy-2,6-dinitrobiphenyl with a considerable amount of tar.

As reported previously, nitrobenzene reacts slowly to give small amounts of 2-nitrobiphenyl.⁴ 1,3,5-Trinitrobenzene gives good results.^{3,6}

The reactions of 2,6-dimethoxyiodobenzene with *m*-dinitrobenzene to give both 2,6-dimethoxy-2',6'-dinitrobiphenyl and 2,6-dimethoxy-2',4'-dinitrobiphenyl show that both the 2- and the 4-positions in 1,3-dinitrobenzene are reactive.

When quinoline was used as a solvent for the reaction between metallic copper, *m*-dinitrobenzene, and iodoarenes, far better yields were obtained than those reported by Forrest.² Thus in reactions conducted at 238° for 2 h, *p*-methoxyiodobenzene gave 63 % yield of 4-methoxy-2',6'-dinitrobenzene plus 12 % yield of 4,4'-dimethoxybiphenyl while 4-iodotoluene gave 49 % 4-methyl-2',6'-dinitrobiphenyl and 16 % 4,4'-dimethylbiphenyl. The formation of symmetrical biphenyls makes this reaction less attractive than the coupling with copper(I) oxide. However, if the reaction temperature is lowered formation of the symmetrical biaryl is suppressed; 4-methoxyiodobenzene

after 2 h at 220° gave 30 % 4-methoxy-2',6'-dinitrobiphenyl with less than 1 % 4,4'-dimethoxybiphenyl. Surprisingly, only negligible amounts (*ca.* 5 % anisole) of dehalogenation products were observed in these experiments.

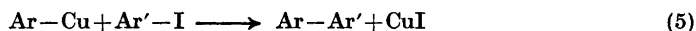
DISCUSSION

The reaction of *m*-dinitrobenzene and iodobenzenes with copper(I) oxide in quinoline thus provides a simple and convenient synthesis of 2,6-dinitrobiphenyls uncontaminated by symmetrical biphenyls. Using di-iodoarenes the reaction may afford also higher polyphenyls as exemplified by 2',5'-dimethoxy-2,2'',6,6''-tetrinitro-*p*-terphenyl and 2,2''',6,6'''-tetrinitro-*p*-quaterphenyl.

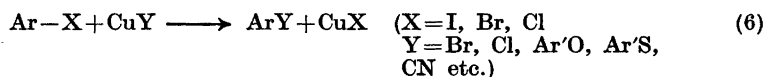
These couplings seem to be closely related to the decarboxylative couplings of 2-nitrobenzoic acids (Eqn. 3). In fact the 2,6-dinitrobiphenyls can also be prepared by decarboxylative coupling of 2,6-dinitrobenzoic acid⁷ but preparatively this seems to offer little advantage.

It seems most likely that all these couplings proceed *via* a common intermediate. The stoichiometry of the couplings with copper(I) oxide seems rather clear-cut (Eqn. 2) but the material balance in the Forrest-type couplings with metallic copper is still not established. The mechanisms must obviously be related to that of the Ullmann biaryl synthesis¹ and to those of other copper-promoted aromatic reactions.⁸

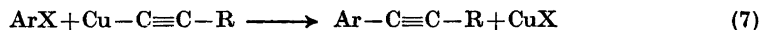
The reaction observed between 2-thienylcopper and iodobenzenes in quinoline solution to give 2-phenylthiophenes⁹ has given support to the hypothesis that Ullmann-type couplings can proceed *via* arylcopper compounds reacting with iodoarenes:¹⁰



This type of reaction is analogous to other well-known copper-promoted aromatic substitutions:⁸



and also to the reaction between iodoarenes and copper(I) acetylides to give arylacetylenes:¹¹



However, *p*-tolylcopper may also be formed in quinoline solutions from metallic copper and *p*-iodotoluene and dimerise to give symmetrical 4,4'-dimethylbiphenyl with elimination of elemental copper¹² showing that another route is also possible:



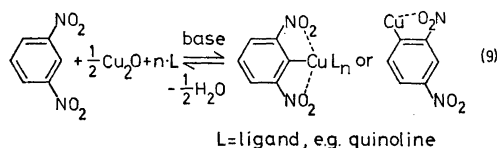
Possibly we have to deal with two competing reactions of the arylcopper compounds. In the present material formation of 2,2',6,6'-tetrinitrobiphenyl

has not been observed and no 2,2'-dinitrobiphenyls were observed in the decarboxylative coupling of *o*-nitrobenzoic acids.

A common feature of the favoured unsymmetrical couplings is the presence of an electronegative group or atom in *o*-position to the coupling site in one nucleus. This could mean that the intermediate arylcopper compounds are stabilised by chelation and show little tendency to self-coupling (Eqn. 8) but preferentially react according to Eqn. 5.

2,6-Dinitrophenylcopper could be an intermediate in the present reactions and would probably be stabilised by chelation of the copper atom by the nitro groups. Its formation (Eqn. 9) would be analogous to that of the σ -cyclopentadienylcopper complex from cyclopentadiene, copper(I) oxide, and triethylphosphine.¹³

1,3-Dinitrobenzene is known to be somewhat acidic and in dimethylformamide-D₂O solution containing a little sodium hydroxide shows a rapid exchange of the 2-proton.¹⁴ The exchange may proceed *via* the anion and spectral data indicate formation of the 4-anion also.¹⁵ Quinoline is a good "soft" ligand for Cu(I) species and its basicity should promote the protolysis. So far, however, our attempts to prepare or isolate 2,6-dinitrophenylcopper have been unsuccessful.



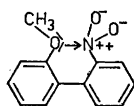
If the formation of 2,6-dinitrophenylcopper were rate-determining the couplings with different iodoarenes would proceed at the same rate. As indicated above, however, the rates seem to differ and it therefore seems probable that also the iodoarene is involved in the rate-determining step.

The tendency of 2,6-dimethoxyiodobenzene to react faster than *p*-methoxyiodobenzene and this in turn faster (and better) than iodonitrobenzenes could suggest a favourable interaction between methoxy groups and nitro groups in the transition state or, stated more generally, the importance of donor-acceptor interactions.

Table 2. Melting points (°C) of some methoxynitrobiphenyls.

2-Methoxy-2'-nitro-	80 — 83
4-Methoxy-2'-nitro-	61 — 63
2-Methoxy-2',6'-dinitro-	146 — 147
4-Methoxy-2',6'-dinitro-	117 — 119
2,6-Dimethoxy-2',6'-dinitro-	198 — 199
2,6-Dimethoxy-2',4'-dinitro-	159 — 161
2,4-Dimethoxy-2',6'-dinitro-	175 — 176
3,4-Dimethoxy-2',6'-dinitro-	134 — 135

This recalls the phenomenon that 2-methoxy-2'-nitrobiphenyls have higher melting points than 4-methoxy-2'-nitrobiphenyls (Table 2) which might be interpreted in terms of attraction between methoxy- and nitro groups causing planarity rather than the expected non-planarity due to steric crowding (10).



(10)

EXPERIMENTAL

The melting points were determined on a Leitz hot stage microscope. Elemental analyses were carried out by Alab, Uppsala, Sweden. The NMR spectra were run on a Varian A60A instrument. For gas chromatography (GLC) an Aerograph 204-1B with hydrogen flame detector was used with SE-30 5% (1.50 m) on Chromosorb W as stationary phase. The chromatogram peak areas were measured by the "height \times width at half-height" method. Internal standard techniques were used, for example 4-methyl-2',6'-dinitrobiphenyl was used as standard when 4-methoxy-2',6'-dinitrobiphenyl was determined. The standard was added after the reaction but before the work-up of the reaction mixture. Thin-layer chromatograms (TLC) were run on silica gel G (Merck) and developed with cyclohexane/benzene mixtures.

The copper used was a lithographic bronze containing *ca.* 0.2–0.5% C₁₈–C₁₈-fatty acids, partly as their copper salts.

The quinoline used generally was a *puriss* quality, "synthetic, min 99%". It was found to contain *ca.* 2% β -methylnaphthalene and *ca.* 1% of a basic impurity possibly isoquinoline (GLC). The commercial quinoline was occasionally purified by extracting its solution in hydrochloric acid with ether. The solution was made alkaline and the recovered quinoline was distilled under reduced pressure from phosphorus pentoxide.

General coupling and work up procedure. The reactants (usually equivalent amounts of *m*-dinitrobenzene, an iodoarene, copper(I) oxide or metallic copper, and excess quinoline) were mixed in a flask equipped with a stirrer and a reflux condenser. The flask was swept with dry oxygen-free nitrogen, though this is generally not necessary. The flask was heated in a thermostated silicone oil or metal bath for 0.5–6 h at 180–240°. When the reaction mixture had cooled, ether was added and the mixture stirred. The yellow crystalline complex of copper iodide and quinoline as well as unreacted copper(I) oxide or copper were filtered off, washed with ether and discarded. The filtrate was extracted with 2 M hydrochloric acid to remove remaining quinoline, washed with water, dried and the solvent evaporated.

Variation of solvent. An autoclave (100 ml) was charged with *m*-dinitrobenzene (0.01 mole), *p*-iodoanisole (0.01 mole), copper(I) oxide (0.005 mole), and quinoline (25 ml). The reactor was heated to 230° and kept at this temperature for 2 h. After the reactor had cooled to room temperature, the reaction mixture was worked up as described above. GLC analysis showed 4-methoxy-2',6'-dinitrobiphenyl in 67% yield (internal standard 4-methyl-2',6'-dinitrobiphenyl).

In an otherwise identical experiment pyridine (25 ml) was used as solvent. GLC analysis showed 4-methoxy-2',6'-dinitrobiphenyl (yield 43%). The crude product was not so dark as when quinoline was used as solvent.

When isoquinoline was used as solvent GLC showed 5% yield of 4-methoxy-2',6'-dinitrobiphenyl. In this case the reaction gave mainly a dark tar. When *N*-dimethylformamide (25 ml) or triphenyl phosphine (25 g) were used as solvents the reactions gave only tars and GLC showed no peaks corresponding to 4-methoxy-2',6'-dinitrobiphenyl.

Sulpholan was also used as solvent under the same conditions. The reaction mixture was worked up largely as described above but water was used for the extraction of sulpholane. GLC showed no peak corresponding to 4-methoxy-2',6'-dinitrobiphenyl.

When the same reaction was run for 3.7 h without any solvent, distillation gave low-boiling material (mainly *p*-iodoanisole and *m*-dinitrobenzene) and a fraction boiling at 140–170°/0.1 mm. Recrystallisation from ethyl acetate gave yellow needles of 4-methoxy-2',6'-dinitrobiphenyl, m.p. and mixed m.p. 119–120° (0.22 g, yield 8 %).

Preparations with copper(I) oxide

2,6-Dinitrobiphenyl, 220°, 2 h. *m*-Dinitrobenzene (0.02 mole), iodobenzene (0.02 mole), copper(I) oxide (0.01 mole), and quinoline (50 ml). Distillation of the reaction product gave low-boiling material (mainly iodobenzene and *m*-dinitrobenzene) and a fraction, b.p. 140–220°/0.2 mm. Recrystallisation from ethanol gave 0.75 g (15 %) 2,6-dinitrobiphenyl, m.p. 189–191° (Forrest² reported 189–190°). Reaction at 238° for 2 h gave a 41 % yield.

4-Methoxy-2',6'-dinitrobiphenyl. *m*-Dinitrobenzene (0.01 mole), *p*-iodoanisole (0.01 mole), copper(I) oxide (0.005 mole), and quinoline (25 ml) were reacted at 238° for 0.5 h. Distillation gave a low-boiling fraction (mainly *p*-iodoanisole and *m*-dinitrobenzene) and a fraction, b.p. 175–195°/0.5 mm. Recrystallisation from ethyl acetate gave yellow needles of 4-methoxy-2',6'-dinitrobiphenyl, m.p. 117–119° (0.77 g, 28 %).

With reaction time 2 h at the same temperature the yield was 1.52 g (55 %). The best result so far, 81 % yield, was obtained after 5 h reaction at 220°.

When the reaction was carried out at 150° for 30 h, GLC showed a small peak corresponding to a 1 % yield of 4-methoxy-2',6'-dimethoxybiphenyl (internal standard).

2-Methoxy-2',6'-dinitrobiphenyl 225°, 3 h. *m*-Dinitrobenzene (0.1 mole), *o*-iodoanisole (0.1 mole), copper(I) oxide (0.05 mole), and quinoline (300 ml). Trituration of the reaction product gave a solid which was recrystallised from methanol to give 7.36 g (27 %) 2-methoxy-2',6'-dinitrobiphenyl, m.p. 146–147° (after sublimation). (Found: C 57.0; H 3.8; N 10.0. Calc. for C₁₃H₁₀N₂O₅: C 56.9; H 3.7; N 10.2).

The reaction conducted at 220° for 2 h in 0.01 mole scale gave 10 % yield (GLC).

2,6-Dimethoxy-2',6'-dinitrobiphenyl, 238°, 0.5 h. *m*-Dinitrobenzene (0.01 mole), 2,6-dimethoxyiodobenzene (0.01 mole), copper(I) oxide (0.005 mole), and quinoline (30 ml).

Table 3. Selected NMR data for methoxynitrobiphenyls and reference compounds. For notations see formulas below (solvent deuteriochloroform).

	τ_{H_A}	τ_{H_B}	τ_{H_C}	J_{AB} H_z	J_{BC}	τ_{OCH_3}
2,6-Dinitrotoluene	2.36	1.93		7.7		
4-Methoxy-2',6'-dinitrobiphenyl	2.45	2.01		7.8		6.32
2-Methoxy-2',6'-dinitrobiphenyl	2.46	2.11		8.4		6.17
3,4-Dimethoxy-2',6'-dinitrobiphenyl	2.45	2.04		6.2		6.33 ³ ; 6.20 ⁴
2,4-Dimethoxy-2',6'-dinitrobiphenyl	2.44	2.13		7.6		6.20 ² ; 6.15 ⁴
2,6-Dimethoxy-2',6'-dinitrobiphenyl	2.33	1.83		7.8		6.30
2,4-Dinitrotoluene	1.19	1.52	2.21	2	9	
2,6-Dimethoxy-2',4'-dinitrobiphenyl	1.10	1.50	2.23	2	8	6.25
2-Methoxyiodobenzene						6.42
4-Methoxyiodobenzene						6.38
2,4-Dimethoxyiodobenzene						6.35 ² ; 6.27 ⁴
2,6-Dimethoxyiodobenzene						6.20

Distillation of the evaporation residue gave a low-boiling fraction (mainly 2,6-dimethoxyiodobenzene and *m*-dinitrobenzene) and a fraction, b.p. 160–250°/0.3 mm. Separation on a silica gel column (cyclohexane/benzene, 6:1) followed by recrystallisation from ethanol and sublimation gave two yellow compounds: A, m.p. 198–199° (1.3 g crude, 46 %) and B, m.p. 159–161° (0.15 g, 5 %). Comparison of their NMR-spectra with spectra of 2,6-dinitrotoluene and 2,4-dinitrotoluene (Table 3) showed the two compounds to be: A, 2,6-dimethoxy-2',6'-dinitrobiphenyl (Found: C 55.2; H 3.9; N 9.2) and B, 2,6-dimethoxy-2',4'-dinitrobiphenyl (Found: C 55.5; H 4.0; N 9.4. Calc. for C₁₄H₁₂N₂O₆: C 55.3; H 4.0; N 9.2). Yields: A 46 %; B 5 %.

2,4-Dimethoxy-2',6'-dinitrobiphenyl, 238°, 2.2 h. *m*-Dinitrobenzene (0.01 mole), 2,4-dimethoxyiodobenzene (0.01 mole), copper(I) oxide (0.005 mole), and quinoline (25 ml). Distillation of the evaporation residue gave low-boiling material (mainly 2,4-dimethoxyiodobenzene and *m*-dinitrobenzene) and a fraction, b.p. 194–212°/0.3 mm. Recrystallisation from ethyl acetate gave yellow needles of 2,4-dimethoxy-2',6'-dinitrobiphenyl, m.p. 175–176° (1.88 g, 59 %). (Found: C 55.2; H 4.0; N 9.2. Calc. for C₁₄H₁₂N₂O₆: C 55.3; H 4.0; N 9.2). IR and NMR-spectra are in agreement with this structure.

3,4-Dimethoxy-2',6'-dinitrobiphenyl, 238°, 2 h. *m*-Dinitrobenzene (0.01 mole), 3,4-dimethoxyiodobenzene (0.01 mole), copper(I) oxide (0.005 mole), and quinoline (25 ml). Distillation gave low-boiling material (mainly 3,4-dimethoxyiodobenzene and *m*-dinitrobenzene) and a fraction, b.p. 160–220°/0.2 mm. Recrystallisation from ethyl acetate gave yellow needles of 3,4-dimethoxy-2',6'-dinitrobiphenyl, m.p. 134–135° (1.75 g, 58 %). (Found: C 55.4; H 4.0; N 9.0. Calc. for C₁₄H₁₂N₂O₆: C 55.3; H 4.0; N 9.2).

4-Methyl-2',6'-dinitrobiphenyl, 230°, 2 h. *m*-Dinitrobenzene (0.01 mole), *p*-iodotoluene (0.01 mole), copper(I) oxide (0.005 mole), and quinoline (30 ml). Distillation gave low-boiling material and a fraction, b.p. 130–220°/0.3 mm. Recrystallisation from ethanol gave yellow needles of 4-methyl-2',6'-dinitrobiphenyl, m.p. 119–121° (Forrest² found m.p. 121–122°) (1.05 g, 40 %). The same experiment run at 225° for 2 h gave 0.77 g 4-methyl-2',6'-dinitrobiphenyl (yield 30 %).

2,4',6-Trinitrobiphenyl, 235°, 6 h. *m*-Dinitrobenzene (0.01 mole), *p*-iodonitrobenzene (0.01 mole), copper(I) oxide (0.005 mole), and quinoline (25 ml). Distillation gave two fractions, the first fraction containing mainly *m*-dinitrobenzene and *p*-iodonitrobenzene, and a second fraction, b.p. 160–240°/0.4 mm. Recrystallisation of the second fraction from ethanol gave yellow needles of 2,4',6-trinitrobiphenyl (1.21 g, 42 %), m.p. 185–187°. (Found: C 50.0; H 2.6; N 14.5. Calc. for C₁₂H₇N₃O₆: C 49.8; H 2.4; N 14.5).

Attempted coupling of m-dinitrobenzene and o-iodonitrobenzene, 235°, 6 h. *m*-Dinitrobenzene (0.01 mole), *o*-iodonitrobenzene (0.01 mole), copper(I) oxide (0.005 mole), and quinoline (30 ml) were reacted and worked up as described earlier. GLC analysis showed two peaks which could be correlated with nitrobiphenyls. These peaks correspond to trace-amounts of material (less than 1 %). A high yield of nitrobenzene was found (about 50 %).

Attempts to couple 1-methoxy-2,4-dinitrobenzene, 1-methoxy-3,5-dinitrobenzene or 3,5-dinitrotoluene, 230°, 1 h. 1-Methoxy-2,4-dinitrobenzene (0.02 mole), 3,4-dimethoxyiodobenzene (0.02 mole), copper(I) oxide (0.01 mole), and quinoline (60 ml). GLC analysis of the almost black evaporation residue showed no peaks which could be correlated to a nitrobiphenyl. When 3,5-dinitrotoluene was reacted with *p*-iodoanisole under the same conditions no biphenyl was detected (GLC). When 1-methoxy-3,5-dinitrobenzene (0.01 mole), *p*-iodoanisole (0.01 mole), copper(I) oxide (0.005 mole), and purified quinoline (25 ml) were heated for 1 h at 230°, separation of the evaporation residue on a silica column (cyclohexane/benzene, 6:1) gave a compound which NMR indicated to be the expected 4,4'-dimethoxy-2,6-dinitrobiphenyl (m.p. 152–153°, 0.15 g, yield 5 %). (Found: C 56.1; H 4.2; N 8.6. Calc. for C₁₄H₁₂N₂O₆: C 55.3; H 4.0; N 9.2). The NMR spectrum showed peaks at $\tau = 6.21$ and $\tau = 6.09$ corresponding to two methoxys, an A₂B₂ spectrum $\tau = 2.86$ and $\tau = 3.13$, $J_{AB} = 9$ cps, and $\tau = 2.57$ corresponding to the protons in the nitro-substituted ring.

*2',5'-Dimethoxy-2,2'',6,6''-tetranitro-*p*-terphenyl, 230°, 5 h.* *m*-Dinitrobenzene (0.02 mole), 1,4-di-iodo-2,4-dimethoxybenzene (0.01 mole), copper(I) oxide (0.015 mole), and quinoline (25 ml). Trituration of the evaporation residue with ether gave 2',5'-dimethoxy-2,2'',6,6''-tetranitro-*p*-terphenyl (*ca.* 0.55 g, 12 %), m.p. 341–343° (after sublimation). (Found: C 51.5; H 2.9; N 12.0. Calc. for C₂₀H₁₄N₄O₁₀: C 51.0; H 3.0; N 11.9). This *p*-terphenyl is very sparingly soluble in ether and a large volume (2 l) was necessary

to prevent crystallisation during the work up procedure. Separation of the material in the mother liquor on a silica gel column with cyclohexane/benzene gave 2,5-dimethoxy-2',6'-dinitrobiphenyl (1.27 g, yield 41%), m.p. 133–135° (after sublimation). (Found: C 55.5; H 4.0; N 9.4. Calc. for $C_{14}H_{12}N_2O_6$: C 55.3; H 4.0; N 9.2).

2,2''',6,6'''-Tetranitro-*p*-quaterphenyl, 220°, 3 h. *m*-Dinitrobenzene (0.015 mole), 4,4'-di-iodobiphenyl (0.075 mole), copper(I) oxide (0.015 mole), and quinoline (50 ml). Trituration of the evaporation residue with methanol gave 2,2''',6,6'''-tetranitro-*p*-quaterphenyl (0.80 g, 22%), m.p. 358–360° (after sublimation). (Found: C 59.7; H 3.0; N 11.5. Calc. for $C_{24}H_{14}N_4O_8$: C 59.3; H 2.9; N 11.5).

Preparations with copper bronze

4-Methoxy-2',6'-dinitrobiphenyl, 238°, 2 h. *m*-Dinitrobenzene (0.01 mole), *p*-iodoanisole (0.02 mole), copper bronze (0.04 mole), and quinoline (25 ml). Distillation of the partly crystalline residue gave a low-boiling fraction (mainly *p*-iodoanisole and *m*-dinitrobenzene) and a fraction, b.p. 150–220°/0.1 mm (1.98 g) which on GLC analysis was shown to be a mixture of 4-methoxy-2',6'-dinitrobiphenyl and 4,4'-dimethoxybiphenyl. Fractional crystallisation from ethanol and sublimation gave 4-methoxy-2',6'-dinitrobiphenyl, m.p. 117–119° (1.72 g, yield 63%, Forrest² reported m.p. 119–120°) and 4,4'-dimethoxybiphenyl, m.p. 177–178° (0.52 g, yield 12%, Forrest² reported m.p. 172°).

When the reaction was run at 220° for 2 h GLC showed 30% 4-methoxy-2',6'-dinitrobiphenyl and less than 1% 4,4'-dimethoxybiphenyl.

4-Methyl-2',6'-dinitrobiphenyl, 238°, 3 h. *m*-Dinitrobenzene (0.01 mole), *p*-iodotoluene (0.02 mole), copper bronze (0.04 mole), and quinoline (25 ml). Distillation of the reaction residue gave a low-boiling fraction (mainly *p*-iodotoluene and *m*-dinitrobenzene) and a fraction b.p. 130–220°/0.3 mm. Fractional crystallisation from ethanol and sublimation gave pure compounds: 4,4-dimethylbiphenyl (0.58 g, 16%), m.p. 119–121° and 4-methyl-2',6'-dinitrobiphenyl, m.p. 119–120° (1.35 g, 49%) (Forrest² reported 121–122°).

Acknowledgements. The work has been supported by *The Swedish Council for Applied Research*. The spectra were recorded by Miss Gurli Hammarberg. The English was checked by Dr. B. R. Thomas.

REFERENCES

1. Fanta, P. E. *Chem. Rev.* **64** (1964) 613.
2. Forrest, J. J. *Chem. Soc.* **1960** 566, 574, 581, 589, 592, 594.
3. Björklund, C. and Nilsson, M. *Tetrahedron Letters* **1966** 675.
4. Nilsson, M. *Acta Chem. Scand.* **20** (1966) 423.
5. Björklund, C. and Nilsson, M. *Unpublished observations*.
6. Björklund, C. and Nilsson, M. *Acta Chem. Scand.* **22** (1968). *In press*.
7. Björklund, C. and Nilsson, M. *Acta Chem. Scand.* **22** (1968). *In press*.
8. Bacon, R. G. R. and Hill, H. A. O. *Quart. Rev. (London)* **19** (1965) 95.
9. Nilsson, M. *Tetrahedron Letters* **1966** 679.
10. Nilsson, M. *Scensk Kem. Tidskr.* **73** (1961) 447.
11. Castro, C. E., Gaugham, E. J. and Owsley, D. C. *J. Org. Chem.* **31** (1966) 4071.
12. Lewin, A. H. and Cohen, Th. *Tetrahedron Letters* **1965** 4531.
13. Wilkinson, G. and Piper, T. S. *J. Inorg. Nucl. Chem.* **2** (1956) 32.
14. Pollitt, R. J. and Saunders, B. C. *Proc. Chem. Soc.* **1962** 176.
15. Pollitt, R. J. and Saunders, B. C. *J. Chem. Soc.* **1965** 4615.

Received March 11, 1968.