

Copper-promoted Arylations of 1,3,5-Trinitrobenzene

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Arylcopper compounds react with 1,3,5-trinitrobenzene in pyridine to form intensely coloured solutions. The colour is apparently due to formation of σ -complexes, Meisenheimer complexes. 2,6-Dimethoxyphenylcopper gives a σ -complex which can be converted to a red pyridinium salt. This salt is relatively stable towards dilute acids in contrast to other Meisenheimer compounds. The σ -complex is easily oxidised to 2,6-dimethoxy-2',4',6'-trinitrobiphenyl. The reactions are compared with those between trinitrobenzene, 2,6-dimethoxyiodobenzene, and copper or copper(I) oxide.

Copper-promoted reactions have increased in importance in the last few years. Organocopper compounds have been used as synthetic intermediates in alkylation,¹⁻³ alkenylation,⁴⁻⁵ alkynylation,^{6,7} as well as in arylation^{3,8-13} reactions of halogen-containing compounds. Organocopper intermediates have also been suggested in decarboxylative couplings of aromatic acids with iodoarenes and copper(I) oxide,^{14,15} and in arylation of polynitroarenes by iodoarenes and copper(I) oxide.^{16,17}

Knowledge about mechanisms for copper-promoted reactions is still rather limited. Some of these reactions are analogous to nucleophilic aromatic substitution reactions. Much of the knowledge about the mechanism for aromatic S_N2 reactions comes from reactions between polynitroarenes and nucleophiles.¹⁸

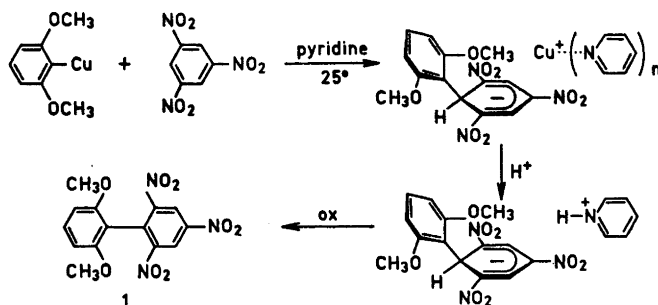
We have therefore investigated the reaction between some arylcopper compounds and *m*-dinitrobenzene or 1,3,5-trinitrobenzene. We also report additional investigations of the arylation of 1,3,5-trinitrobenzene by iodoarenes and copper(I) oxide. The present work connects previous investigations of phenylcopper⁹ with those of copper(I) oxide-promoted couplings of nitroarenes with iodoarenes.^{16,17}

RESULTS

Phenylcopper reacts exothermally with 1,3,5-trinitrobenzene in pyridine or quinoline at room temperature to form intensely coloured solutions. The reaction is very slow or absent in other types of solvents tried. The colour

most probably is due to a σ -complex – a Meisenheimer compound. The visible spectrum of the solution showed strong absorptions at 444 nm and 522 nm, corresponding to *ca.* 50 % conversion to the Meisenheimer compound, assuming $\epsilon = 2.6 \times 10^4$ l cm⁻¹ mol⁻¹ at 444 nm for the pure compound. No stable products or intermediates have, however, yet been isolated from the reaction mixture.

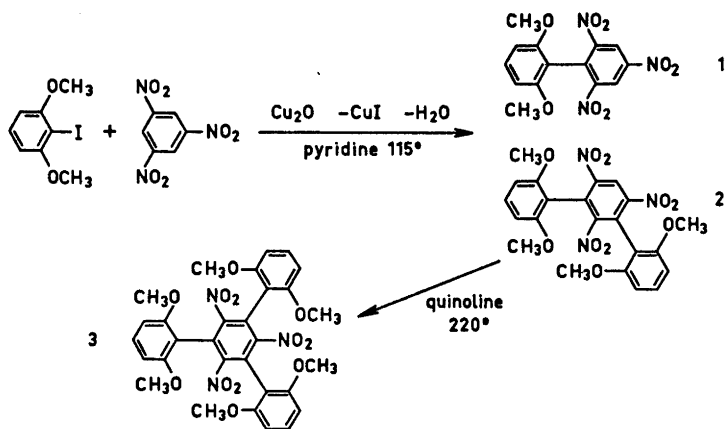
2,6-Dimethoxyphenylcopper is thermally more stable than phenylcopper and reacts more slowly with air and moisture. It reacts with 1,3,5-trinitrobenzene in pyridine to form a deep red solution. Acidification with acetic acid gives a red precipitate which on washing with warm benzene gives a red microcrystalline compound identified as the pyridinium salt of the Meisenheimer anion. The salt is easily oxidised to 2,6-dimethoxy-2',4',6'-trinitrobiphenyl (**1**) (Scheme 1).



2,6-Dimethoxyphenylcopper also reacts with *m*-dinitrobenzene in pyridine at 50° to form a blue solution from which 2,6-dimethoxy-2',4'-dinitrobiphenyl can be obtained in 6 % yield. 2,2',6,6'-Tetramethoxybiphenyl is the major product.

2,6-Dimethoxyphenylcopper reacts slowly with picryl chloride in dimethylformamide suspension and 2,6-dimethoxy-2',4',6'-trinitrobiphenyl (36 %) is formed. The weak colour of the reaction mixture indicates that no intermediate σ -complex is accumulated. In pyridine a complex reaction mixture is obtained. The solvent has, as also reported elsewhere,⁹ a decisive influence on many arylcopper reactions.

Iodoarenes react with *m*-dinitrobenzene or 1,3,5-trinitrobenzene and copper or copper(I) oxide in quinoline at 220° to give unsymmetrical biphenyls.^{16,17} When 1,3,5-trinitrobenzene and 2,6-dimethoxyiodobenzene are used it is possible to carry out the reaction at lower temperature, and products are isolated from reactions in boiling pyridine. In this case the mono- and the diarylated trinitrobenzenes **1** and **2** are formed while triarylation (to **3**) requires higher temperature. Biphenyl **1** is the main product when copper(I) oxide is used but the terphenyl **2** dominates when metallic copper is used. A preliminary experiment indicates that the symmetric phenyl-*m*-terphenyl (**3**) is formed in low yield in quinoline solution at 220° (Scheme 2).



DISCUSSION

Reactions between polynitroarenes and nucleophiles have been the subject of several reviews¹⁹⁻²² recently. The structures of the initially formed, strongly coloured σ -complexes, Meisenheimer compounds, have been determined by spectroscopic methods and in a few cases they have also been confirmed by X-ray investigations.

The aryl part of the arylcopper apparently adds to 1,3,5-trinitrobenzene to form a stable σ -complex in analogy with many other nucleophilic reagents.

Analogous reactions also proceed with 2,6-dimethoxyphenylsilver in pyridine.²³ Phenylethynylcopper and phenylethynylsilver also give σ -complexes with 1,3,5-trinitrobenzene in the same solvent.²³

Reactions with organocopper compounds have been suggested to proceed *via* homopolar²⁴ as well as heteropolar cleavage of the copper-carbon bond. Concerted reactions are also possible in some cases.

Though the details of the mechanism are still obscure we believe that the present reactions proceed *via* a concerted mechanism or a heteropolar copper-carbon bond cleavage rather than *via* free radicals.

Arylation of *m*-dinitrobenzene and 1,3,5-trinitrobenzene with iodoarenes and copper(I) oxide or metallic copper has been reported earlier. An organocopper intermediate from the nitroarene was considered.^{16,17} However, the present experimental results are not in agreement with such a simple model for the reaction.

The approximate order of increasing reactivity for iodobenzenes towards phenylcopper for various substituents is: 4-methoxy, 2,6-dimethoxy, 2-methoxy, none, 2-chloro, 2-fluoro, 4-methoxycarbonyl, 2-methoxycarbonyl, and 2-nitro.²⁵ Essentially the same order has been observed in reactions between 2-thienylcopper and iodobenzenes.²⁶ The corresponding order for iodobenzenes towards *m*-dinitrobenzene in the presence of copper(I) oxide is: 4-nitro, none, 4-methyl, 2-methoxy, 4-methoxy, and 2,6-dimethoxy. 2-Nitroiodobenzene gives no biphenyl at all.¹⁶

Another model must also be considered, in which copper reacts with the iodoarene and an arylcopper compound and copper iodide are formed. The arylcopper compound reacts quickly with the nitroarene to an intermediate σ -complex which on oxidation by copper(I) oxide could give the biphenyl and metallic copper. The latter would then react with the iodoarene. Further analogous reactions could lead to *m*-terphenyls and phenyl-*m*-terphenyls.

If an arylcopper compound were formed from the iodoarene, it would be expected to react with the iodo compound present to give a symmetric biphenyl. We therefore tried to react 2,6-dimethoxyiodobenzene with copper or copper(I) oxide in boiling pyridine, even in presence of the *m*-terphenyl (II), but no tetramethoxybiphenyl was formed. However, at higher temperature symmetric biphenyls are formed in moderate amounts from iodoarene and copper in the presence of *m*-dinitrobenzene.¹⁶ In quinoline at 220° 2,6-dimethoxyiodobenzene and copper slowly give resorcinol dimethylether, but so far no 2,2',6,6'-tetramethoxybiphenyl has been observed.

Nucleophilic attack on *m*-dinitrobenzene should occur *para* to a nitro group,²⁰ as was also observed in the reaction with 2,6-dimethoxyphenylcopper. 2,6-Dimethoxyiodobenzene, *m*-dinitrobenzene, and copper(I) oxide in quinoline give, however, mainly the product from attack *ortho* to both nitro groups.¹⁶

Attempts have been made, by spectroscopic methods, to observe intermediate σ -complexes in the reaction between 2,6-dimethoxyiodobenzene, 1,3,5-trinitrobenzene, and copper. When the compounds were stirred in pyridine at 50°, a deep red colour appeared within an hour. The visible spectrum of the solution showed two strong absorption peaks at 436 nm and 517 nm. However, the same visible spectrum was obtained if 2,6-dimethoxyiodobenzene was excluded. The colour most probably is due to the copper-catalyzed formation of a Meisenheimer complex between 1,3,5-trinitrobenzene and pyridine, in analogy to the formation of a similar complex from triethyl amine and 1,3,5-trinitrobenzene.²⁷ The intensity of the absorption at 436 nm corresponds to ca 20 % conversion to the Meisenheimer complex, assuming $\epsilon = 2.5 \times 10^4 \text{ l cm}^{-1} \text{ mol}^{-1}$.

In conclusion we can describe the situation as follows:

(a) 1,3,5-Trinitrobenzene and copper in pyridine give strongly coloured solutions at 50° (probably due to the formation of a Meisenheimer complex between 1,3,5-trinitrobenzene and pyridine).

(b) 2,6-Dimethoxyphenylcopper adds to 1,3,5-trinitrobenzene in pyridine solution to give a salt of 2,6-dimethoxy-2',4',6'-trinitro-1',*x*'-dihydrobiphenyl which is readily converted to 2,6-dimethoxy-2',4',6'-trinitrobiphenyl.

(c) Reactions between 2,6-dimethoxyiodobenzene, 1,3,5-trinitrobenzene, copper(I) oxide or copper in refluxing pyridine give high yields of biphenyl 1 and terphenyl 2.

(d) No evidence has been obtained for reaction of 2,6-dimethoxyiodobenzene with copper(I) oxide or copper in boiling pyridine to give 2,2',6,6'-tetramethoxybiphenyl.

None of the simple hypotheses seem to explain the experimental facts. Thus further work must consider the interaction between pyridine, nitro compound, iodoarene, copper or copper(I) oxide in the rate-determining step(s).

EXPERIMENTAL

Organometallic compounds were prepared in ether, freshly distilled from lithium aluminium hydride. Pyridine (A.R.) and quinoline (A.R.) were distilled from phosphorus pentoxide before use. All reactions were run under oxygen-free nitrogen. Extracts were dried over sodium sulphate. The products were identified by comparison with authentic samples (m.p. and IR) unless otherwise stated. NMR spectra were run at 60 MHz and chemical shifts are given as τ -values.

Phenylcopper and 1,3,5-trinitrobenzene. Phenylcopper prepared essentially according to Costa *et al.*²⁸ from copper(I) bromide (2.87 g), was mixed with 1,3,5-trinitrobenzene (3.2 g) dissolved in 150 ml pyridine. The mixture was kept at -10° for 2 h. The visible spectrum of the mixture diluted 1 to 1000 recorded after 15 min and 60 min showed two strong absorptions at 444 nm and 522 nm (absorbance 1.29 and 0.86, respectively).

No 2,4,6-trinitrobiphenyl was obtained from the reaction mixture after air oxidation or chromium trioxide oxidation or acidification.

2,6-Dimethoxyphenylcopper. Dimethoxyphenyl-lithium (0.05 mol), prepared from resorcinol dimethyl ether and butyl-lithium, was suspended in ether (250 ml) at room temperature. Dry, powdered copper(I) bromide (0.045–0.050 mol) was added and the reaction mixture stirred for 24 h. A fine, grey precipitate was slowly formed. The precipitate was filtered off, washed several times with dry ether to remove most of the lithium bromide and dried in vacuum. However, 2,6-dimethoxyphenylcopper always retained some unreacted copper(I) bromide and lithium compounds. Analysis of products from different runs gave: Found: C 41.2–44.8; H 4.1–4.5; Cu 27.8–31.1. Calc. for $C_8H_{10}O_2Cu$: C 48.0; H 4.5; Cu 31.7. The IR spectrum of the product in KBr showed that only traces of resorcinol dimethyl ether and 2,2',6,6'-tetramethoxybiphenyl were present. The most characteristic frequencies in cm^{-1} are: 1558s, 1490m, 1450s, 1415s, 1232s, 1093s, 768s and 714s. 2,6-Dimethoxyphenylcopper was used without further purification. The amount of reactants and the yield in the reactions are calculated assuming a pure aryl-copper compound.

2,6-Dimethoxyphenylcopper and m-dinitrobenzene. 2,6-Dimethoxyphenylcopper (2.2 g, 11 mmol) and *m*-dinitrobenzene (1.8 g, 11 mmol) were reacted in pyridine (50 ml) at 50° . A blue colour developed slowly. After 5 h the colour changed to violet and finally to brown after 20 h. Ether was added to the cooled reaction mixture and pyridine was removed by extraction with acid. The solution was dried and the solvent evaporated. The residue (2.47 g) was chromatographed on silica gel to give 2,2',6,6'-tetramethoxybiphenyl (0.63 g, 42 %, m.p. $170-175^\circ$), 2,6-dimethoxy-2',4'-dinitrobiphenyl (0.21 g, 6 %, m.p. $155-160^\circ$ ¹⁴) and unreacted *m*-dinitrobenzene (1.4 g, 78 %).

2,6-Dimethoxyphenylcopper and 1,3,5-trinitrobenzene. 2,6-Dimethoxyphenylcopper (1.6 g, 8 mmol) and 1,3,5-trinitrobenzene (1.7 g, 8 mmol), respectively, suspended and dissolved in 5 ml pyridine each, were mixed under cooling. The pyridine was evaporated *in vacuo* after 20 min. The residue was stirred in glacial acetic acid (50 ml) for 20 h and the red precipitate (2.5 g) filtered off, washed with acetic acid and with ether and dried in a vacuum. Part of the residue (0.5 g) was extracted with boiling benzene (50 ml) for 10 min to dissolve the copper(II) acetate-pyridine complex present. The microcrystalline, dark red, insoluble material (0.25 g, 37 %) was dried and found to be identical (IR spectrum) with the product from 2,6-dimethoxyphenylsilver and 1,3,5-trinitrobenzene.²⁸

The compound decomposes quickly at 150° . Heated in vacuum, it (0.4 g) decomposed slowly at 110° to give 2,6-dimethoxy-2',4',6'-trinitrobiphenyl (0.23 g, 70 %) together with a yellow compound (probably a primary amine according to the IR spectrum) apparently through a disproportionation reaction.

Analytical and spectroscopical data for the red compound are in agreement with those expected for the pyridinium salt of 2,6-dimethoxy-1',*x'*-dihydro-2',4',6'-trinitrobiphenyl. (Found: C 53.4; H 4.2; N 13.0. Calc. for $C_{19}H_{18}N_4O_8$: C 53.0; H 4.2; N 13.0). The visible spectrum in pyridine shows two strong absorption peaks at 475 nm ($\epsilon=27\ 000$) and 585 nm ($\epsilon=13\ 000$), typical for Meisenheimer compounds.²⁸ The IR spectrum (KBr) shows the expected absorption peak at $1485\ cm^{-1}$ due to the nitro groups in Meisenheimer compounds.²⁸ The NMR spectrum (in dimethylsulphoxide- d_6) shows the following characteristics: singlet at 1.63, multiplets at 2.87 and 3.43, singlet at 3.67, and singlet at 6.30. The pyridine spectrum was hidden in the background.

2,6-Dimethoxyphenylcopper (1.0 g, 5 mmol) and 1,3,5-trinitrobenzene (1.1 g, 5 mmol) were reacted for 24 h at 50° in pyridine (25 ml). Ether was added to the cooled reaction mixture and insoluble material filtered off. Pyridine was removed by extraction with acid. The insoluble residue was boiled with benzene. 2,6-Dimethoxy-2',4',6'-trinitrobiphenyl (0.81 g, 46 %) was isolated from this solution and recrystallised from ethanol, m.p. 170–173°. The ether phase was analysed by GLC and found to contain 1,3,5-trinitrobenzene (0.11 g, 10 %), 2,2',6,6'-tetramethoxybiphenyl (0.09 g, 13 %) and 2,6-dimethoxy-2',4',6'-trinitrobiphenyl (0.15 g, 9 %).

2,6-Dimethoxyphenylcopper and 2,4,6-trinitrochlorobenzene. 2,6-Dimethoxyphenylcopper (1.6 g, 8 mmol) and 2,4,6-trinitrochlorobenzene (2.0 g, 8 mmol) were reacted at 25° in dry dimethylformamide (20 ml) for 24 h. Ether was added to the reaction mixture and dimethylformamide removed by washing with water. The ether solution was dried and the solvent evaporated. The residue was recrystallised from ethanol to give 2,6-dimethoxy-2',4',6'-trinitrobiphenyl (1.0 g, 36 %) m.p. 170–173°.

2,6-Dimethoxyiodobenzene, 1,3,5-trinitrobenzene, and copper(I) oxide. 1,3,5-Trinitrobenzene (0.05 mole), 2,6-dimethoxyiodobenzene (0.05 mol), copper(I) oxide (0.05 mol), and dry pyridine (30 ml) were heated at 115° (oil bath) under nitrogen for 10 h. Within 10 min the reaction mixture turned dark red and during the reaction the colour changed to dark brown. The mixture was allowed to cool, ether was added and unreacted copper(I) oxide and precipitated copper(I) iodide-pyridine complex was filtered off. The filtrate was extracted with hydrochloric acid (2 M) to remove remaining pyridine, washed with water, dried and the ether evaporated. GLC (with internal standard) showed peaks corresponding to 2,6-dimethoxy-2',4',6'-trinitrobiphenyl (1, yield 45 %) and 2,2',6,6''-tetramethoxy-2',4',6'-trinitro-*m*-terphenyl (2, yield 7 %) but no peak with retention time equal to 2,2',6,6''-tetramethoxybiphenyl.

Fractional crystallisation (ethanol) of the crude product gave a small amount of pale yellow crystals of compound 2, m.p. 297–298⁵ (after sublimation), and yellow crystals of compound 1, m.p. 171–173°.

The NMR spectrum of the biphenyl (1) (in deuteriochloroform) showed the following characteristics: singlet at 1.1 (2 H), triplet at 2.6 (1 H), doublet at 3.4 (2 H), $J=9$ Hz, and a sharp singlet at 6.3 (6 H). The mass spectrum showed the parent ion at m/e 349 as expected, and the fragmentation pattern characteristic of an aromatic nitro compound.

The NMR spectrum of the *m*-terphenyl (2) showed the following characteristics: singlet at 1.3 (ca. 1 H), triplet at 2.6 (2 H), doublet at 3.4 (4 H), $J=9$ Hz, and a sharp singlet at 6.3 (12 H). The mass spectrum showed the parent ion at m/e 485 as expected, and a fragmentation pattern as expected for an aromatic nitro compound.

NMR and mass spectra thus support the structures 2,6-dimethoxy-2',4',6'-trinitrobiphenyl (1) and 2,2',6,6''-tetramethoxy-2',4',6'-trinitro-*m*-terphenyl (2), respectively.

2,6-Dimethoxyiodobenzene, 2,6-dimethoxy-2',4',6'-trinitrobiphenyl, and copper(I) oxide. 2,6-Dimethoxy-2',4',6'-trinitrobiphenyl (1, 0.01 mol), 2,5-dimethoxyiodobenzene (0.01 mol), copper(I) oxide (0.01 mol) and pyridine (30 ml) were heated at 115° for 20 h under nitrogen.

The reaction mixture was allowed to cool, ether (200 ml) was added and the solids filtered off.

The solids were extracted with hydrochloric acid (2 M), washed with water, dried and finally extracted with acetone. The acetone solution gave on evaporation a light brown-yellow product (0.92 g, m.p. 295–297°). Sublimation gave yellow crystals of 2,2',6,6''-tetramethoxy-2',4',6'-trinitro-*m*-terphenyl (2) m.p. 297–298° (0.80 g).

The filtrate was extracted with hydrochloric acid (2 M), washed with water and dried. After evaporation of the ether, fractional crystallisation (ethanol) gave brown-yellow crystals [mainly starting material and *m*-terphenyl (2), 2.34 g]. Fractional sublimation gave yellow crystals of 2,2',6,6''-tetramethoxy-2',4',6'-trinitro-*m*-terphenyl (2), m.p. 296–298° (1.00 g).

The total yield of *m*-terphenyl (2) was 37 %. GLC showed no peak corresponding to 2,2',6,6''-tetramethoxybiphenyl.

*2,6-Dimethoxyiodobenzene, 2,2',6,6''-tetramethoxy-2',4',6'-trinitro-*m*-terphenyl and copper(I) oxide.* 2,2',6,6''-Tetramethoxy-2',4',6'-trinitro-*m*-terphenyl (2, 0.4 g), 2,6-dimethoxyiodobenzene (0.25 g), copper(I) oxide (0.25 g), and quinoline (10 ml) were heated at 220° for 10 h under nitrogen. The reaction mixture was allowed to cool and ether (30

ml) was added. Filtration gave a small amount of yellow copper(I) iodide-quinoline complex. The filtrate was extracted with hydrochloric acid (2 M), washed with water and dried. GLC and TLC showed the presence of the starting materials only.

The filter cake was extracted with dilute hydrochloric acid, washed with water and dried. The residue was sublimed (0.1 mm, 280°) and gave a pale yellow compound, m.p. > 360° (4 mg).

The IR spectrum showed the presence of an aromatic compound with nitro and methoxy groups. The mass spectrum showed the parent ion at m/e 621, a double-charged ion at m/e 310.5, and a fragmentation pattern analogous to the *m*-terphenyl (2) and biphenyl (1). The isolated compound therefore apparently is the expected 2,2'',6,6''-tetramethoxy-5'(2,6-dimethoxyphenyl)-2',4',6'-trinitro-*m*-terphenyl (3, yield ca. 1%). When the same experiment was carried out in pyridine solution (115°, 20 h), no product (3) could be found.

2,6-Dimethoxyiodobenzene, 1,3,5-trinitrobenzene, and copper. 1,3,5-Trinitrobenzene (0.01 mol), 2,6-dimethoxyiodobenzene (0.01 mol), copper bronze (1 g), and pyridine (50 ml) was heated on an oil bath at 115° for 10 h. A strong red colour appeared within a few minutes. The reaction mixture was allowed to cool and ether (100 ml) was added. Filtration gave a brown filtrate and a brown solid (6.03 g).

Pyridine was removed from the solid by extraction with hydrochloric acid (2 M). Extraction of the solid with acetone gave a brown solution and a residue (copper bronze and copper(I) iodide, 2.4 g). Evaporation of the acetone gave a light brown solid (0.64 g) which on sublimation gave yellow crystals of 2,2'',6,6''-tetramethoxy-2',4',6'-trinitro-*m*-terphenyl m.p. 295–297° (0.6 g).

The ether filtrate was treated with hydrochloric acid (2 M), washed with water and dried. Fractional crystallisation of the residue after evaporation gave a yellow solid, m.p. 295–297° (0.13 g), shown by GLC and TLC to be 2,2'',6,6''-tetramethoxy-2',4',6'-trinitro-*m*-terphenyl.

Finally, evaporation gave a crystalline residue (0.66 g). GLC showed it to be starting material, 2,6-dimethoxy-2',4',6'-trinitrobiphenyl (1, ca. 0.19 g), and a small amount of 2,2'',6,6''-tetramethoxy-2',4',6'-trinitro-*m*-terphenyl (2, ca. 0.01 g). Total yields: 2,6-dimethoxy-2',4',6'-trinitrobiphenyl (1, ca. 0.19 g, 8%), 2,2'',6,6''-tetramethoxy-2',4',6'-trinitro-*m*-terphenyl (2, ca. 1.89 g, 78%). No 2,2',6,6'-tetramethoxybiphenyl could be found by GLC.

1,3,5-Trinitrobenzene and copper in pyridine. 1,3,5-Trinitrobenzene (0.001 mol) and copper (0.002 mol) was stirred in 100 ml pyridine at 50° under nitrogen. Small samples were withdrawn and diluted 1 to 100. The visible spectrum after 3 h showed absorptions at 436 nm and 517 nm (absorbance=0.49 and 0.28, respectively). Essentially the same spectrum was obtained in presence of 2,6-dimethoxyiodobenzene (0.001 mol).

2,6-Dimethoxyiodobenzene and copper in pyridine. 2,6-Dimethoxyiodobenzene (0.01 mol), copper (electrolytical grade, 1 g) and pyridine (30 ml) were heated on an oil bath for 6 h at 115° under nitrogen. After cooling ether was added, and the solid material (only copper, 0.98 g) filtered off.

The ether solution was extracted with hydrochloric acid (2 M), washed with water, dried, and the ether evaporated. The residue was 2,6-dimethoxyiodobenzene (2.46 g, *i.e.* 93%, recovered). GLC showed no 2,2',6,6'-tetramethoxybiphenyl and less than 1% 1,3-dimethoxybenzene.

When the experiment was run in quinoline at 220° 40% of 2,6-dimethoxyiodobenzene could be recovered together with 25% 1,3-dimethoxybenzene. No 2,2',6,6'-tetramethoxybiphenyl could be found.

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REFERENCES

1. House, H. O., Respass, W. L. and Whitesides, G. M. *J. Org. Chem.* **31** (1966) 3128.
2. Corey, E. J. and Posner, G. H. *J. Am. Chem. Soc.* **89** (1967) 3911; **90** (1968) 5615.
3. Whitesides, G. M., Fischer, W. F., Jr., Filippo, J. S., Jr., Bashe, R. W. and House, H. O. *J. Am. Chem. Soc.* **91** (1969) 4871.

4. Nilsson, M. and Wahren, R. *J. Organometal. Chem.* **16** (1969) 515.
5. Vig, O. P., Kapur, J. C. and Sharma, S. D. *J. Indian Chem. Soc.* **45** (1968) 734; **45** (1968) 1026.
6. Castro, C. E., Gaughan, E. J. and Owsley, D. C. *J. Org. Chem.* **31** (1966) 4071.
7. Castro, C. E., Havlin, R., Honwad, V. K., Malte, A. and Mojé, S. *J. Am. Chem. Soc.* **91** (1969) 6464.
8. Gilman, H. and Straley, J. M. *Rec. Trav. Chim.* **55** (1936) 821.
9. Nilsson, M. and Wennerström, O. *Tetrahedron Letters* **29** (1968) 3307.
10. Cairncross, A. and Sheppard, W. A. *J. Am. Chem. Soc.* **90** (1968) 2186.
11. Vig, O. P., Sharma, S. D. and Kapur, J. C. *J. Indian Chem. Soc.* **46** (1969) 167.
12. DePasquale, R. J. and Tamborski, C. *J. Org. Chem.* **34** (1969) 1736.
13. Jukes, A. E., Dua, S. S. and Gilman, H. *J. Organometal. Chem.* **21** (1970) 241.
14. Björklund, C. and Nilsson, M. *Acta Chem. Scand.* **22** (1968) 2585.
15. Nilsson, M. and Ullenius, C. *Acta Chem. Scand.* **22** (1968) 1998.
16. Björklund, C. and Nilsson, M. *Acta Chem. Scand.* **22** (1968) 2338.
17. Björklund, C. and Nilsson, M. *Acta Chem. Scand.* **22** (1968) 2581.
18. Miller, J. *Aromatic Nucleophilic Substitution*, Elsevier, Amsterdam 1968.
19. Crampton, M. R. *Advan. Phys. Org. Chem.* **7** (1969) 211.
20. Buck, P. *Angew. Chem.* **81** (1969) 136.
21. Buncel, E., Norris, A. R. and Russell, K. E. *Quart. Rev.* **22** (1968) 123.
22. Foster, R. and Fyfe, C. A. *Rev. Pure Appl. Chem.* **16** (1966) 61.
23. Wennerström, O. *Acta Chem. Scand.* **25** (1971). *In press.*
24. Hashimoto, H. and Nakano, T. *J. Org. Chem.* **31** (1966) 891.
25. Nilsson, M. and Wennerström, O. *Acta Chem. Scand.* **24** (1970) 482.
26. Nilsson, M. and Ullenius, C. *Acta Chem. Scand.* **24** (1970) 2379.
27. Servis, K. L. *J. Am. Chem. Soc.* **89** (1967) 1508.
28. Costa, G., Camus, A., Gatti, L. and Marsich, N. *J. Organometal. Chem.* **5** (1966) 568.

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