

Mono-, Di- and Triarylation of 1,3,5-Trinitrobenzene

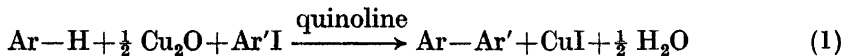
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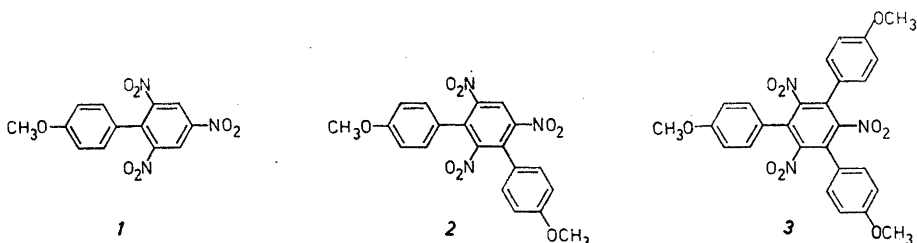
The reaction of 1,3,5-trinitrobenzene with *p*-iodomethoxybenzene and copper(I) oxide in quinoline solution for successively longer times or higher temperatures leads, in turn, to 4-methoxy-2',4',6'-trinitrobiphenyl, 4,4''-dimethoxy-2',4',6'-trinitro-*m*-terphenyl and 4,4''-dimethoxy-5'(4-methoxyphenyl)-2',4',6'-trinitro-*m*-terphenyl.

The reaction on *m*-dinitrobenzene with iodoarenes and copper(I) oxide in quinoline solution gives 2,6-dinitrobiphenyls and occasionally 2,4-dinitrobiphenyls also.^{1,2}

This reaction seems fairly general (Eqn. 1) and we have preliminarily reported such an arylation of 1,3,5-trinitrobenzene to give both a 2,4,6-trinitrobiphenyl and a 2',4',6'-trinitro-*m*-terphenyl.¹



The present work is a further examination of the reaction between 1,3,5-trinitrobenzene, *p*-iodomethoxybenzene, and copper(I) oxide in quinoline solution.



Using equivalent amounts of starting materials the reaction gave a 72 % yield of 4-methoxy-2',4',6'-trinitrobenzene (*1*) already after 1 h at 180°. Reaction with an excess of *p*-iodomethoxybenzene for 2 h at 180° gave 58 % of the biphenyl *1* and 8 % yield of 4,4''-dimethoxy-2',4',6'-trinitro-*m*-terphenyl (*2*). When the reaction temperature was raised and the reaction time prolonged the yield of the biphenyl *1* decreased (to *ca.* 12 %), the yield of the *m*-ter-

phenyl increased somewhat (to *ca.* 10 %) and in addition a triarylation product, 4,4''-dimethoxy-5'(4-methoxyphenyl)-2',4',6'-trinitro-*m*-terphenyl (**3**) was formed (16 % yield after 4 h at 220°).

Thus, it seems possible to control the reaction so as to give either mono-, di-, or triarylation by using the correct temperatures, reaction times, and proportions of reactants.

The reaction between trinitrobenzene, *p*-iodomethoxybenzene, and copper(I) oxide to give 4-methoxy-2',4',6'-trinitrobiphenyl seems to be considerably faster than the corresponding reaction with *m*-dinitrobenzene (*cf.* Ref. 2). This difference is larger than is to be expected solely on statistical grounds and may have some bearing on the reaction mechanism. We have assumed that the coupling of 1,3-dinitrobenzene proceeds *via* an intermediate of the 2,6-dinitrophenylcopper type, stabilized by the chelating influence of the nitro group. There are, however, indications that the iodoarene may also be involved in the rate-determining step and that donor-acceptor interaction between the iodoarene and the nitroarene may be important.² 1,3,5-Trinitrobenzene is undoubtedly a stronger electron acceptor than *m*-dinitrobenzene. On the other hand trinitrobenzene is a poor proton acid and does not exchange its protons under conditions where 1,3-dinitrobenzene rapidly exchanges at least its 2-proton with heavy water (dimethylformamide, D₂O, NaOH). There is some evidence that 1,3-dinitrobenzene on reaction with base may lose one proton and form an anion, whereas 1,3,5-trinitrobenzene seems to form a complex with the base (OH⁻ ion).^{3,4}

However, the non-catalysed decarboxylation of 2,4,6-trinitrobenzoic acid proceeds by unimolecular loss of CO₂ from the 2,4,6-trinitrobenzoate ion to give presumably the 2,4,6-trinitrophenyl anion.^{5,6}

It remains to be tested whether these differences are relevant to the mechanism of the copper(I) oxide-promoted reactions between nitroarenes and iodoarenes.

In any case the results illustrate the connection between the copper(I) oxide promoted couplings of nitroarenes and iodoarenes, the decarboxylative couplings of 2-nitro-, 2,4-dinitro-, and 2,6-dinitrobenzoic acids,^{7,8} and the copper-promoted reactions in the thiophene series.^{9,10}

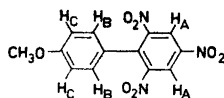
The successive introduction of 4-methoxyphenyl substituents on the trinitrobenzene nucleus changes its properties. This is clearly demonstrated by the colour changes, the biphenyl **1** is orange, the *m*-terphenyl **2** yellow, and trisubstitution product **3** almost colourless. The spectral evidence in Table 1 illustrates this and indicates that both the 4-methoxyphenyl groups and the nitro groups are gradually forced out of the plane.

The changes seem to parallel the decreasing reactivity of 1,3,5-trinitrobenzene and its successive substitution products. Due to the steric crowding the catalytic hydrogenation of the nitro groups in compound **3** proceeds very slowly.

EXPERIMENTAL

Melting points were determined with a Leitz hot stage microscope. Elemental analyses were carried out by Alab, Uppsala, Sweden. The UV spectra were measured in 99.5 % ethanol with a Beckman DK 2 instrument. The NMR spectra were run on a Varian A

Table 1. UV and NMR data illustrating the effects of successive substitution by 4-methoxyphenyl groups on 1,3,5-trinitrobenzene. In all relevant compounds $J_{BC} = 9$ Hz. For notations, see the formula below.



Substance	UV				NMR			
	λ_1 nm	λ_2 nm	$\log \epsilon_1$	$\log \epsilon_2$	τ_{H_A}	τ_{H_B}	τ_{H_C}	τ_{OCH_3}
Methoxybenzene	222	271	3.86	3.33				6.22
4-Methoxybiphenyl		260 ¹		ca. 4.25 ¹		ca. 2.60	3.11	6.25
1,3,5-Trinitrobenzene	222	ca. 300 sh ca. 340 sh	4.45		0.73			
4-Methoxy-2',4',6'-trinitro-biphenyl (1)	227	340	4.47	3.61	1.35	2.87	3.05	6.18
4,4'-Dimethoxy-2',4',6'-trinitro-m-terphenyl (2)	227	305	4.62	3.75	1.64	2.83	3.09	6.22
4,4'-Dimethoxy-5'(4-methoxyphenyl)-2',4',6'-trinitro-m-terphenyl (3)	224	279	4.78	4.22	—	2.74	3.11	6.25

60-A instrument (in deuterochloroform). Gas chromatography (GLC) was carried out on an Aerograph 204-1B with flame detector using SE-30, 5% (1.50 m), on Chromosorb W as stationary phase.

Coupling of 1,3,5-trinitrobenzene with p-iodoanisole, 180°, 1 h. 1,3,5-Trinitrobenzene (0.01 mole), *p*-iodoanisole (0.01 mole), copper(I) oxide (0.005 mole), and quinoline (25 ml) were mixed in a reaction flask and heated with stirring in a silicone-oil bath.

The reaction mixture was allowed to cool and ether (200 ml) was added. The yellow, crystalline complex of copper iodide and quinoline, as well as unreacted copper(I) oxide, were filtered off, washed with ether and discarded. The filtrate was extracted with 2 M hydrochloric acid to remove the remaining quinoline, washed with water, dried ($\text{Na}_2\text{SO}_4 \cdot \text{H}_2\text{O}$), and the solvent evaporated.

Distillation of the residue gave starting material and a fraction, b.p. 140–220°/0.3 mm. Recrystallisation of the latter from ethanol and sublimation gave 4-methoxy-2',4',6'-trinitrobiphenyl (1) as orange needles, m.p. 143–145°, (2.25 g, 72%). (Found: C 49.2; H 2.8; N 12.8. Calc. for $\text{C}_{15}\text{H}_9\text{N}_3\text{O}_5$: C 48.9; H 2.8; N 13.2).

Coupling at 180°, 2 h. 1,3,5-Trinitrobenzene (0.01 mole), *p*-iodoanisole (0.03 mole), copper(I) oxide (0.02 mole), and quinoline (25 ml) were reacted and the reaction mixture worked up as described above. Separation of the reaction product on an alumina column with light petroleum (b.p. 40–60°)/benzene gave 4-methoxy-2',4',6'-trinitrobiphenyl (1.84 g, 58%), m.p. 135–140° (after sublimation m.p. 142–144°), and yellow needles of 4,4'-dimethoxy-2',4',6'-trinitro-m-terphenyl (2), m.p. 231–240°, after sublimation m.p. 238–240° (0.33 g, 8%). (Found: C 56.6; H 3.6; N 9.9. Calc. for $\text{C}_{20}\text{H}_{11}\text{N}_3\text{O}_8$: C 56.5; H 3.6; N 9.9).

Coupling at 220° for 4 h. 1,3,5-Trinitrobenzene (4 g), *p*-iodoanisole (13 g), copper(I) oxide (4 g) (molar ratio about 1:2.3:1.2), and quinoline (60 ml) were reacted and worked up as described above. Trituration of the product with methanol gave yellow crystals. Recrystallisation from ethyl acetate and sublimation gave nearly white crystals of 4,4'-dimethoxy-5'(4-methoxyphenyl)-2',4',6'-trinitro-m-terphenyl (3), m.p. 310–311° (2.01 g, 16% yield based on trinitrobenzene). (Found: C 61.3; H 4.0; N 7.9. Calc. for $\text{C}_{22}\text{H}_{21}\text{N}_3\text{O}_9$: C 61.0; H 4.0; N 7.9). GLC analysis of the mother liquor gave peaks corresponding to 4-methoxy-2',4',6'-trinitrobiphenyl (ca. 0.9 g, 12%) and 4,4'-dimethoxy-2',4',6'-trinitro-m-terphenyl (ca. 1.0 g, 10%). The mother liquor was dark red, probably due to the presence of nitroarylamines also.

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