Contribution to the Study of the Mechanism of the Ullmann Biaryl Condensation. The Reaction of 2,3-Dichloronitrobenzene

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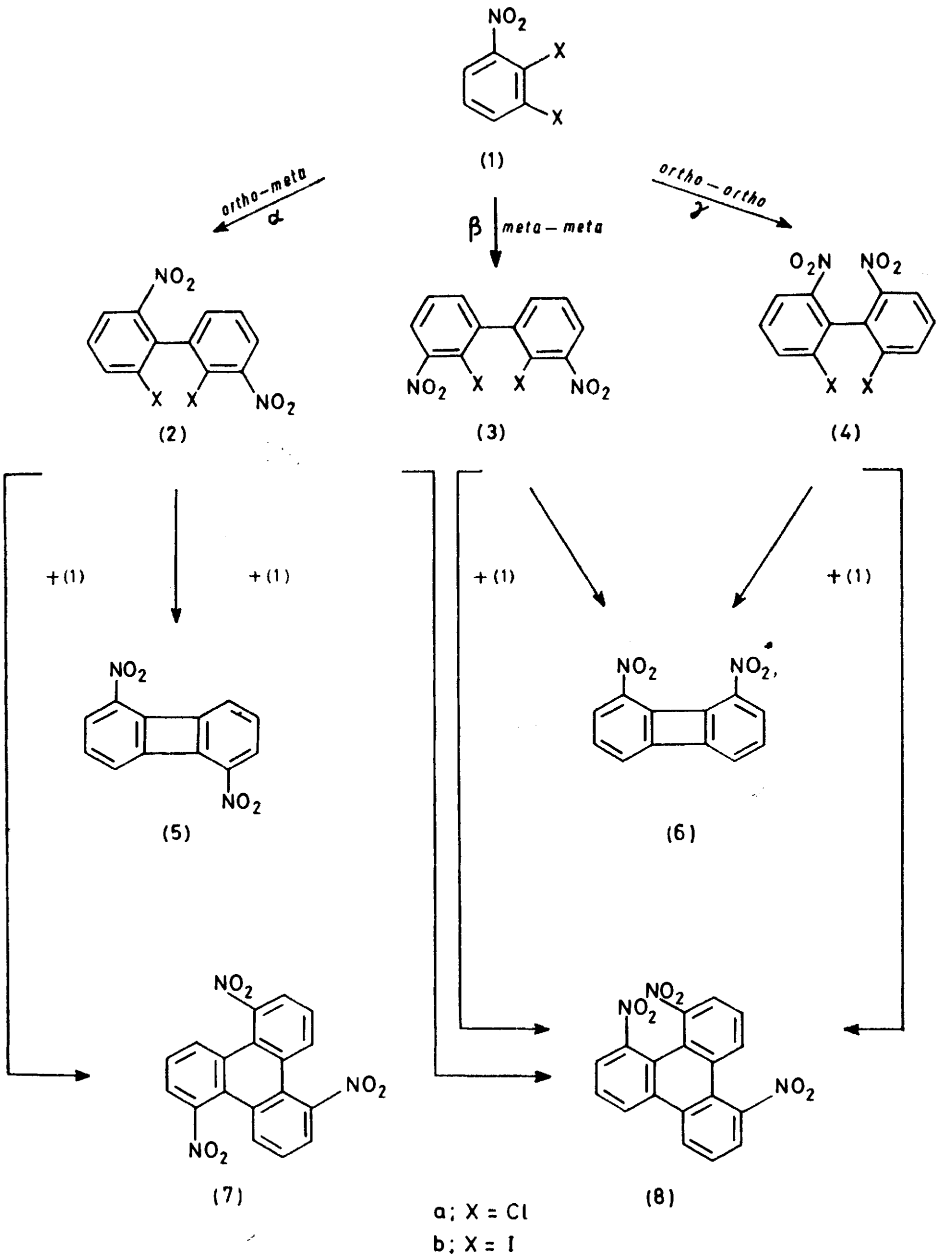
The reaction of 2,3-dichloronitrobenzene with copper bronze gives, in a total yield of 100%, 1,5-dinitrobiphenylene and 1,5,9-trinitrotriphenylene. The formation of these compounds necessarily implies an initial *ortho–meta* coupling, which rules out a free-radical process, and a mechanism involving the coupling of two molecules of an organocopper intermediate. The results are, on the contrary, in good accord with the ionic mechanism, proposed by Fanta, according to which the organocopper intermediate reacts with a molecule of the aryl halide.

THE mechanism of the Ullmann biaryl condensation has been the subject of a large amount of discussion.[1] Three main reaction schemes have been proposed, the first being a free-radical mechanism. Secondly, an ionic mechanism has been suggested. The rate-determining step is the formation of an arylcopper compound, which

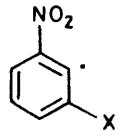


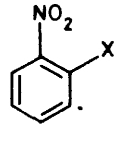
SCHEME 1

subsequently reacts with a molecule of the aryl halide. According to Fanta,[1a] the first stage is governed mainly by the susceptibility of the aromatic halide to nucleophilic attack, whereas the second step is more sensitive to steric factors. Finally, a mechanism involving the coupling of the molecules of the above mentioned organocopper intermediate has been proposed.[2] Although most of the experimental data seems to be in favour of the ionic mechanism, this is still a matter of controversy.[1d,3] We report here results which bring new evidence in confirmation of this mechanism.

RESULTS AND DISCUSSION

The reaction of 2,3-dichloronitrobenzene (1a) with copper bronze gives, in a total yield of 100%, 1,5-dinitrobiphenylene (5) and 1,5,9-trinitrotriphenylene (7).


(9)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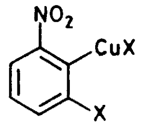
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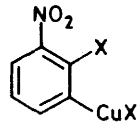

(12)

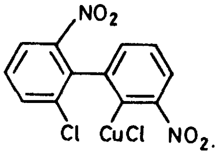
a; X = Cl
b; X = I

Compound (7) was characterized by analysis, mass and n.m.r. spectra, and dipole moment. The latter is 1.22 D, which is much lower [4] than that, 7.4 D, calculated for the isomer (8).

All possible, successive, bimolecular reactions yielding bi- and tri-condensed compounds are given in Scheme 1. The formation of (5) and (7) necessarily implies initial *ortho-meta* coupling (with reference to the nitro-group) along path α. This result rules out the first and third mechanisms. For example, in the case of a radical mechanism, two successive processes would have to take place: first, 50% of each radical (9a) and (10a) would have to be formed; secondly, one molecule of (9a) would have to react exclusively with one molecule of (10a), since no product derived form symmetrical coupling (paths β and γ) is found experimentally, and since the yield of (5) and (7) is 100%. The probability that these successive events occur is practically nil.

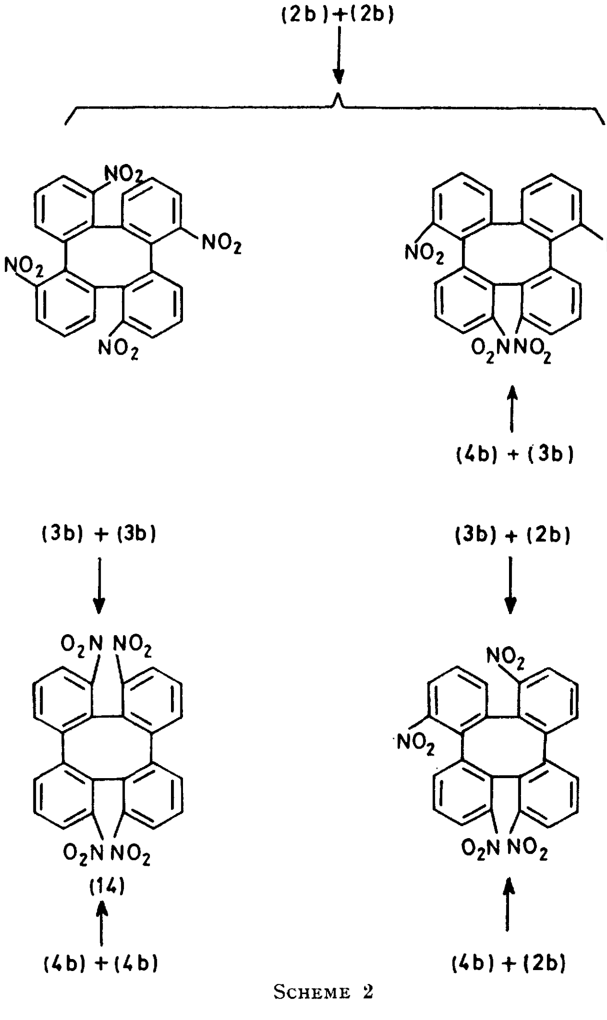
The same reasoning can be repeated for the organocopper compounds (11a) and (12a).

The experimental results can be explained very easily on the basis of an ionic mechanism. The initial formation of the organocopper compound (11a) by nucleophilic attack of the copper on the carbon–halogen bond is facilitated by the electron-attracting effect of the neighbouring nitro-group, in agreement with the views of Fanta. Compound (11a) then reacts with (1a) to give the intermediate (2a). The reaction takes place with the chlorine *meta* to the nitro-group of (1a), which is again in keeping with Fanta's predictions according to which steric factors play a major role during this step.


(13)

Despite several attempts, we have not been able to isolate 2,2′-dichloro-3,6′-dinitrobiphenyl (2a).

The formation of 1,5,9-trinitrotriphenylene (7) implies a subsequent reaction either between the organocopper compound (13) and 2,3-dichloronitrobenzene (1a), or between the organocopper derivative (11a) and compound (2a). The first possibility seems to be the more probable for two reasons: first, compound (2a), which has chlorine *ortho* to a nitro-group should be as reactive as (1a) towards copper, which explains why we could not isolate it; secondly, (13) must be an intermediate in the formation of 1,5-dinitrobiphenylene (5).



SCHEME 2

Our results help to clarify some of the data found in the literature. The Ullmann condensation has been carried out[5] with the iodo analogue of (1a), 2,3-di-iodonitrobenzene (1b). The reaction yields a mixture of 1,5-dinitrobiphenylene (5), which can be obtained solely *via* initial *ortho–meta* coupling (Scheme 1) and 4,5,12,13-tetranitro*tetra*phenylene (14), which can be formed only through initial *ortho–ortho* or *meta–meta* coupling (Scheme 2). As with the chloro derivative, an iodocopper compound (11b) is probably formed initially. The second stage of the reaction, however, occurs partly in the *ortho*- and partly in the *meta*-position of 2,3-di-iodonitrobenzene, because the greater lability of iodine partially compensates for the influence of steric factors. This hypothesis is confirmed by the fact that during the reaction of 3-bromo-2-iodo-5-methylnitrobenzene, only the product of *ortho–ortho* coupling could be isolated.[6] The formation of 1,5-dinitrobiphenylene (5) can be explained quite easily by the possibility of initial *ortho–meta* coupling as in the case of the chloro compound, and the hypothesis of a benzyne intermediate[5] is not necessary.

EXPERIMENTAL

^{1}H N.m.r. spectra were recorded with a JEOL FX 100 spectrometer ($CDCl_3$ as solvent, tetramethylsilane as internal standard). Mass spectra were obtained on a Finnigan 3003 spectrometer. The dipole moment was determined in dioxan at 27.4 °C.

Materials.—Dimethylformamide (HP quality), copper bronze (Merck), and 2,3-dichloronitrobenzene (Fluka) were used.

The Ullmann Reaction.—To a solution of 2,3-dichloronitrobenzene (10 g, 52.08 mmol) in dimethylformamide (80 ml) was added copper bronze (20 g). The mixture was heated to reflux with stirring for 2 h and the copper bronze was filtered off and washed with methylene chloride. The filtrate was poured into water, filtered on alumina, and dried ($MgSO_4$). After removal of the solvent the residue was dissolved in acetone (1 000 ml). 25 ml of this solution were partly evaporated and chromatographed on a silica gel thin layer, using benzene–hexane (2 : 3) as eluant, which yielded two bands. The first band gave 1,5-dinitrobiphenylene (72.5 mg, 0.3 mmol), m.p. 272 °C (lit.,[5] 272—274 °C), *m/e* 242 (M^+), δ 7.56 (1 H, dd, 2-H), 7.36 (1 H, dd, 4-H), and 7.11 (1 H, dd, 3-H), $J_{2.3}$ 8.8, $J_{2.4}$ 0.75, and $J_{3.4}$ 6.5 Hz.

1,5,9-Trinitrotriphenylene, in the second band (revealed by u.v.), was desorbed with acetone and the solution was filtered on charcoal and evaporated, affording product (100 mg, 0.27 mmol). It was recrystallised from acetone as *needles*, m.p. 305—307 °C (Found: C, 59.4; H, 2.7; N, 11.8. $C_{18}H_9N_3O_6$ requires C, 59.4; H, 2.5; N, 11.7%), δ 8.15 (1 H, dd, 10-H), 7.93 (1 H, dd, 12-H), and 7.66 (1 H, t, 11-H), $J_{10.11} = J_{11.12} = 8$, $J_{10.12}$ 1.2 Hz, *m/e* 363 (M^+), μ 1.22 D.[4]

Larger amounts of 1,5-dinitrobiphenylene and 1,5,9-trinitrotriphenylene can be obtained by column chromatography, but the separation is more difficult. The relative yields of 1,5-dinitrobiphenylene and 1,5,9-trinitrotriphenylene vary from one experiment to the other, but the total yield is always 100%.

We thank Professor H. Lumbroso, Université de Paris VI, for the determination of the dipole moment of 1,5,9-trinitrotriphenylene and Dr. C. Moïse for the n.m.r. spectra.

[8/1965 *Received*, 10*th November*, 1978]

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