
The Synthesis of Diarylamines by Nitro-group Displacement. Activation of Anilines containing Electron-withdrawing Groups by Potassium Carbonate

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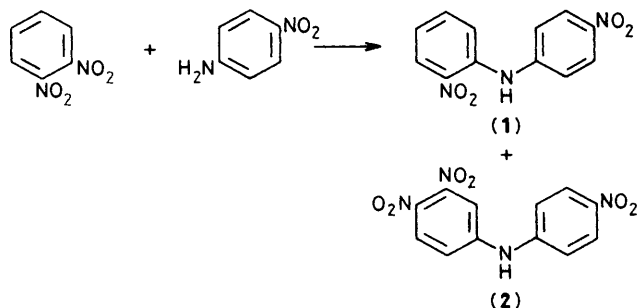
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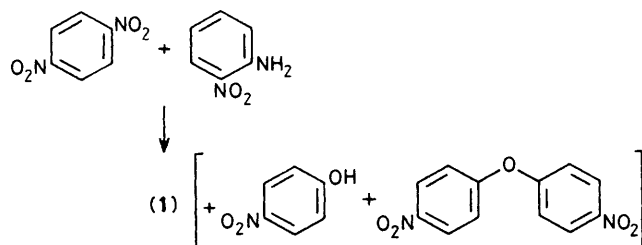
Anilines of enhanced *N*-acidity can displace activated aromatic nitro-groups in dipolar aprotic solvents in the presence of potassium carbonate; the resulting diarylamines are generally obtained free of triarylamine and of the hydrogen displacement product.

Anilines whose *N*-acidity is enhanced by *ortho* or *para* electron-withdrawing groups in dipolar aprotic solvents at 120—130 °C undergo activation by potassium carbonate so that they can displace aromatic nitro-groups whose nucleofugality is similarly enhanced. This activation presumably originates in hydrogen-bonding between the NH₂ group and CO₃²⁻ anions, in association with the K⁺ cation, with induced

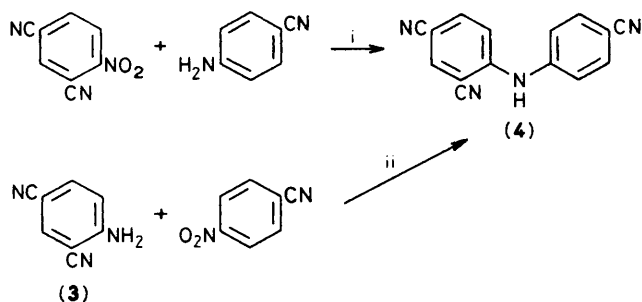
development of negative charge on the nitrogen atom; it does not appear to involve full proton transfer leading to the HCO₃⁻ anion and free nitranion since, in comparable cases, attack by the nitranion is found to be less selective for nitro-group displacement, tending to remove concurrently some other displaceable group, *e.g.* hydrogen, itself activated by the nitro-group. Thus it has been reported¹ that the anion



Scheme 1. Reaction conditions, Bu^tOK, hexamethylphosphoramide, 6 h, 30 °C.¹



Scheme 2. Reaction conditions, K₂CO₃ in dimethylformamide or DMSO, 5 h, 120–130 °C.

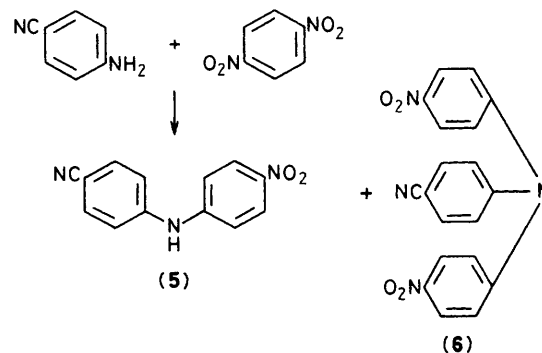


Scheme 3. Reaction conditions, i, Bu^tOK, DMSO, 17 h, 25 °C, ii, K₂CO₃, DMSO, 5 h, 120–130 °C.

of *p*-nitroaniline reacts with *o*-dinitrobenzene (Scheme 1) to give the nitro-displacement product (1) and the hydrogen displacement product (2) in a mean molecular ratio of approximately 2:1. When this reaction was conducted in dimethylformamide (DMF) at 120–130 °C in the presence of K₂CO₃, the diarylamine (1) was obtained (24%) free of (2) (the low yield is attributable to the ready hydroxydenitration² of *o*-dinitrobenzene). The alternative synthesis (Scheme 2) from *p*-dinitrobenzene and *o*-nitroaniline using K₂CO₃ in dimethylsulphoxide (DMSO) or DMF gave the diarylamine (1) in yields of 65–70% and 45–50% respectively. In contrast, sodium carbonate under the same conditions in DMSO showed very slight catalytic activity, while lithium carbonate was almost ineffective.[†]

In a series of about 25 similar reactions between aromatic nitro-compounds and anilines, variously *ortho*- or *para*-substituted by NO₂, CN, PhCO, or as 1- and 3-xanthen-9-one derivatives, all in DMSO at 120–130 °C in the presence of K₂CO₃, the secondary amine of type (1) was obtained, in moderate to good yields, free of the hydrogen displacement product, type (2). On the other hand, in a corresponding series of reactions using potassium *t*-butoxide in DMSO at

[†] Note added in proof: Caesium carbonate (Cs₂CO₃) however was somewhat more effective than K₂CO₃.



Scheme 4. Reaction conditions, K₂CO₃ in DMSO, 120–130 °C.

20–25 °C, displacement of the nitro-group as the sole reaction was found only with more highly activated nitro-compounds. Thus the diarylamine (4) was formed (>80% yield) under these conditions (Scheme 3, i) with no detectable hydrogen displacement product.[‡]

Since the *N*-acidity of a diarylamine such as (5) should be greater than that of the parent arylamine, the formation of triarylamine might logically be expected; in fact the reaction shown in Scheme 4, in which (5) (*ca.* 50% yield) was accompanied by the triarylamine (6) (*ca.* 3%), was the only instance encountered.[§] Possibly the bulk of the displaceable nitro-group normally hinders further reaction. Such a steric effect should not be present in activated fluoro-compounds and indeed the triarylamine (6) was the major product (64% yield) together with (5) (5%) when *p*-dinitrobenzene was replaced by *p*-fluoronitrobenzene, although a 400% excess of the primary amine was employed. In halogen displacements of this latter type, potassium carbonate has been routinely used,⁵ in the presence of a copper catalyst, to remove hydrogen halide; in such circumstances any catalytic action exerted by the carbonate *per se* would not have been apparent.

The formation of (4) under the alternative conditions (Scheme 3, ii) from *p*-cyanonitrobenzene and *o,p*-dicyanobenzene (3) (K₂CO₃, DMSO, 120–130 °C) was competitive with a concurrent oligomerisation of the primary amine (3). This new instance of carbonate activation is under investigation.

I am grateful to Professor Emeritus W. B. Whalley and to Professor W. A. Gibbons for laboratory facilities.

Received, 25th October 1984; Com. 1546

References

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[‡] It is not immediately clear why attack by the nitrone at a moderately activated nitro-group seems sluggish in comparison with attack by OR⁻ and, particularly, the more polarizable SR⁻ anion.³ Presumably repulsion by the electron cloud of the NO₂ group diverts attack elsewhere,⁴ since hydrogen displacement is not specially favoured, involving as it does concomitant reduction of substrate and/or product by the liberated hydride ion (or by the intermediate adduct).

[§] Admittedly the primary amines were used in 150% excess with the object of minimising any such effect; yields are based on the activated nitro-compounds.