

Direct Nucleophilic Substitution of Hydrogen in Nitrobenzene with Some Carbanions

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Summary Phenylalkylacetonitriles react with nitrobenzene in the presence of bases, yielding products of nucleophilic substitution of the hydrogen in the *para*-position of nitrobenzene.

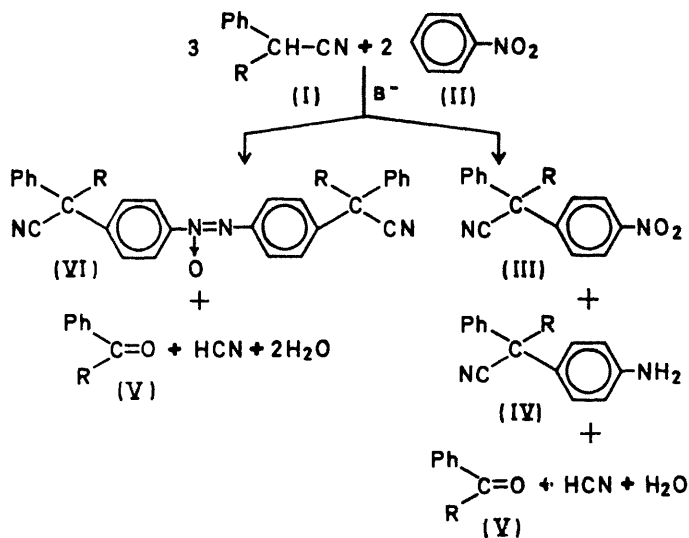
NUCLEOPHILIC substitution in mononitro-aromatic compounds proceeds easily when the leaving group forms a relatively stable anion. There are few reactions in which the nucleophilic agent substitutes a hydrogen atom, *i.e.* a

formal expulsion of hydride ion takes place.¹ Complex redox processes generally occur in these reactions.

Although only few examples of reactions between carbanions and aromatic mononitro-compounds have been described, some of them are of great practical value.²

We report a new direct nucleophilic substitution of a hydrogen atom in nitrobenzene (II), in a reaction with phenylalkylacetonitrile (I) anions. Nitrobenzene reacts exothermically with nitriles (Ia, R = Me); Ib, R = Et) in the presence of strong bases (NaOH, NaNH₂, or CH₃ONa) in several solvents (liquid ammonia, methanol, Me₂SO, tetrahydrofuran) yielding mixtures of (III), (IV), (V), and (VI) (Scheme 1). The composition of the mixture varies with the reaction parameters (solvent, base, temp.).

In liquid NH₃ or THF at -60-30°, the product consisted of (mole %): (III) (15), (IV) (15), (V) (30), and (VI) (30); in methanol with NaOH or NaOMe the composition was (VI) (60%), (V) (30%), and small quantities of (III) and (IV).



SCHEME 1

About 50% yield of the amino-nitrile (IV) was obtained from the reaction mixture after (V) and some unchanged (I) and (II) were removed and the residue reduced.

All compounds gave satisfactory analytical data. Their m.ps. were: (IIIa) 77°, (IIIb) 96°, (IVa) 69°, (IVb) 78°, (VIa) 146°, and (VIb) 181°. Nitro- and amino-nitriles (IIIa,b) and (IVa,b) were identical with the products obtained by nitroarylation of (Ia,b) with *p*-chloronitrobenzene, followed by reduction. Compounds (VIa,b) were prepared by reduction of (IIIa,b) with NaOMe in methanol.³ Compounds (Va,b) were identified by means of

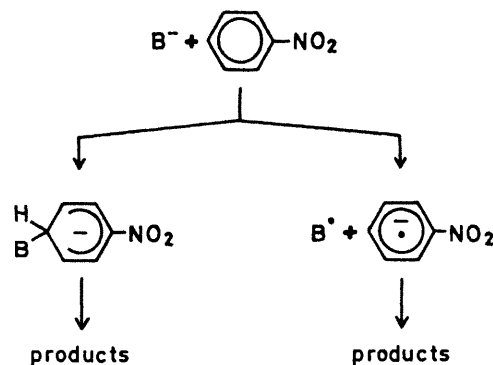
their 2,4-dinitrophenylhydrazones and their relative proportions determined by g.l.c.

Cyanide ions were found in the reaction mixture; their amount was always about 30 mole % with respect to the nitrile consumed, *i.e.* approximately equivalent to the ketone produced.

These results led to the assumption that the molar ratio of nitrile anion to nitrobenzene participating in the reaction was 3:2.

The use of an excess of (I) or (II) did not change the amounts of the substrate consumed.

Formation of ketones (V) by oxidation of anions of (I) with oxygen has frequently been observed,⁴ OCN⁻ ions being formed. It seems that in our case the reaction proceeds *via* the ketone-cyanohydrin. The ketone content determined in the reaction product by g.l.c. is often lower than that of the CN⁻ anions. This results from the condensation of the ketone with an excess of nitrobenzene—such reaction products were observed by t.l.c.



SCHEME 2

On the other hand, diphenylacetonitrile reacts with nitrobenzene yielding only tetraphenylsuccinonitrile (m.p. 212°; nearly quantitative) and aniline.

According to Russell,⁵ the electron transfer from organic anions to an aromatic nitro-compound may proceed in two main directions (Scheme 2), whereby a Meisenheimer-type complex (well known for polynitro-compounds) or a radical anion and a free radical are formed. When B represents anions (Ia,b), the reactions proceed in the former manner, yielding products (III), (IV), (V), and (VI).

The stability of the diphenylcyanomethyl radical favours the second reaction course with (I; R = Ph).

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