

The Reaction of Nitrobenzenes with Sodium Borohydride; a Novel Reductive Coupling to Diphenylamine Derivatives

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Dale, J. and Vikersveen, L., 1988. The Reaction of Nitrobenzenes with Sodium Borohydride; a Novel Reductive Coupling to Diphenylamine Derivatives. – Acta Chem. Scand., Ser. B 42: 354–361.

The reduction of mono-, di- and trinitro-substituted benzenes by NaBH₄ in hydroxylic solvents gives very different products depending on structure and reaction conditions. In addition to known reactions, such as formation of azoxybenzene and azobenzene derivatives, displacement of nitro groups by hydrogen, and ring reduction, a novel coupling reaction with loss of one nitro group was observed. From 1,3-dinitrobenzene and 1,3,5-trinitrobenzene, diphenylamine derivatives were obtained in reactions that are clean and of preparative value when the nitro compound is present in excess. From 1,2-dinitrobenzene the diphenylhydroxylamine derivative was obtained in a much slower, but equally clean reaction. Possible mechanisms are discussed, and an aromatic *ipso* radical substitution of a nitro group by a phenylnitroxide intermediate is proposed.

In attempts to prepare Meisenheimer complexes from 1,3-dinitrobenzene and 1,3,5-trinitrobenzene by hydride addition using NaBH₄, it was discovered that reductive coupling took place, accompanied by the loss of one nitro group, leading to 3,3'-dinitrodiphenylamine and 3,3',5,5'-tetranitrodiphenylamine, respectively, in preparative yields. This reaction is synthetically interesting because of the particular *meta* substitution pattern, considering that electrophilic nitration of diphenylamine can only give *ortho-para* substitution. The reaction is also of mechanistic interest, since reduction of nitrobenzenes would normally be expected to lead to simple nitroso-, hydroxylamino- or amino-derivatives, or to coupling products without loss of nitrogen, such as azoxy-, azo- or hydrazobenzenes. To examine the scope of the new coupling reaction, in particular to establish whether the *meta* relationship of the nitro groups is a prerequisite, a comparative study of nitrobenzene, 1,2-, 1,3- and 1,4-dinitrobenzene, and 1,2,4- and 1,3,5-trinitrobenzene was undertaken.

Previous work on borohydride reduction of nitrobenzenes

In 1962 the statement was made¹ that until then, nitro groups had been reported to be reduced either with difficulty or not at all by borohydrides. Nevertheless, in 1956, Weill and Panson² had obtained smooth reduction of nitrobenzene to azoxybenzene by NaBH₄ in diglyme at 90–100°C. Using KBH₄ in refluxing ethanol, Shine and Mallory¹ reported in 1962 that a series of 3- and 4-substituted nitrobenzenes were reduced to give azoxy compounds. The same authors obtained large amounts of red-brown solids from 1,3- and 1,4-dinitrobenzene, but no products were isolated or identified. Also in 1962, Severin and Schmitz³ observed an easy reduction of 1,3,5-trinitrobenzene with NaBH₄ in water/methanol at 0°C, but surprisingly, the reduction took place in the aromatic nucleus to give 1,3,5-trinitrocyclohexane. Likewise, ring reduction was reported for 1,3-dinitrobenzene, but only to the dinitrocyclohexene stage.³ Analogous reduction of 1-chloro-2,4-dinitrobenzene and similar derivatives with NaBH₄ gave the corresponding substituted dinitrocyclohexene.⁴ Further surprising

observations were made in 1964 by Kaplan⁵ in a study of the reaction between NaBH_4 and chlorinated 1,3,5-trinitrobenzenes. With the 2,4,6-trichloro derivative a stepwise denitration occurred, seemingly occurring by nucleophilic displacement of the nitro group (as nitrite) by hydride ion. In contrast, with the 2,4-dichloro and the 2-chloro derivative full dechlorination and subsequent reduction of the aromatic nucleus occurred to give in both cases 1,3,5-trinitrocyclohexane.⁵ Displacement by hydride of one nitro group has been reported to take place to some extent also in the reaction of NaBH_4 with 1,4-dinitrobenzene in DMSO.⁶ With 1-methoxy-2,4-dinitrobenzene, hydride displacement of the 2-nitro group, or ring reduction, is observed.⁶ NaBH_4 reduction of nitrobenzene was taken up again in 1970, and although only electron transfer to give the radical anion was observed by ESR for nitrobenzene itself in water/methanol at room temperature,⁷ a range of conventional reduction products were obtained when the solvent was DMSO at 85°C or sulfolane at 100°C.⁸ These products arise from a normal reductive attack on the nitro group, and most significantly they appear in a clear sequence. Thus, azoxybenzene is formed from nitrobenzene very rapidly and converted in a slower step to azobenzene, while aniline appears only after accumulation of azobenzene. Presumably, aniline is formed via hydrazobenzene, which does not accumulate. Other necessary or likely early intermediates, such as nitrosobenzene and phenylhydroxylamine, were not observed.

Present work

Our experimental conditions leading exclusively to reductive coupling with loss of one nitro group were such that a large excess of the nitro compound was always present, a suspension of NaBH_4 in methanol containing NaOH being added dropwise to a solution of an equimolar quantity of the nitro compound in refluxing methanol (Method A). The conditions used by Severin³ to obtain exclusively reduction of the aromatic ring of 1,3,5-trinitrobenzene were just the opposite: a solution of the nitro compound in THF was added dropwise to a five-fold molar excess of NaBH_4 suspended in methanol/water at 0°C (Method B).

For our comparative study, both these ex-

trêmes of experimental conditions were first selected for use with each nitrosubstituted benzene. Additional variations of conditions were tried in selected cases.

The results of the two series of parallel experiments for the six nitrobenzenes are briefly presented in the following and summarized in Fig. 1.

Nitrobenzene. Using Method A, no reaction occurred. Even replacement of methanol with ethylene glycol gave no reaction within 5 days at 100°C. With Method B, traces (<1%) of azoxybenzene (**1**) could be identified.

1,2-Dinitrobenzene. The only reaction product obtained by both methods was bis(2-nitrophenyl) hydroxylamine (**4**), and the yield in both cases was 16%, the remainder being unchanged starting material.

1,3-Dinitrobenzene. Using Method A, 3,3'-dinitrodiphenylamine (**5**) was isolated in a yield of 32%. No other product was present, only unchanged starting material. In contrast, with Method B a variety of accompanying products were also obtained, although different in two separate experiments (24 h or 42 h). The yield of 3,3'-dinitrodiphenylamine was the same in both these cases (30%). The other products were nitrobenzene (40%) and 3-nitroaniline (20%) in the former case, and 3,3'-dinitroazoxybenzene (**2**, 30%) and 3,3'-dinitroazobenzene (15%) in the latter case. Insufficient temperature control may account for the difference.

1,4-Dinitrobenzene. Using Method A, 4,4'-dinitroazobenzene (**3**) was isolated in a yield of 56%, the remainder being unchanged starting material. Method B led to nearly the same result; in addition to 4,4'-dinitroazobenzene (49%) and unreacted starting material, some 4-nitroaniline (6%) was identified, together with traces of 4,4'-dinitroazoxybenzene.

1,2,4-Trinitrobenzene. Neither of the methods induced coupling to diphenylamine derivatives or reduction to cyclohexane derivatives. Method A gave 1,3-dinitrobenzene (35%) and 1,4-dinitrobenzene (24%), as well as 2,4-dinitrophenol (22%). Method B gave mainly unchanged starting material, with 1,4-dinitrobenzene and 2,4-dinitroaniline as minor products.

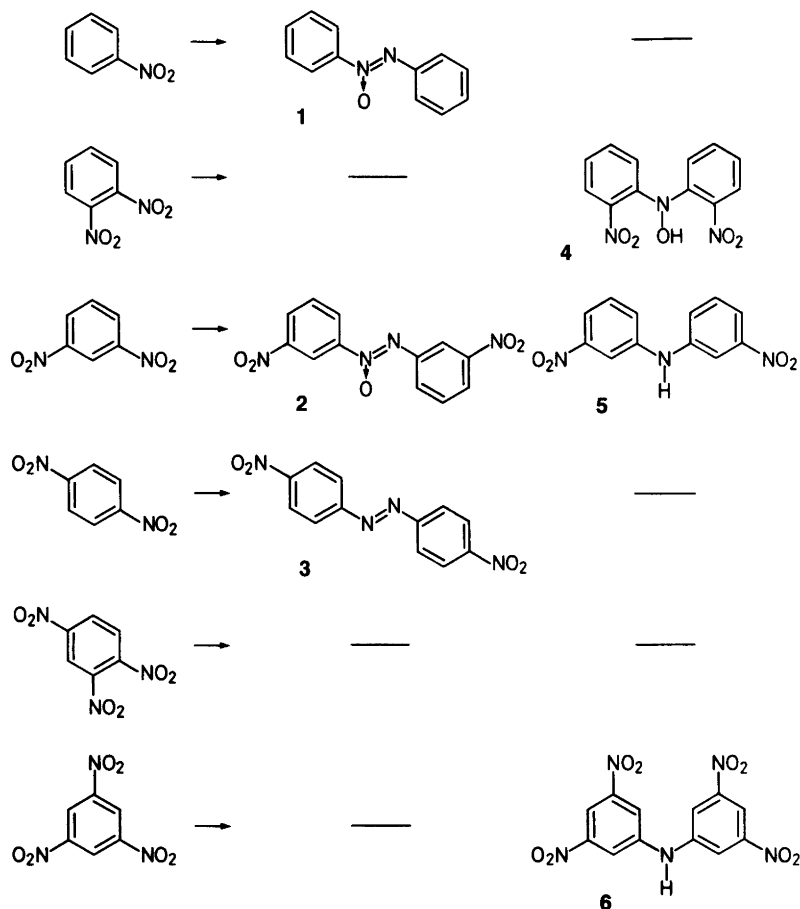


Fig. 1. Main coupling products in NaBH_4 reduction of nitrobenzenes without and with loss of NO_2 .

1,3,5-Trinitrobenzene. Using Method A, 3,3',5,5'-tetranitrodiphenylamine (**6**) was isolated in a yield of 58%. The remainder was unreacted starting material, with only traces of 3,5-dinitroaniline. Method B gave 1,3,5-trinitrocyclohexane (*cis* + *trans*, ~1:1) in 18% yield, the remainder being mainly starting material.

The observation was made that in the case of 1,2-di-, 1,3-di- and 1,3,5-trinitrobenzene the initial colouring of the reaction mixture was dark blue-violet, while for mono-, 1,4-di-, and 1,2,4-trinitrobenzene the colour was red.

Preparative aspects

It is clear from our results (Fig. 1) that the novel

reductive coupling to diphenylamine by NaBH_4 occurs only with 1,3-dinitrobenzene and 1,3,5-trinitrobenzene. The yields can obviously be improved, since almost no by-products are formed when Method A is used. With Method B, 1,3-dinitrobenzene still furnishes the diphenylamine derivative, but it is accompanied by a variety of "normal" reduction products. No reduction to dinitrocyclohexenes, as reported by Severin,^{3,4} is observed under our conditions. 1,3,5-Trinitrobenzene on the other hand is reduced cleanly to 1,3,5-trinitrocyclohexane using Method B, and in a high yield based on converted material. No coupling products are obtained from 1,2,4-trinitrobenzene, even though two of the nitro groups have a *meta* relationship; only prepara-

tively uninteresting product mixtures are obtained. 1,4-Dinitrobenzene undergoes reductive coupling to 4,4'-dinitroazobenzene in good yield and especially cleanly using Method A. Most unexpectedly, using either method 1,2-dinitrobenzene gives a very clean coupling with loss of one nitro group, but the product is a diphenylhydroxylamine derivative instead of a diphenylamine derivative. The reaction is, however, slow, and the product is difficult to isolate from unreacted 1,2-dinitrobenzene. Finally, practically no reduction takes place with nitrobenzene; only traces of azoxybenzene are produced by Method B.

Mechanistic aspects

The variety of products obtained in the reaction of nitrobenzenes with borohydrides, and the dramatic changes in reaction paths as a result of relatively minor changes of conditions makes the formulation of plausible mechanisms difficult.

The first step could, in principle, be the transfer of an electron, a hydrogen radical or a hydride ion. The isolation and characterization by NMR of stable Meisenheimer complexes from the reaction of 1,3,5-trinitrobenzene with tetramethylammonium borohydride,⁹ and the observation by NMR of the formation of unstable Meisenheimer complexes from 1,3-dinitrobenzene with NaBH₄ would indicate direct hydride transfer. However, radical anions can be easily prepared from nitrobenzenes quite generally,^{7,10,11} and from 1,3,5-trinitrobenzene particularly, and studied by ESR.¹¹⁻¹³ It cannot therefore be excluded that apparent hydride transfer is actually initiated by the transfer of an electron followed by the transfer of a hydrogen radical. This implies that the BH₄ radical can be formed from NaBH₄, and this has in fact been realized by radiolysis.¹⁴ Even the apparent transfer of a hydrogen radical could occur in two steps, since it has been shown that the borohydride anion after photolytic loss of an electron can lose a proton to form the BH₃ radical anion.¹² For simplicity, we shall limit the discussion to the hydride anion and the hydrogen radical.

Considering the acceptor, it is difficult to establish whether the hydride initially attacks the positively charged nitrogen or the aromatic nucleus, and whether there is a subsequent 1,3-shift. Whatever the case may be, when the Mei-

senheimer complex picks up a proton from the solvent, the aromatic structure is destroyed and the next step in the ring reduction can proceed much faster, although only by one step per extra nitro group (conjugate addition). This explains why reduction of 1,3-dinitrobenzene stops at the cyclohexene stage, and why only 1,3,5-trinitrobenzene yields the cyclohexane derivative.^{3,4} The present picture is in conflict with the existence of intermediate di- and trianions as formulated by Severin,^{3,4} but these have never been documented. Only mono-anions are seen by NMR in solution.⁶

To facilitate hydride attack on the benzene ring, it is of course essential that the nitro groups are coplanar with the aromatic nucleus in order to delocalize the negative charge. This was also advanced by Kaplan⁵ as an explanation of his observation that although normal nucleophilic displacement of chlorine by hydride, followed by ring reduction to 1,3,5-trinitrocyclohexane, took place with the 2-chloro and the 2,4-dichloro derivative of 1,3,5-trinitrobenzene, it did not happen with the 2,4,6-trichloro derivative. Instead, the nitro groups were displaced so as to give 1,3,5-trichlorobenzene. All three nitro groups are encumbered from both sides by the Cl substituents and rotated perpendicular to the aromatic plane, so that the activation of the 2-, 4- and 6-carbons is lost. The observed *ipso* substitution was considered as a displacement of nitrite ion by hydride ion,⁵ but a radical mechanism cannot be excluded. Displacement of a nitro radical by authentic carbon radicals to give aromatic *ipso* substitution has been firmly established.¹⁶ In 1-X-2,4-dinitrobenzenes, displacement by NaBH₄ of the 2-nitro group occurs along with ring reduction, and in our own experiments, displacement of the 1-nitro- or 2-nitro group in 1,2,4-trinitrobenzene and of one nitro group in 1,3-dinitrobenzene is particularly marked. Surprisingly, it does not occur in 1,2-dinitrobenzene.

The important question regarding the coupling reactions is what happens with the initially formed nitroso group? This is shown in Fig. 2 for nitrobenzene as an example, although more than one nitro group may actually be needed. Further reduction by other reagents is known to produce species such as the nitrosobenzene radical anion (in strongly basic medium), the phenylnitroxide radical, and phenylhydroxylamine.¹⁷ Azoxybenzene has been shown to form rapidly in basic

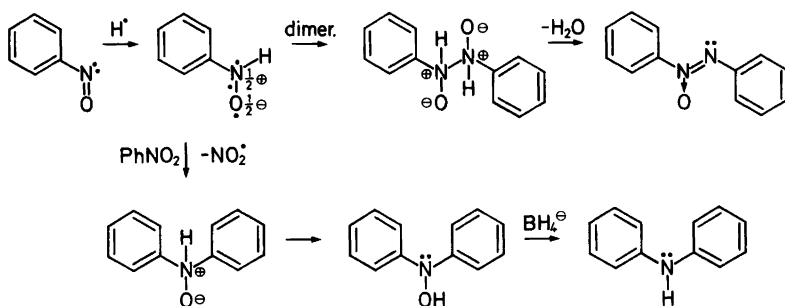


Fig. 2. Secondary reduction products from nitrosobenzenes, substituents not involved being omitted.

medium from a mixture of nitrosobenzene and phenylhydroxylamine.¹⁷ On the other hand, the same mixture in the absence of added base gives rise to a low concentration of the phenylnitroxide radical,¹⁷ and this same radical, prepared independently, disproportionates rapidly to nitrosobenzene and phenylhydroxylamine.¹⁸ The final coupling to give azoxybenzene occurs in a slow reaction, but according to Ingold¹⁸ "there would seem to be no way of determining whether azoxybenzene is actually produced from two phenylnitroxide radicals or from nitrosobenzene and phenylhydroxylamine". We are inclined to believe that coupling of two radicals (Fig. 2) is the more likely mechanism because of the indications of a radical mechanism for our alternative coupling reaction to give diphenylamine derivatives.

Our main argument for radical involvement using NaBH_4 is that the corresponding reduction of nitrobenzene or nitrosobenzene with LiAlH_4 , although known to give azobenzene when an excess of aluminumhydride is used, produces not only the phenylnitroxide radical but also the more stable diphenylnitroxide radical when the nitro or nitroso compound is in excess.¹⁹ The diphenylnitroxide radical can hardly arise from anything other than *ipso* substitution on excess nitro or nitroso compound by the initially formed phenylnitroxide radical, with displacement of the NO or NO_2 radical and subsequent loss of a hydrogen radical or stabilization as diphenylhydroxylamine. When LiAlH_4 is in excess, the aromatic substrate is not available and a high concentration of the phenylnitroxide radical builds up, leading to slow dimerization to azoxybenzene. Further reduction gives azobenzene, hydrazobenzene and aniline, in that sequence.

This is exactly what is found in our NaBH_4 reduction of 1,3-dinitrobenzene. With excess of nitro compound (Method A), the assumed 3-nitrophenylnitroxide radical displaces one nitro group of an unchanged 1,3-dinitrobenzene molecule in a rapid reaction to give the diphenylhydroxylamine derivative which is then further reduced to the diphenylamine (Fig. 2). When an excess of NaBH_4 is used (Method B), also dimerization of 3-nitrophenylnitroxide radicals can occur. Similarly, in the case of 1,3,5-trinitrobenzene, the 3,5-dinitrophenylnitroxide radical is formed and effects *ipso* substitution of a nitro group of the unchanged nitro compound when this is in excess (Method A), but now ring reduction takes over when the borohydride is in excess (Method B).

Since 3-nitroaniline and 3,5-dinitroaniline were obtained as minor products, it could of course be argued that in both these cases it is an intermediate hydroxylamino or amino derivative that effects a nucleophilic displacement; however, the substitution pattern would in both cases be irreconcilable with this. An experiment showed that 3,5-dinitroaniline gave absolutely no reaction with 1,3,5-trinitrobenzene in methanol at 60°C. The mesomeric effect of the nitro groups should produce a strong alternation of electron density on the ring carbons, i.e. positive charge on carbons 2, 4 and 6, and negative charge on carbons 1, 3 and 5. That nucleophiles like amines and the hydride ion should therefore attack carbons 2, 4 or 6 is textbook knowledge. It may be less widespread knowledge that the best electronic description according to Linnett²⁰ of the nitroxide radical puts one-half positive charge on nitrogen (Fig. 2). Such radicals should therefore attack

carbons 1, 3 or 5. Non-polar radicals like hydrogen and carbon radicals¹⁶ would be less selective. Furthermore, in 1,3-dinitrobenzene the mesomeric polarization effects of the two nitro groups should reinforce each other, whereas in 1,4-dinitrobenzene the effects should counteract each other and create no alternation of charge density. This explains nicely why our coupling reaction is observed in the former but not in the latter case, and neither in 1,2,4-trinitrobenzene. In 1,2-dinitrobenzene the mesomeric effect is much reduced since the nitro groups are rotated 40° out of the aromatic plane.²¹ The observed, although unexpected, coupling can thus be explained *a posteriori*. Interestingly, it is not the diphenylamine derivative, but the diphenylhydroxylamine derivative that is formed here. Presumably, reduction to the amine is blocked by the steric hindrance exerted by the two *ortho* nitro substituents. The intermediacy of the diphenylhydroxylamine derivative in the other coupling examples is thereby strongly supported.

Experimental

Starting materials. The nitrobenzenes, except 1,2,4-trinitrobenzene, were commercial products of sufficient purity to be used directly.

1,2,4-Trinitrobenzene was prepared in the following manner: To trifluoroacetic acid (10 ml) at room temperature was added dropwise 35% hydrogen peroxide (3.3 ml, 33 mmol). 2,4-Dinitroaniline (1.15 g, 6.5 mmol) was then added in one portion and the mixture heated to 50°C and stirred for 24 h. After cooling, more hydrogen peroxide (2 ml, 20 mmol) was added and the mixture was then heated for 1 h, cooled and poured into ice-water (50 ml). The precipitated 1,2,4-trinitrobenzene was filtered off and recrystallized from methanol. Yield: 1.06 g (80%), m.p. 60–62°C (lit.²² 60°C). MS (EI, 70 eV): 213 (83, *M*). ¹H NMR (300 MHz, CDCl₃): δ 8.16 (1H, d, *J* 8.7 Hz), 8.68 (1H, dd, *J* 2.4, 8.7 Hz), 8.85 (1H, d, *J* 2.3 Hz).

An analogous procedure, using a mixture of acetic acid and sulfuric acid instead of trifluoroacetic acid, gave nearly the same yield. With acetic acid alone, no reaction took place.

General procedure for reduction method A. To a stirred solution of the nitro compound (9 mmol)

in methanol (25 ml) at 60°C was added dropwise a suspension of sodium borohydride (0.36 g, 9 mmol) in methanol (10 ml) made alkaline with sodium hydroxide. The mixture was stirred until no further change could be observed when analyzed by TLC. The products were isolated by filtration or by chromatography on silica. Separate experiments showed that varying the quantity of NaOH has no observable effect.

General procedure for reduction method B. To a stirred suspension of sodium borohydride (2 g, 50 mmol) in water (25 ml) and methanol (25 ml) at 0°C was added dropwise a solution of the nitro compound in tetrahydrofuran. The reaction mixture was acidified with tartaric acid and extracted with dichloromethane. The organic layers were washed with water, dried over CaCl₂ and evaporated. The products were purified by recrystallization or by chromatography on silica.

Reduction of nitrobenzene. With Method A, no reaction could be observed after 120 h. Using method B, the mixture was analysed by GLC after 24 h and showed 99% unchanged nitrobenzene. Evidence for the presence of azoxybenzene (**1**) was obtained by MS (EI, 70 eV): 198 (27, *M*), 77 (100, *M*–C₆H₅N₂O).

Reduction of 1,2-dinitrobenzene. The products obtained using Method A (2 h) and Method B (24 h) were shown by TLC to be identical. Separation by thick-layer chromatography (Merck Kieselgel 60 PF₂₅₄, toluene/ethanol, 12:1) gave unchanged 1,2-dinitrobenzene and a compound identified as bis(2-nitrophenyl)hydroxylamine (**4**); yield ~16%. MS (EI, 70 eV): 275 (100, *M*), 183 (16, *M*–2NO₃), 153 (16, *M*–C₆H₄NO₂).

Reduction of 1,3-dinitrobenzene. Using Method A, after 114 h the reaction mixture was cooled to give a precipitate which was filtered off. The mother liquor was evaporated, and the residue separated by thick-layer chromatography (Merck Kieselgel 60 PF₂₅₄, toluene/ethanol, 10:1) into unreacted 1,3-dinitrobenzene and more of the initially precipitated product. This was recrystallized from acetonitrile and shown to be 3,3'-dinitrodiphenylamine (**5**). Yield 32%, m.p. 185–187°C (lit.²³ 188°C). MS (EI, 70 eV): 259 (100, *M*), 213 (5, *M*–NO₂), 167 (54, *M*–2NO₂). ¹H NMR (300 MHz, DMSO-*d*₆): δ 7.55 (4H, m),

7.72 (2H, m), 7.86 (2H, d, J 2.4 Hz), 9.28 (1H, s). ^{13}C NMR (75 MHz, DMSO- d_6): δ 110.8, 115.1, 123.0, 130.7, 143.5, 148.7. UV (ethanol): 337 (ϵ 1000), 289 (ϵ 10360), 272 nm (ϵ 10610).

Using Method B, two experiments were made, and in both cases the crude reaction product contained several substances that could not easily be separated by chromatography and were therefore analysed by GLC/MS. A reaction time of 42 h gave 3,3'-dinitrodiphenylamine (**5**) in ~30% yield [MS (CI, isobutane): 289 (100, $M+1$), 288 (12, M)] and 3,3'-dinitroazobenzene in ~15% [MS: 273 (76, $M+1$), 272 (18, M)]. A reaction time of 24 h also gave 3,3'-dinitrodiphenylamine (**5**) in ~30% yield, but now, surprisingly, 3-nitroaniline in ~20% and nitro-benzene in ~40% yield.

Reduction of 1,4-dinitrobenzene. With Method A, a precipitate was formed during the reaction. After 48 h, this was filtered off, recrystallized from acetic acid and identified as 4,4'-dinitroazobenzene (**3**). Yield 56%, m.p. 227–229° (lit.²⁴ 222°C). MS (EI, 70 eV): 272 (35, M), 150 (64, $M-\text{C}_6\text{H}_4\text{NO}_2$), 122 (100, $M-\text{C}_6\text{H}_4\text{N}_3\text{O}_2$). ^1H NMR (300 MHz, DMSO- d_6 + CDCl_3 , 60°): δ 8.13 (4H, d, J 9.5 Hz), 8.43 (4H, d, J 8.6 Hz). ^{13}C NMR (75 MHz, DMSO- d_6 + CDCl_3 , 60°C): δ 124.4, 125.4, 150.1, 155.8. UV (ethanol): 331 nm (ϵ 16600). The mother liquor contained only unreacted 1,4-dinitrobenzene.

A precipitate also formed with Method B. After 24 h it was filtered off and the product, 4,4'-dinitroazobenzene (**3**), was recrystallized from acetic acid; yield 49%. After evaporation of the mother liquor, the residue was separated by thick-layer chromatography (Merck Kieselgel 60 PF₂₅₄, toluene/ethanol, 5:1). In addition to a fraction containing unreacted 1,4-dinitrobenzene, a fraction containing mostly 4-nitroaniline was collected, yield 6%. The mass spectrum indicated the presence of small amounts of 4,4'-dinitroazobenzene [MS (EI, 70 eV): 288 (M)].

Reduction of 1,2,4-trinitrobenzene. Using Method A, the reaction was stopped after 75 h, and the reaction mixture filtered through silica and evaporated. Separation was performed with a Chromatotron (silica gel, PF₂₅₄, with $\text{CaSO}_4 \cdot 1/2 \text{H}_2\text{O}$, ether/petrol ether). Three components were collected and identified by MS and ^1H NMR:

1,3-dinitrobenzene, 35%, MS (CI, isobutane): 169 (100, $M+1$), ^1H NMR (300 MHz, acetone- d_6): δ 8.17 (1H, t, H 8.2 Hz), 8.82 (2H, dd, J 2.2, 8.2 Hz), 9.09 (1H, t, J 2.2 Hz); 1,4-dinitrobenzene, 24%, MS: 169 (100, $M+1$), ^1H NMR: δ 8.65 (4H, s); 2,4-dinitrophenol, 22%, MS: 184 (100, M), ^1H NMR: δ 7.54 (1H, dd, J 2.4, 9.2 Hz), 8.12 (1H, d, J 2.4 Hz), 8.41 (1H, d, J 9.3 Hz).

Using Method B, the reaction was stopped after 7 h and worked up as described above. Attempted separation of the components by preparative chromatography was unsuccessful, but GLC and TLC showed that unreacted 1,2,4-trinitrobenzene was the main component, with 2,4-dinitroaniline and 1,4-dinitrobenzene as minor products.

Reduction of 1,3,5-trinitrobenzene. With Method A, a precipitate was formed during the reaction. The mixture was cooled after 90 h, and the precipitate filtered off; after recrystallization from acetonitrile it was identified as 3,3',5,5'-tetranitrodiphenylamine (**6**). Yield 58%, m.p. 208–209°C. MS (CI, isobutane): 350 (100, $M+1$), 349 (37, M), 320 (56, $M+1-\text{NO}$), 319 (13, $M-\text{NO}$). ^1H NMR (300 MHz, DMSO- d_6): δ 8.31 (4H, d, J 1.9 Hz), 8.39 (2H, t, J 1.9 Hz), 10.11 (NH). ^{13}C NMR (75 MHz, DMSO- d_6): δ 110.7 (C-4), 117.1 (C-2, C-6), 144.1 (C-1), 149 (C-3, C-5). UV (ethanol): 336 (ϵ 41700), 268 nm (ϵ 25700).

The filtrate was taken to dryness and the residue separated by preparative chromatography (Merck Kieselgel 60 PF₂₅₄, toluene/ethanol, 5:1) into unreacted 1,3,5-trinitrobenzene (main component) and traces of 3,5-dinitroaniline; MS: 184 (54, $M+1$).

With Method B, the reaction was stopped after 7 h. The crude product was recrystallized from 2-propanol to give a non-separable solid mixture of *cis*- and *trans*-1,3,5-trinitrocyclohexane (ratio ~1:1). Yield 18%, m.p. 121–122°C (lit.³ 125°C). MS (CI, isobutane): 220 (7, $M+1$), 174 (9, $M+1-\text{NO}_2$), 173 (100, $M-\text{NO}_2$). ^1H NMR (300 MHz, CD_3CN): δ 2.53 (6H, m), 2.96 (6H, m), 4.90 (3H, m), 5.19 (3H, m). ^{13}C NMR (75 MHz, CD_3CN): δ 31.4 (C-2, C-4, C-6, *cis*), 32.8 (C-2, C-4, *trans*), 33.5 (C-6, *trans*), 78.6 (C-1, C-3, C-5, *cis*), 79.0 (C-3, *trans*), 79.8 (C-1, C-5, *trans*).

The mother liquor contained traces of 3-nitrohydroxylamine as evidenced by MS (EI, 70 eV): 154 (29, M), 137 (16, $M-\text{OH}$), 108 (18,

$M-\text{NO}_2$), 107 (23, $M-\text{HNO}_2$). No product could be isolated.

This experiment (Method B) was repeated with sodium hydroxide added, but the products and yields were the same. Higher temperatures caused total destruction and no products could be isolated.

Acknowledgement. We thank Alf Bjerke's Legat, Oslo for financial support to L.V.

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Received December 7, 1987.