

The Autoxidation of *o*- and *p*-Nitrotoluene under Basic Conditions

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The autoxidation of *o*- and *p*-nitrotoluene in DMSO and DMF under basic conditions resulted in the formation of 1,2-di(nitrophenyl)-ethanol (2), presumably *via* the corresponding nitrobenzaldehydes. According to the reaction conditions, compounds of type 2 could be isolated, oxidized further to the ketones, or dehydrated to the nitrostilbenes. Autoxidation under basic conditions in *t*-butanol resulted in the formation of dinitrobenzyl. The different reaction paths in the two types of solvents were believed to be related to different rates of ionization and different degrees of ion separation.

The autoxidation of *p*-nitrotoluene under basic conditions was studied by Russell *et al.*¹ as a part of the extensive work of the Russell group on autoxidation of hydrocarbons under basic conditions.^{2,3}

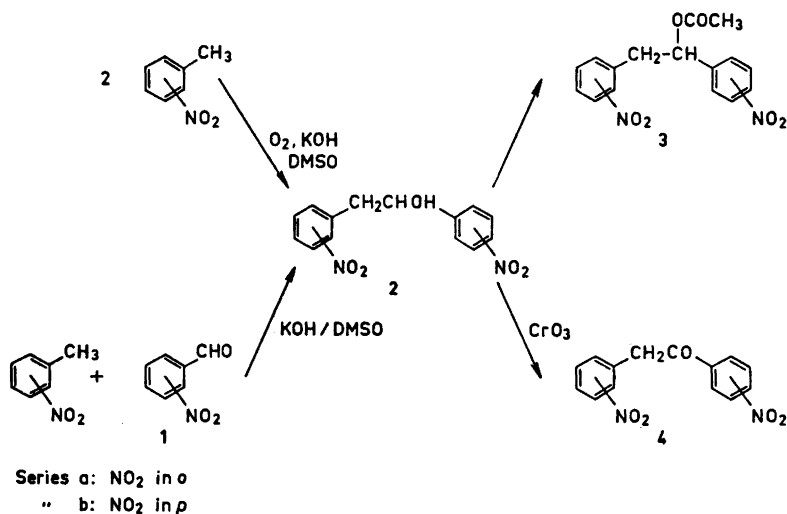
When Russell *et al.*¹ oxidized *p*-nitrotoluene in dimethyl sulfoxide (DMSO)/*t*-butanol with potassium *t*-butoxide as base, they obtained *p,p'*-dinitrostilbene as the major neutral product. They assumed the stilbene to have been formed by dehydrogenation of *p,p'*-dinitrobenzyl and not by condensation of the nitrobenzyl anion with the nitrobenzaldehyde as proposed for the oxidations of some other substituted toluenes.⁴

While our studies of the chemistry of nitro compounds^{5,6} were in progress, Russell *et al.*¹ reported their results for the autoxidation of *p*-nitrotoluene.¹ Our investigation of the autoxidation of *o*-nitrotoluene had given a result different from that which would have been expected from the work of Russell *et al.*¹ Our study was therefore extended to include *p*-nitrotoluene.

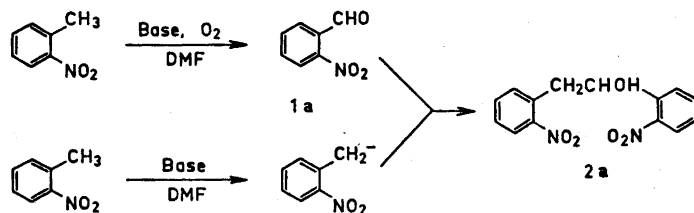
Oxidation of *o*-nitrotoluene was performed by passing oxygen through a dimethyl formamide (DMF) solution containing potassium hydroxide as base. The oxidation gave two main neutral products. One was *o*-nitrobenzaldehyde (1a) and the other 1,2-di(*o*-nitrophenyl)-ethanol (2a). The structure of 2a was deduced from spectroscopic evidence. The IR spectrum showed the com-

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pound to contain OH and NO₂ groups and the mass spectrum indicated the molecular weight to be 288. The electronic spectrum showed that the product was not a stilbene (λ_{\max} 260 nm). The formation of derivatives gave further support to the proposed structure: acetylation gave an acetate (3a) and oxidation a ketone (4a), both exhibiting the expected data. The structure of 2a was further confirmed by its synthesis from *o*-nitrotoluene and *o*-nitrobenzaldehyde.⁷



The proportion of *o*-nitrobenzaldehyde to 1,2-di(*o*-nitrophenyl)-ethanol (1a/2a) depended on the initial concentration of *o*-nitrotoluene. This proportion decreased with increasing initial concentration (Table 1). This fact, together with the results from the additions of nitrotoluenes to aldehydes⁷ and the results of Russell *et al.* on oxidation of other substituted toluenes,⁴ suggested the following path of formation for compound 2a:



When the oxidation of *o*-nitrotoluene was tried at low concentrations in dimethyl sulfoxide, the decomposition products from the reaction of *o*-nitrotoluene with base were obtained. At higher concentrations, 2a was isolated in 23 % yield. The results at low concentrations are probably due to a higher activity of the base in DMSO than in DMF.

As our results for the oxidation of *o*-nitrotoluene indicated the reaction to go *via* the aldehyde even in nitrotoluenes, the oxidation of *p*-nitrotoluene was investigated.

Autoxidation at high concentration in DMSO with potassium hydroxide as base gave 1,2-di(*p*-nitrophenyl)-ethanol (*2b*) in 40 % yield. The structure was assigned on the basis of spectral evidence and from the formation of an acetate (*3b*) and a ketone (*4b*). The structure of compound *2b* and its mode of formation were further indicated by the synthesis from *p*-nitrotoluene and *p*-nitrobenzaldehyde (*1b*).

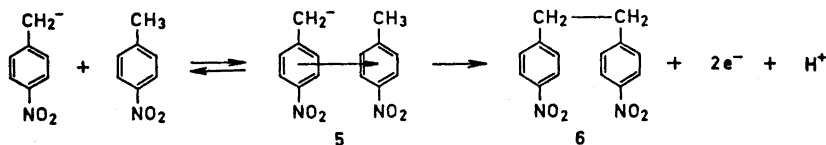
Reinvestigation of the oxidation of *p*-nitrotoluene under the conditions of Russell *et al.*¹ (*i.e.* potassium *t*-butoxide as base, low concentration of *p*-nitrotoluene in DMSO: *t*-butanol 80:20) confirmed their results with *p,p'*-dinitrostilbene as the major neutral product. However, thin layer chromatography of the reaction mixture revealed one further compound to be present in approximately 10 % of the amount of dinitrostilbene. This compound was isolated by crystallization and proved to be the ketone *4b*.

Oxidation of *p,p'*-dinitrobenzyl under the same conditions gave *p,p'*-dinitrostilbene as the major product, and no trace of the ketone *4b* could be detected by TLC. On the other hand, oxidation of 1,2-di(*p*-nitrophenyl)-ethanol (*2b*) under these conditions gave a product mixture of the same composition as that from oxidation of *p*-nitrotoluene, *i.e.* *ca.* 90 % *p,p'*-dinitrostilbene and *ca.* 10 % *p*-nitrobenzyl *p*-nitrophenyl ketone (*4b*).

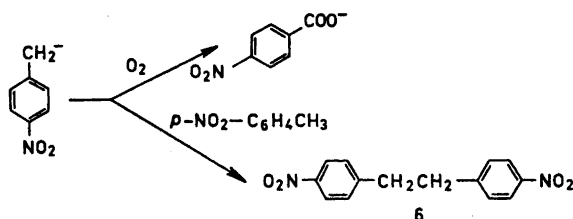
From these results, it seemed evident that the autoxidation of *o*- and *p*-nitrotoluene in DMSO (or solvent composition with DMSO as major constituent) gave the corresponding nitrobenzaldehydes which could react with the nitrobenzyl anions to give the alcohols *2a* and *2b*. These latter could react further or might be isolated, depending on the reaction conditions. Our results did not exclude the possibility that part of the nitrostilbene originated from dinitrobenzyl. The similar composition of the reaction mixtures from oxidation of *p*-nitrotoluene and of 1,2-di(*p*-nitrophenyl)-ethanol (*2b*) nevertheless indicated a major path to be *via* the alcohol *2*.

The autoxidation of *p*-nitrotoluene in *t*-butanol with potassium *t*-butoxide as base resulted in the formation of *p,p'*-dinitrobenzyl (*6*).¹ Duplication of the experiments of Russell *et al.*¹ substantiated this result. The autoxidation of *p*-nitrotoluene under basic conditions was thus solvent dependent.

Russell *et al.* have explained the oxidation of *p*-nitrotoluenes as proceeding *via* a charge-transfer complex (*5*). This complex gave *p,p'*-dinitrobenzyl (*6*) by the loss of a proton and two electrons which were removed by nitrotoluene or oxygen. In DMSO solution, dinitrobenzyl (*6*) could be further oxidized to dinitrostilbene.¹

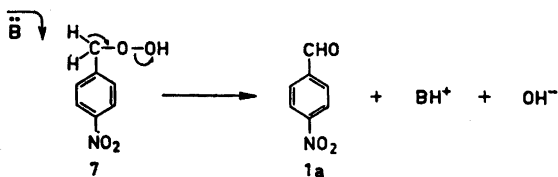


The formation of *p*-nitrobenzoic acid was explained by a competition between oxygen and *p*-nitrotoluene for the nitrobenzyl anion.⁸



When DMSO was used as solvent, the formation of *p*-nitrobenzoic acid was explained by further oxidation of dinitrostilbene.¹

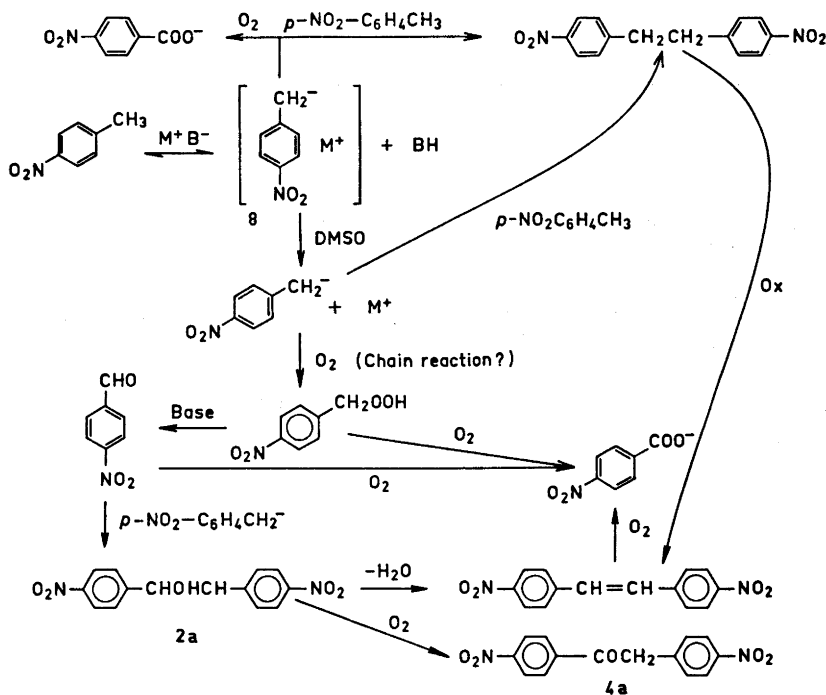
Our results from the oxidation in DMF and DMSO provide new evidence as to the reaction mechanism. The intermediate nitrobenzaldehyde (*1*) was probably formed from nitrobenzyl hydroperoxide (*7*),⁹ indicating that the peroxide was also an important intermediate in the formation of some of the neutral products:



DMSO is a polar, aprotic solvent. On the other hand, *t*-butanol is a non-polar, protic solvent,¹⁰ and these differences are probably the clue to the different reaction paths in the two types of solvent. What follows might be one explanation.

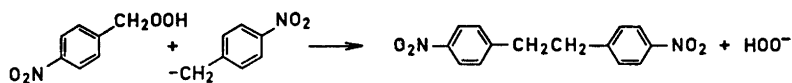
In *t*-butanol, the formation of the nitrobenzyl anion will be slow, and the anion will exist as a part of an ion pair or be hydrogen bonded by the solvent (symbolized by *8*). The nonpolar oxygen molecule will probably not be as reactive towards this anion as the polar nitrotoluene will be. At low oxygen pressures, a high yield of dinitrostilbene is therefore obtained. At higher pressures, oxygen competes more successfully and a higher yield of nitrobenzoic acid is obtained.¹ Because of the low activity of the base in *t*-butanol, no aldehyde is trapped by the nitrobenzyl anion to give the alcohol *2*.

On the other hand, in DMSO the formation of the nitrobenzyl anion is rapid, and the anion will be separated from the cation. Under these conditions, oxygen competes more successfully with nitrotoluene for the anion. This results in the more rapid oxidation in DMSO than in *t*-butanol.¹ The nitrobenzyl hydroperoxide formed by the oxidation is converted to the nitrobenzaldehyde. Because of the rapid formation of the nitrobenzyl anion, some of the aldehyde is trapped and gives the alcohol *2*. Part of the aldehyde will be further oxidized to nitrobenzoic acid:



The reaction is probably more complex than indicated above. The rate of formation and the equilibrium constant of the charge-transfer complex 5 in different solvents may be part of the explanation. The solubility of oxygen in *t*-butanol is not known, but if it is very different from that in DMSO this may also be part of the explanation of the different reaction paths. Some of the nitrobenzaldehyde formed during the oxidation may undergo a Cannizzaro reaction resulting in nitrobenzoic acid and nitrobenzyl alcohol, the latter being oxidized further to aldehyde or acid.

The possibility that *p,p'*-dinitrobenzyl is formed by a substitution reaction of the *p*-nitrobenzyl hydroperoxide cannot be excluded:



This appears rather unlikely, however, in view of the work of Davis *et al.*¹¹ They showed alkyl hydroperoxides with strongly electron-releasing alkyl groups to undergo alkyl-oxygen heterolysis under mildly acidic conditions, *i.e.* conditions opposite to those encountered in the present reaction.

On the grounds of the presented evidence the reaction chart above is therefore believed to indicate the major reaction steps in the autoxidation of *o*- and *p*-nitrotoluenes. The results also show a useful synthetic route to the 1,2-di(nitrophenyl)-ethanols *2a* and *2b* and derivatives of these.

EXPERIMENTAL

The IR spectra were recorded on a Perkin-Elmer infrared spectrophotometer Model 257 and the electronic spectra were recorded on a Beckman DK-2 spectrophotometer. NMR spectra were recorded on a Varian A 60 spectrometer, using tetramethylsilane as internal standard. The chemical shifts are given in δ -units. Gas chromatographic separations were made on a Perkin-Elmer F 11 gas chromatograph, equipped with an SE-30 column and a hydrogen flame ionisation detector. Mass spectra were recorded on an A.E.I. MS 902 mass spectrometer.

The oxidation of o-nitrotoluene in DMF solution. Potassium hydroxide (0.25 g in 1.75 ml ethanol) was added to *o*-nitrotoluene (3.0 g, 0.14 M) in DMF (141 ml) at -40° . Oxygen was passed through the solution at -40° for 1 h. TLC of the reaction mixture showed only *o*-nitrotoluene to be present. The temperature was then raised to -10° and the oxidation continued for 3 h. The mixture was poured into water and extracted 3 times with ether. The ether phase was washed 3 times with water, dried (Na_2SO_4) and evaporated, yield 2.3 g of a partly crystalline mixture. The crystals [1,2-di(*o*-nitrophenyl)-ethanol (*2a*)] (0.6 g) were separated and the oil chromatographed on silica gel (eluted with chloroform.) Yield: *o*-nitrotoluene 0.66 g (22 % of starting material); *o*-nitrobenzaldehyde 0.8 g (30 % of reacted *o*-nitrotoluene, IR and m.p. identical with authentic material); 1,2-di(*o*-nitrophenyl)-ethanol (*2a*) 0.2 g. Total yield of *2a* was thus 0.8 g (m.p. $153-155^\circ$) 30 % of reacted material). 1,2-Di(*o*-nitrophenyl)-ethanol had IR (KBr): 3550, 3060, 2950, 2860, 2840, 1610, 1580, 1520, 1450, 1360, 1340, 1310, 1050, 1040, 860, 790, 780, 740, 710, 700, 660 cm^{-1} . The electronic spectrum (ethanol) had λ_{max} 260 nm (ϵ_{max} : 8500 $\text{M}^{-1} \text{cm}^{-1}$). The mass spectrum had peaks m/e 288 (5×10^{-4} %), 270 (10^{-3} %), 152 (28 %), 137 (43 %), 120 (100 %).

Oxidations at different concentrations were carried out in an analogous way. The results are given in Table 1.

Table 1. Autoxidation of *o*-nitrotoluene in DMF at -10° in presence of KOH (0.2 mol KOH/mol *o*-nitrotoluene).

Start concentration of <i>o</i> -nitrotoluene, M	Reacted <i>o</i> -nitrotoluene, %	Yields of reacted <i>o</i> -nitrotoluene, %	
		<i>o</i> -Nitrobenzaldehyde	Dimer (<i>2a</i>)
0.014	85	50	25
0.14	78	30	30
1.2	33	0	35

1,2-Di(o-nitrophenyl)-ethyl acetate (3a). Acetic anhydride (0.5 ml) was added to 1,2-di(*o*-nitrophenyl)-ethanol (102 mg) in pyridine (5 ml). After 24 h at 20° , the mixture was poured into water, stirred for 0.5 h to destroy excess acetic anhydride, extracted with ether, the ether phase washed with dilute HCl followed by NaHCO_3 , dried (Na_2SO_4) and evaporated, yield 90 mg with m.p. $115-116^\circ$. Recrystallization from chloroform/petroleum ether raised m.p. to $116-117^\circ$. IR (CHCl_3) had no band near 3550, but bands at 1740 and 1240 cm^{-1} (acetate), and at 1520 and 1350 cm^{-1} (NO_2). The NMR spectrum (CDCl_3) had signals at 2.0 (singlet, 3H); the AB part of an ABX spectrum with signals

between 3.3 and 4.1 (2 protons, methylene with $J_{AB} = 14$ Hz), the X part of the ABX spectrum with 4 equally strong signals between 6.35 and 6.6 (1 proton, methine); and a complex signal pattern for the aromatic protons: 5 protons between 7.3 and 7.75 and 2 protons between 7.75 and 8.1 (the protons *ortho* to the NO_2 group).

o-Nitrobenzyl *o*-nitrophenyl ketone (4a). CrO_3 (1 g) in 90 % acetic acid/water (10 ml) was added to a suspension of 1,2-di(*o*-nitrophenyl)-ethanol (1 g) in 90 % acetic acid/water (20 ml) at 0°. After 3 h at 20°, the mixture was poured into water, extracted with ether, the ether phase washed with NaHCO_3 , dried (Na_2SO_4) and evaporated. Yield 0.5 g. The product was recrystallized from chloroform, yield 0.2 g of *o*-nitrobenzyl *o*-nitrophenyl ketone, m.p. 157–159°. IR (KBr): 3090, 2860, 1710, 1610, 1580, 1520, 1410, 1350, 1220, 1000, 860, 850, 760, 740, 710, 700, 670 cm^{-1} . The NMR spectrum (d_6 -DMSO) had signals at 4.7 (2 protons, methylene singlet) and a complex pattern from 7.3 to 8.3 (8 protons). The intensity of methylene to the aromatic protons signals (2:8) was altered to 1.2:8 protons on addition of D_2O to the solution.

Autoxidation of o-nitrotoluene in DMSO. Oxygen was passed through a solution of *o*-nitrotoluene (46 g) in DMSO (160 ml) containing solid KOH (10 g) (stirring). The mixture was poured into water after oxidation for 3 h at 30°, and unreacted *o*-nitrotoluene (17 g, 37 % of starting material) and 1,2-di(*o*-nitrophenyl)-ethanol (2a) (11 g, 23 % of starting material) were obtained.

Autoxidation of p-nitrotoluene at high concentration. Oxygen was passed through a stirred solution of *p*-nitrotoluene (46 g) in DMSO (160 ml) with KOH pellets (10 g) added. The reaction temperature was kept below 30°. After 4 h, the reaction mixture was poured into water and the product isolated by filtration, washing with water, and drying. The product (41.4 g) contained 42 % *p*-nitrotoluene (determined by GLC, internal standard method) corresponding to 17.4 g (38 % starting material). The reaction product was washed with chloroform to remove unreacted *p*-nitrotoluene. The residue (12.8 g) had m.p. 183–185° and was pure as judged by TLC (R_F 0.15 as compared to R_F 0.76 for *p*-nitrotoluene, eluted with chloroform). Recrystallization from chloroform raised the m.p. to 184–186°. The product (1,2-di(*p*-nitrophenyl)-ethanol, 2a) had IR spectrum (KBr): 3530, 3100, 3080, 2960, 2920, 2890, 2840, 1610, 1600, 1520, 1350, 1210, 1160, 865, 855, 790, 750, 700 cm^{-1} . The mass spectrum had peaks at m/e 288(0.04 %), 271(0.3 %), 152(12 %), 137(100 %), 120(10 %), 107(3 %), 90(3 %).

1,2-Di(p-nitrophenyl)-ethyl acetate. To 2a (0.175 g) in pyridine (10 ml), acetic anhydride (0.5 ml) was added. The mixture was poured into water after 20 h at room temperature, and the product isolated by filtration, washing with water, drying and recrystallization from chloroform/petroleum ether. Yield 0.06 g, m.p. 161–161.7°. The product was pure as judged by TLC (R_F 0.53, eluted with chloroform) and had IR (KBr): 3110, 2960, 2840, 1750, 1615, 1605, 1520, 1350, 1240, 1220, 1110, 1030, 940, 860, 800, 750, 700 cm^{-1} . The NMR spectrum (CDCl_3) had signals at 2.1 (singlet, 3 protons); 3.3 (doublet, $J = 7$ Hz, 2 protons, methylene); 6.1 (triplet, $J = 7$ Hz, 1 proton, methine); 7.27 (doublet, $J = 9$ Hz); 7.40 (doublet, $J = 9$ Hz); 8.13 (doublet, $J = 9$ Hz), 8.20 (doublet, $J = 9$ Hz); total number of aromatic protons 8.

p-Nitrobenzyl *p*-nitrophenyl ketone. To a suspension of 2a (0.5 g) in acetic acid containing 10 % water (10 ml) was added a solution of CrO_3 (0.5 g) in acetic acid (with 10 % water, 5 ml). After 3.5 h at 20° the mixture was poured into water. The product was isolated by filtration, washing with water, drying and recrystallization from chloroform/petroleum ether. The product (0.5 g) was pure as judged by TLC, had m.p. 135.5–136.4°. IR (KBr): 3100, 3080, 3050, 2940, 2920, 2860, 1700, 1600, 1520, 1350, 1220, 1205, 1100, 1000, 880, 865, 860, 820, 790, 750, 740, 710, 690 cm^{-1} . Electronic spectrum: λ_{max} 268 nm (ϵ_{max} 26 800 $\text{M}^{-1} \text{cm}^{-1}$). NMR (DMSO- d_6 , green solution) had signals at 4.7 (singlet, 2 protons, methylene), 7.6 (2 protons, doublet, $J = 9$ Hz), 8.2 (doublet, $J = 9$ Hz) and 8.35 (singlet). The last two signals corresponded to 6 protons. The signal at 4.7 disappeared on addition of D_2O , the other signals remained unchanged.

Oxidation of p-nitrotoluene in dilute solution. Oxygen was passed through a solution of *p*-nitrotoluene (1.37 g) in dry DMSO (80 ml) for 5 min. A solution of potassium *t*-butoxide (2.24 g) in *t*-butanol (20 ml) was added and the oxygenation continued for 2.5 h. The mixture was then poured into water. Isolation of the product by filtration, washing with water, and drying gave a product (0.63 g) which TLC indicated to consist of *p,p'*-dinitrostilbene and *p*-nitrobenzyl *p*-nitrophenyl ketone in an approximate ratio of 9:1. The product was extracted three times with ethanol and gave an insoluble substance

(0.43 g) which was recrystallized from chloroform to give yellow crystals of *p,p'*-dinitrostilbene (131 mg, m.p. 280–282°). IR (KBr): 3100, 3040, 1610, 1600, 1510, 1340, 1110, 1080, 1060, 860, 850, 760, 690, cm^{-1} . The ethanol solution gave 0.11 g on evaporation which contained ca. 80 % of *p*-nitrobenzyl *p*-phenyl ketone and ca. 20 % dinitrostilbene. After three recrystallizations from chloroform/petroleum ether, *p*-nitrobenzyl *p*-nitrophenyl ketone (20 mg) was obtained which had m.p., mixed m.p. and IR spectrum identical to those reported above.

Oxidation of p,p'-dinitrobibenzyl. *p,p'*-Dinitrobibenzyl (0.5 g) was oxidized as described above for the case of *p*-nitrotoluene in dilute solution. The neutral product (0.29 g) contained only *p,p'*-dinitrostilbene and traces of starting material as judged by TLC and IR spectroscopy.

Oxidation of 1,2-(p-dinitrophenyl)-ethanol (2b). Oxygen was passed through a solution of 1,2-di(*p*-nitrophenyl)-ethanol (1.44 g) in DMSO (80 ml) for 5 min. Potassium *t*-butoxide (2.24 g) in *t*-butanol (20 ml) was added, and the oxidation continued for 2.5 h. The product was isolated as described for the oxidation of *p*-nitrotoluene in dilute solution and contained ca. 90 % *p,p'*-dinitrostilbene and 10 % *p*-nitrobenzyl *p*-nitrophenyl ketone as judged by TLC. The two compounds were separated by crystallization. *p,p'*-Dinitrostilbene (145 mg) and *p*-nitrobenzyl *p*-nitrophenyl ketone (12 mg after 5 crystallizations) had the physical data of the pure substances.

Oxidation of p-nitrotoluene in dilute DMSO solution with KOH as base. This oxidation was performed analogously with the one in DMSO/*t*-butanol, but with pure DMSO as solvent and KOH as base. The result of the oxidation was the same as when potassium *t*-butoxide was used as base in dilute DMSO *t*-butanol solution: the product consisted of *p,p'*-dinitrostilbene with ca. 10 % *p*-nitrobenzyl *p*-phenyl ketone.

Oxidation of p-nitrotoluene in t-butanol. Oxygen was passed through a solution of *p*-nitrotoluene (3 g) in dry *t*-butanol (65 ml) for 5 min. A solution of potassium *t*-butoxide (4 g) in *t*-butanol was added, and the oxidation continued for 3 h. The product was isolated by pouring the reaction mixture into water, filtering, washing the crystals with water and drying. Yield 1.3 g. Crystallization from chloroform gave 0.9 g *p,p'*-dinitrobibenzyl, m.p. 182–183°. IR (KBr): 3110, 3080, 2940, 2860, 2840, 1610, 1605, 1600, 1520, 1345, 1183, 1178, 1110, 1100, 865, 855, 790, 750, 700 cm^{-1} .

Reaction of p-nitrotoluene with p-nitrobenzaldehyde. A solution of *p*-nitrotoluene (2.3 g) and *p*-nitrobenzaldehyde (2.63 g) in DMSO (16 ml) containing KOH-pellets (1 g) was stirred for 6 h. The product was isolated by pouring the reaction mixture into water, filtering, washing with water and drying. Yield 2.2 g of a product with m.p. 175–205°. TLC of the product indicated a composition of 90 % 1,2-di(*p*-nitrophenyl)-ethanol and 10 % *p,p'*-dinitrostilbene. Recrystallization from chloroform gave 1,2-di(*p*-nitrophenyl)-ethanol with m.p. and IR identical to those described above.

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Received February 20, 1971.