[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, UNIVERSITY OF WESTERN AUSTRALIA, AND FROM THE CHEMISTRY DEPARTMENT, UNIVERSITY OF ADELAIDE]

THE S_N MECHANISM IN AROMATIC COMPOUNDS, PART XI. SOME REACTIONS OF AMINODINITRODIARYL ETHERS

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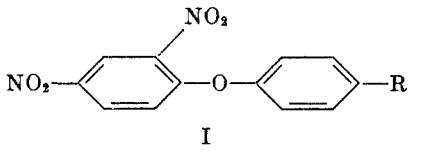
As a further preliminary [see also (1)] to commencing kinetic investigations of the nucleophilic attack on aryl ethers, it was decided to investigate the mode of attack on compounds closely related to 2,4-dinitro-4′-aminodiphenyl ether (Ia)



I

a R = NH_2
b R = $NHSO_2$—C$_6$H$_4$—CH_3
c R = $NHCH_3$
d R = $N(CH_3)_2$
e R = $N(CH_3)SO_2$—C$_6$H$_4$—CH_3
f R = $NH{\cdot}COCH_3$
g R = $N(CH_3)COCH_3$

We have prepared a number of such compounds and subjected them to attack by methoxide ion, and also in some cases by electrically neutral nucleophilic reagents.

The purpose was to find suitable compounds for kinetic studies, and also to determine whether any of these compounds, other than Ia, underwent initial fission of the ether linkage, followed by recombination to form substituted diphenylamines (1).

The amino compound (Ia) was prepared by an improvement of the original method used by Reverdin and Dresel (2).

The *p*-toluenesulfonyl derivative (Ib) was prepared by two methods—from the parent amine, and, more conveniently, by reaction between N-(*p*-toluenesulfonyl)-*p*-aminophenol and 1-chloro-2,4-dinitrobenzene. In preparing the mono- and di-methylamino compounds (Ic and Id), direct methylation of the primary amine (Ia) was not found to be satisfactory and alternative routes were followed. The sodium salt of 2,4-dinitro-4′-[N-(*p*-toluenesulfonyl)amino]diphenyl ether (Ib) reacted with methyl sulfate readily to give the methyl sulfonamide (Ie) which was smoothly hydrolyzed to the desired monomethylamino compound (Ic).

The dimethylamino compound (Id) was prepared by reaction between 1-chloro-2,4-dinitrobenzene and *p*-dimethylaminophenol in ethanolic sodium hydroxide. Since *p*-dimethylaminophenol was unavailable at the time, it was prepared *in situ* by prior methylation of *p*-aminophenol with methyl sulfate.

Methylation of the tertiary amine (Id) with methyl sulfate and picric acid

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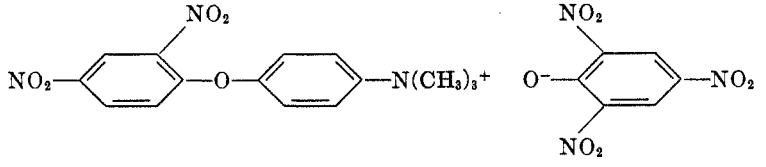
[2] For reprints.

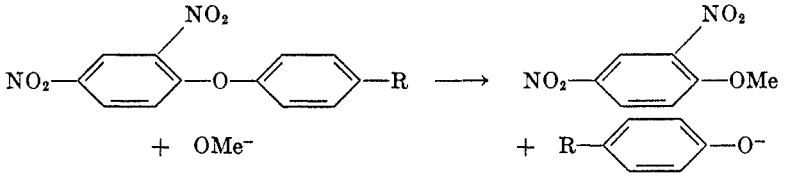
produced 2,4-dinitro-4′-trimethylammonium picrate (II). This compound was also prepared directly by reaction between N-(2,4-dinitrophenyl)pyridinium chloride and *p*-hydroxyphenyltrimethylammonium picrate in ethanolic sodium



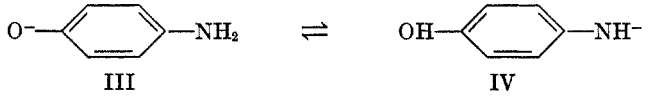
II

hydroxide. Despite the high reactivity of the pyridinium salt it was not attacked by the free phenol.

All the ethers described above were reacted with sodium methoxide in absolute methanol. In every case, except Ia as previously described (1), the products were 2,4-dinitroanisole and the appropriate phenol, corresponding to the simple reaction



The rearrangement occurring with Ia was due to attack on the 2,4-dinitroanisole by the *p*-hydroxy anilide ion (IV), formed by prototropic rearrangement



III IV

of the *p*-aminophenoxide ion (III). Compounds Id and Ie have no H available for prototropic rearrangement to the anilide ion and acylanilide ion respectively.

With acyl substituents on the N atom (Ib and If) the acylamide ions have insufficient nucleophilic power to attack 2,4-dinitroanisole. Steric effects may also play a part.

In the case of the N-methyl amino compound (Ic) there is no obvious reason why rearrangement should not occur, with subsequent attack on the dinitroanisole, unless there is a steric hindrance to the final stage. The absence of rearrangement to a diphenylamine is therefore ascribed to this cause.*

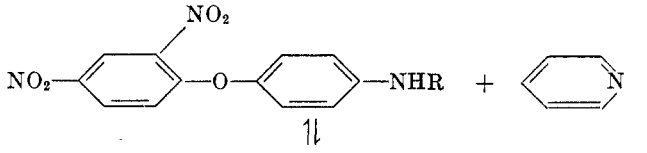
The possibility of attack by pyridine on these compounds was also investigated, since any N-(2,4-dinitrophenyl)pyridinium ion formed would be very susceptible to further attack. Bolto and Miller have already shown kinetically the ease of replacement of cationic groups (3).

* *Added in proof:* As pointed out by a referee, the methyl group would decrease the stability of the anilide ion, and the lower yield of 2,4-dinitroanisole in this case may indicate slight rearrangement.

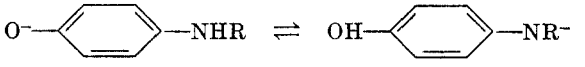
The three compounds Ia, Ib, and Ic were each refluxed with pyridine, but in every case only unchanged starting material was recovered.

The lack of detectable reaction could be due simply to the forward reaction

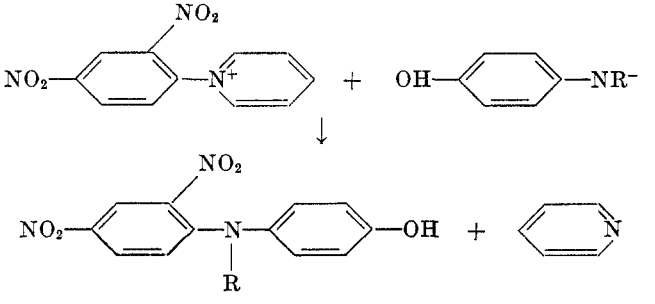
(a)



(b)



(c)



(a) being too slow under the experimental conditions or to reverse action (a) being so much faster than forward reaction (b) that insufficient *p*-hydroxyanilide ions formed for reaction (c) to occur. To see which was correct, the *p*-toluenesulfonylamino compound (Ib) was refluxed with pyridine in the presence of *p*-toluenesulfonyl chloride, which should react with any of the phenoxide ion formed by forward reaction (a). Since no di-*p*-toluenesulfonyl-*p*-aminophenol could be detected it was concluded that pyridine does not react with these deactivated ethers under the conditions used by us. This was expected from the kinetic results of Lantzke, Leahy, and Miller (4).

The quaternary ammonium salt (II) is expected to be highly reactive and correlation of the results of Bolto and Miller (3) and Beckwith and Miller (5) suggests that it should have a reactivity comparable with but less than 1-chloro 2,4-dinitrobenzene (6).

The reaction with pyridine under the conditions used was expected to be slow (4) but detectable.

The reaction between the ether (II) and pyridine was carried out in the presence of phenol since any N-(2,4-dinitrophenyl)pyridinium ion formed should react with phenol under the conditions of the experiment. The production of 2,4-dinitrodiphenyl ether confirmed that pyridine had in fact reacted.

Finally the reaction between diethylamine and some of these ethers was investigated.

The *p*-amino ether (Ia) was refluxed in methanol with diethylamine. Besides unchanged starting material, the rearrangement product 2,4-dinitro-4′-hydroxydiphenylamine was obtained. However this could not have been obtained from 2,4-dinitrodiethylaniline since, as was expected, it was shown separately to be resistant to attack by *p*-aminophenol and *p*-aminophenoxide ion.

It appears therefore that reaction proceeds *via* 2,4-dinitroanisole [as in (1)] which is here formed by solvolysis. This is further confirmed, since in benzene, the ether is almost completely unattacked by diethylamine.

Ethers of greater reactivity are attacked normally by this reagent: both 2,4,4′-trinitrodiphenyl ether and even 2,4-dinitro-4′-acetylaminodiphenyl ether (Ic) give 2,4-dinitrodiethylaniline when heated with methanolic diethylamine.

EXPERIMENTAL

M.p.s are corrected. Analyses are by Dr. Zimmermann, Melbourne.

2,4-Dinitro-4′-acetylaminodiphenyl ether (If). N-Acetyl-*p*-aminophenol (10 g.) and 1-chloro-2,4-dinitrobenzene were dissolved in ethanol (100 ml.) and to the hot solution was added, in small portions with stirring, a solution of sodium hydroxide (2.5 g.) in water (10 ml.). The mixture was gently refluxed for five minutes and then cooled in ice. The product was filtered off, washed with water, and crystallized from acetone/ethanol as thin colorless plates (16.5 g., 88%), m.p. 196° [Reverdin and Dresel (2) give m.p. 195°].

2,4-Dinitro-4′-aminodiphenyl ether (Ia). To a refluxing solution of the above acetamide (7.0 g.) in glacial acetic acid (50 ml.) was added 10 ml. of concentrated hydrochloric acid. After one hour another 10-ml. portion of acid was added and refluxing was continued for a further hour. The mixture then was cooled, diluted with water (100 ml.), and the amine liberated by the addition of ammonia. Crystallization from ethanol gave orange plates (5.8 g., 95%), m.p. 146° [Reverdin and Dresel (2) give m.p. 144°].

N-(p-Toluenesulfonyl)-p-aminophenol. p-Aminophenol (5.0 g.), hydrated sodium acetate (6.3 g.), and *p*-toluenesulfonyl chloride (8.7 g.) were refluxed in ethanol (20 ml.) and water (15 ml.) for 30 minutes. The mixture was cooled and poured into 10% hydrochloric acid and the precipitate was collected. After washing the product was crystallized from aqueous ethanol as colorless needles (10.1 g., 84%), m.p. 145° [Troeger and Uhlmann (7) give m.p. 143°].

2,4-Dinitro-4′-[N-(p-toluenesulfonyl)amino]diphenyl ether (Ib). (*i*). 2,4-Dinitro-4′-aminodiphenyl ether (2.2 g.), *p*-toluenesulfonyl chloride (2.5 g.), and pyridine (20 ml.) were gently heated to the boiling point. There was a color change from red to yellow. The excess chloride was destroyed by the dropwise addition of water and the product was obtained by pouring the mixture into 10% hydrochloric acid (200 ml.). After washing with water the *sulfonamide* was carystallized from acetone/ethanol as thin colorless plates (2.72 g., 79%), m.p. 202°.

Anal. Calc'd for $C_{19}H_{15}N_3O_7S$: C, 53.15; H, 3.52.
Found: C, 53.42; H, 3.55.

(*ii*). N-(*p*-Toluenesulfonyl)-*p*-aminophenol (6.5 g.) and 1-chloro-2,4-dinitrobenzene (4.5 g.) were dissolved in ethanol (35 ml.) and to the hot solution was added with stirring sodium hydroxide (0.93 g.) in water (15 ml.). After five minutes reflux, the mixture was cooled, acidified, and diluted with water (20 ml.). The precipitate was collected, washed, and crystallized from dilute acetic acid. Yield 8.0 g. (84%), m.p. and mixture m.p. 202°.

2,4-Dinitro-4′-[p-toluenesulfonyl)methylamino]diphenyl ether (Ie). The previously mentioned sulfonamide (6.1 g.) was suspended in cold ethanol (50 ml.) and to it was added sodium hydroxide (0.61 g.) in water (15 ml.). As soon as all the solid had dissolved dimethyl sulfate (2.0 g.) was added and the mixture was gently boiled for three minutes. The mixture

was acidified, diluted with water (30 ml.), and cooled in ice. The *methyl-sulfonamide* was collected, washed with cold ethanol, and crystallized from acetone as thin colorless plates (5.9 g., 94%), m.p. 175°.

Anal. Calc'd for $C_{20}H_{17}N_3O_7S$: C, 54.18; H, 3.87; N, 9.47.
Found: C, 54.35; H, 3.89; N, 9.04.

2,4-Dinitro-4'-methylaminodiphenyl ether (Ic). The above N-methyl sulfonamide (6.0 g.) was refluxed in acetic acid (60 ml.) with hydrochloric acid (10 ml.) for 1.5 hours. A further 20-ml. portion of hydrochloric acid then was added and the mixture was refluxed for another 6.5 hours. After cooling, the solution was diluted with water (100 ml.) and the free amine was precipitated with sodium hydroxide solution. The amine then was taken up in 100 ml. of 10% hydrochloric acid, filtered from insoluble impurities, and precipitated by the slow addition of ammonia. Crystallization from methanol gave pale yellow plates (3.8 g., 97%), m.p. 104°.

Anal. Calc'd for $C_{13}H_{11}N_3O_5$: C, 53.95; H, 3.83; N, 14.53.
Found: C, 54.35; H, 4.04; N, 14.54.

The *acetyl* derivative (Ig) was obtained by maintaining a solution of the amine (340 mg.) in pyridine (5 ml.) and acetic anhydride (2 ml.) at 50° for five minutes. The product crystallized from aqueous methanol as colorless needles (325 mg., 84%), m.p. 142°.

Anal. Calc'd for $C_{15}H_{13}N_3O_6$: C, 54.38; H, 3.95; N, 12.69.
Found: C, 54.47; H, 3.94; N, 12.54.

2,4-Dinitro-4'-dimethylaminodiphenyl ether (Id). To a solution of *p*-aminophenol (2.8 g.) and anhydrous sodium acetate (5.0 g.), refluxing under nitrogen, methyl sulfate was added dropwise (6.5 g.). After the addition the mixture was refluxed a further 20 minutes. 1-Chloro-2,4-dinitrobenzene (6.5 g.) then was added, followed by 3.2 g. of sodium hydroxide in water (15 ml.) added in small portions. After a further five minutes' reflux the mixture was cooled, acidified, and poured into 50 ml. of iced-water. The insoluble materials were filtered off and the amine was precipitated by the addition of ammonia to the filtrate. After washing with a little warm ethanol the *dimethylamine* was crystallized from acetone/ethanol as red prisms (2.8 g., 36%), m.p. 142°.

Anal. Calc'd for $C_{14}H_{13}N_3O_5$: C, 55.44; H, 4.32; N, 13.86.
Found: C, 55.83; H, 4.41; N, 14.07.

The tarry acid-insoluble residue was taken up in acetone, charcoaled, and cooled to deposit yellow crystals of 4'-(2,4-dinitrophenoxy)-2,4-dinitrodiphenylamine (1.5 g.), m.p. and mixture m.p. 228°.

When the diphenylamine (420 mg.) was refluxed with 12 ml. of 0.32 *N* sodium methoxide in absolute methanol for 15 minutes, cooled, and poured into iced-water a precipitate of 2,4-dinitroanisole (115 mg., 61%), m.p. 94° was obtained. The filtrate on acidification deposited a crystalline precipitate of 2,4-dinitro-4'-hydroxydiphenylamine (230 mg., 88%), m.p. and mixture m.p. 196°.

N-p-Hydroxyphenyltrimethylammonium picrate. *p*-Aminophenol (5.0 g.), methyl sulfate (15 ml.), anhydrous sodium acetate (10 g.), and ethanol (30 ml.) were gently heated together under reflux. After the initial vigorous reaction had subsided the mixture was refluxed for 30 minutes, cooled, and poured into 120 ml. of water. Picric acid (11 g.) was added and the solution was reduced in bulk by evaporation until on cooling the product was precipitated. The *quaternary salt* crystallized from a large volume of methanol as yellow needles (15.3 g., 87%), m.p. 185°.

Anal. Calc'd for $C_{15}H_{16}N_4O_8$: C, 47.36; H, 4.24; N, 14.73.
Found: C, 47.57; H, 4.13; N, 13.97.

N-p-(2,4-Dinitrophenoxy)phenyltrimethylammonium picrate (II). (*a*). 2,4-Dinitro-4'-dimethylaminodiphenyl ether (2.0 g.) and methyl sulfate (5 ml.) were heated on the water-bath for 30 minutes. The mixture was diluted with ethanol, an aqueous solution of picric acid (2 g.) was added, and the mixture was evaporated until on cooling the *quaternary salt* was precipitated. Crystallization from acetone/ethanol gave yellow prisms (3.25 g., 90%), m.p. 196°.

Anal. Calc'd for $C_{21}H_{18}N_6O_{12}$: C, 46.15; H, 3.32; N, 15.38.
Found: C, 46.51; H, 3.52; N, 15.40.

(*b*). To a suspension of N-*p*-hydroxyphenyltrimethylammonium picrate (1.7 g.) in ethanol (20 ml.) was added 1.3 ml. of 3 *N* sodium methoxide in methanol. On heating and stirring a clear solution was obtained. To the solution was added N-(2,4-dinitrophenyl)-pyridinium chloride (1.4 ml.) in methanol (10 ml.) and the mixture was refluxed for 30 minutes. After cooling in ice the product was filtered off and crystallized from acetone/ethanol. Yield 1.95 g. (92%), m.p. and mixture m.p. 196°.

When the experiment was conducted in the absence of sodium methoxide there was an immediate precipitate of N-(2,4-dinitrophenyl)pyridinium picrate, m.p. 146°.

O,N-Di(p-toluenesulfonyl)-p-aminophenol. *p*-Aminophenol (1.0 g.) and *p*-toluenesulfonyl chloride (4 g.) were refluxed in pyridine (10 ml.) for five minutes, cooled and poured into 100 ml. of 10% hydrochloric acid. The *p*-toluenesulfonyl derivative crystallized from ethanol as colorless needles (3.7 g., 96%), m.p. 169°.

Anal. Calc'd for $C_{20}H_{19}NO_5S_2$: C, 57.55; H, 4.59; N, 3.36.
Found: C, 57.74; H, 4.74; N, 3.45.

2,4,4'-Trinitrodiphenyl ether. 1-Chloro-2,4-dinitrobenzene (3.0 g.) was heated with pyridine (5 ml.) until a vigorous reaction occurred and the solution turned solid. A solution of *p*-nitrophenol (3 g.) in alcohol (25 ml.) was added, followed by 6.0 ml. of 3.0 *N* sodium methoxide solution, and the mixture was refluxed for 30 minutes. The cooled mixture was poured into iced dilute hydrochloric acid, and the precipitate was crystallized from acetone/ethanol as colorless prisms (3.5 g., 78%), m.p. and mixture m.p. 116°.

Fission of the diphenyl ethers with sodium methoxide. (*i*). *2,4-Dinitro-4'-acetylaminodiphenyl ether* (If). The diphenyl ether (1.50 g.) was refluxed for 15 minutes with 30 ml. of 0.34 *N* sodium methoxide in methanol, cooled, and poured into water (150 ml.). The precipitate after washing and drying was identified as 2,4-dinitroanisole (0.85 g., 91%) m.p. and mixture m.p. 94°. The phenolic product was not isolated. When the experiment was repeated with 3 hours' reflux there was still no indication of a rearrangement product.

(*ii*). *2,4-Dinitro-4'-[N-(p-toluenesulfonyl)amino]diphenyl ether* (Ib). The diphenyl ether (1.63 g.) was treated as in (*i*) with 15 ml. of 0.7 *N* sodium methoxide. The yield of 2,4-dinitroanisole, m.p. 94°, was 0.69 g. (92%). The alkaline filtrate, after removal of the dinitroanisole was acidified. On heating the resultant precipitate dissolved and on cooling N-(*p*-toluenesulfonyl)-*p*-aminophenol came down as colorless needles (0.94 g., 94%), m.p. and mixture m.p. 145°. When the experiment was repeated with 2.5 hours' reflux there was still no indication of a rearrangement product.

(*iii*). *2,4-Dinitro-4'-[N-(p-toluenesulfonyl)methylamino]diphenyl ether* (Ie). The diphenyl ether (1.32 g.) was refluxed in the usual way for seven minutes with 15 ml. of 0.7 *N* sodium methoxide to give 0.56 g. (96%) of 2,4-dinitroanisole and 0.76 g. (93%) of N-(*p*-toluenesulfonyl)-*p*-methylaminophenol as colorless rods from methanol, m.p. 138°.

Anal. Calc'd for $C_{14}H_{15}NO_3S$: C, 60.61; H, 5.45; N, 5.05.
Found: C, 60.42; H, 5.41; N, 4.63.

(*iv*). *2,4-Dinitro-4'-methylaminodiphenyl ether* (Ic). The diphenyl ether (0.44 g.) was treated in the usual way for 30 minutes with 10 ml. of 0.35 *N* sodium methoxide under nitrogen to yield 0.24 g. (80%) of 2,4-dinitroanisole. The phenolic product was not isolated and there was no rearrangement product. When the reaction was repeated with 4 hours' reflux there was still no indication of a rearrangement product.

(*v*). *2,4-Dinitro-4'-dimethylaminodiphenyl ether* (Id). The diphenyl ether (1.1 g.) was refluxed for 10 minutes with 12 ml. of 0.35 *N* sodium methoxide under nitrogen, acidified, and poured into iced water. The precipitate consisted of 2,4-dinitroanisole (0.69 g., 96%). When the filtrate was shaken with *p*-toluenesulfonyl chloride and alkali there was obtained a precipitate of *p*-dimethylaminophenyl-*p*-toluenesulfonate which crystallized from methanol as thin colorless plates (0.35 g., 33%), m.p. 130°.

Anal. Calc'd for $C_{15}H_{17}NO_3S$: C, 61.84; H, 5.88; N, 4.81.
Found: C, 62.03; H, 5.85; N, 4.80.

(*vi*). *N-p-(2,4-Dinitrophenoxy)phenyltrimethyl-ammonium picrate* (II). The quaternary salt (1.1 g.) was refluxed with 20 ml. of 0.35 *N* sodium methoxide for 10 minutes and was poured into iced-water to give a precipitate of 2,4-dinitroanisole (0.38 g., 95%). In a second experiment the quaternary salt (1.45 g.) was refluxed for 10 minutes with 10 ml. of 0.35 *N* sodium methoxide, acidified with a little acetic acid, and cooled in ice. *p*-Hydroxyphenyltrimethylammonium picrate was deposited in yellow needles (0.76 g., 74%), m.p. and mixture m.p. 185°.

Fission of diphenyl ethers with pyridine. (*i*). *2,4-Dinitro-4'-aminodiphenyl ether* (Ia). The diphenyl ether (680 mg.) was refluxed with A.R. pyridine (15 ml.) for 4 hours under oxygen-free nitrogen, cooled, and poured into iced 20% hydrochloric acid. A dark powder (45 mg.) which resisted purification and was not alkali-soluble was thrown down. After filtration the liquors were made alkaline with ammonia and unchanged starting material (570 mg.) was recovered.

(*ii*). *2,4-Dinitro-4'-(p-toluenesulfonyl)amino]diphenyl ether* (Ib). The diphenyl ether (0.5 g.) was refluxed for 90 minutes with *p*-toluenesulfonyl chloride (0.5 g.) and pyridine (15 ml.), cooled, and poured into iced dilute hydrochloric acid. The precipitate was collected, dried, and triturated with 10 ml. of cold ethanol. The ethanol extract was slowly evaporated to yield a crystalline solid (25 mg.). The m.p. of the solid was 166° but mixed with authentic O,N-di[*p*-toluenesulfonyl]-*p*-aminophenol it showed a depression of 18°.

(*iii*). *2,4-Dinitro-4'-methylaminodiphenyl ether.* When the diphenyl ether (0.5 g.) was refluxed for 45 minutes with pyridine the only product was unchanged starting material (0.46 g.).

(*iv*). *N-p-(2,4-Dinitrophenoxy)phenyltrimethylammonium picrate.* The quaternary salt (1.05 g.) and phenol (0.5 g.) were refluxed in pyridine (15 ml.) for one hour, cooled, and poured into iced dilute hydrochloric acid. On scratching the precipitated oil solidified and was filtered off. The solid was extracted with hot methanol (20 ml.). On cooling the extract a precipitate of unchanged starting material was thrown down. After this had been removed the extract was heated and diluted dropwise with water to give a crystalline precipitate of 2,4-dinitrodiphenyl ether (135 mg.), m.p. and mixture m.p. 72°.

Fission of diphenyl ethers with diethylamine. (*i*). *2,4-Dinitro-4'-aminodiphenyl ether* (Ia). The diphenyl ether (1.35 g.) and diethylamine (2.0 ml.) were refluxed in absolute methanol (20 ml.) under nitrogen for 5 hours, cooled, and poured into iced dilute hydrochloric acid. The precipitated dark red oil was removed by extraction with chloroform and the acid liquors were made alkaline with ammonia to yield a precipitate of unchanged starting material (730 mg.). The chloroform extract was evaporated and the residual oil was triturated with sodium hydroxide solution. The alkaline solution was filtered to remove a small amount of tarry impurities and was acidified. The precipitated 2,4-dinitro-4'-hydroxydiphenylamine crystallized from methanol as red prisms (440 mg.), m.p. and mixture m.p. 196°.

(*ii*). *2,4-Dinitro-4'-aminodiphenyl ether* (Ia) (*in benzene*). The diphenyl ether (1.34 g.) was refluxed in dry benzene (12 ml.) and diethylamine (1.2 ml.) for five hours, cooled, and poured into dilute hydrochloric acid. The insoluble amine hydrochloride was filtered off and well washed with benzene. The filtrate and washings were combined, and the benzene layer was collected and washed with water. After evaporation of the benzene the oily residue was taken up in petroleum ether, and on standing yellow needles of the labile form of 2,4-dinitrodiethylaniline (15 mg.) m.p. and mixture m.p. 69° were deposited. The solid amine hydrochloride was taken up in hot aqueous ethanol, the aqueous filtrate was added, and the free amine was deposited by the addition of ammonia solution. The yield of unchanged starting material was 1.22 g.

(*iii*). *2,4,4'-Trinitrodiphenyl ether.* The diphenyl ether (1.60 g.) was refluxed for 30 minutes with methanol (10 ml.) and diethylamine (3 ml.), cooled, and poured into iced dilute hydrochloric acid. The precipitate of 2,4-dinitrodiethylaniline was collected and crystallized from methanol as yellow rods (1.19 g., 81%), m.p. and mixture m.p. 69°.

The aqueous filtrate was extracted with chloroform, evaporated, and taken up in ether. On addition of petroleum ether and standing, crystals of unchanged starting material (*circa* 35 mg.) and *p*-nitrophenol were deposited separately and were collected by hand.

(*iv*). *2,4-Dinitro-4'-acetylaminodiphenyl ether* (If). The diphenyl ether (0.92 g.) was refluxed with diethylamine (3.0 ml.) in absolute methanol (10 ml.) for 2.5 hours, cooled, and poured into cold dilute hydrochloric acid. The precipitate was filtered off and was fractionally crystallized from methanol. The first two crops yielded unchanged starting material (320 mg.), m.p. 195°, while later crops gave, after recrystallization, yellow needles of 2,4-dinitrodiethylaniline (0.36 g.), m.p. and mixture m.p. 69°.

The attempted reaction between 2,4-dinitrodiethylaniline and p-aminophenol. (*i*). *p*-Aminophenol (0.80 g.), 2,4-dinitrodiethylaniline (825 mg.), and diethylamine (1.5 ml.) were refluxed in absolute methanol under nitrogen for five hours, cooled, and poured into dilute hydrochloric acid. The precipitate was unchanged starting material (0.77 g.), m.p. 69°. There was no indication of any alkali-soluble product.

(*ii*). A similar result was obtained when the above experiment was conducted in the presence of 1.0 ml. of 3 *N* sodium methoxide.

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(5) Unpublished results of BECKWITH AND MILLER.
(6) MILLER, *J. Chem. Soc.*, 3550 (1952).
(7) TROEGER AND ULLMANN, *J. prakt. Chem.*, [2] **57**, 438 (1895).