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

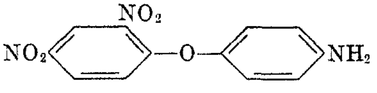
THE S_N MECHANISM IN AROMATIC COMPOUNDS. PART IX. SOME REACTIONS OF POLYNITRODIARYL ETHERS

ATHELSTAN. L. BECKWITH[1] AND JOSEPH MILLER[2]

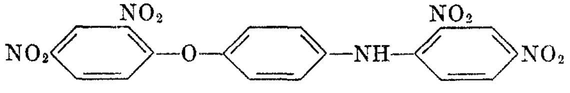
Received March 1, 1954

Before commencing kinetic investigations of the nucleophilic attack on aryl ethers it was felt necessary to clear up a number of relevant points in the chemistry of these compounds.

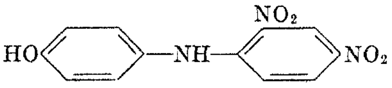
One compound required by us was 2,4-dinitro-4′-aminodiphenyl ether (I) which contains the powerfully deactivating NH_2 group (1–3).



I



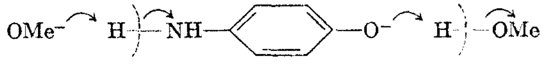
II



III

The literature contains conflicting reports of the physical properties of I. Reverdin and Dresel (4) gave it as having m.p. 144°, whereas Roberts, de Worms, and Clark (5) gave it as 223°. It appeared that the compound described by the latter workers was actually 2,4-dinitro-4′-(2,4-dinitrophenoxy)diphenylamine (II), and we have prepared this compound by an unequivocal synthesis, finding it to have m.p. 228° and to react with methanolic sodium methoxide in the expected manner to give 2,4-dinitro-4′-hydroxydiphenylamine (III) and 2,4-dinitroanisole.

The true 2,4-dinitro-4′-aminodiphenyl ether (I) did not however give the expected products with OMe^-, but gave III instead. We regard the reaction as giving initially the normal products, *viz.* 2,4-dinitroanisole and *p*-aminophenoxide ion which then undergo a secondary irreversible reaction. The *p*-aminophenoxide ion in methanolic sodium methoxide will be in equilibrium with



IV

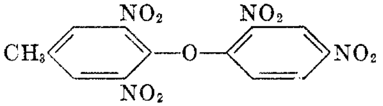
---

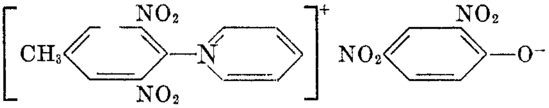
[1] Present address: University of Adelaide, South Australia.

[2] Fulbright Visiting Lecturer/Research Scholar at University of California, Berkeley, during Spring Semester, 1954.

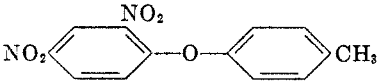
a small amount of the very powerfully nucleophilic *p*-hydroxyanilide ion (IV), which will readily attack 2,4-dinitroanisole to give III and OMe^-. The compound III has very low reactivity towards nucleophilic reagents. This mechanism is fully supported by the fact that III is also formed if 2,4-dinitroanisole and *p*-aminophenol are reacted in the presence of methanolic sodium methoxide.

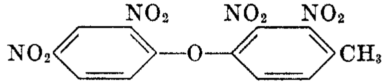
From the general discussion by one of us in Part I (1), *c.f.* Bunnett and Zahler (6), it is seen that the expected point of attack in a diaryl ether is in the ring which is more activated by substituents for nucleophilic attack. Bunnett and Zahler (6) quote some results of Borrows, Clayton, Hems, and Long (7) as contradicting this rule. The latter reported 2,2′,4′,6-tetranitro-4-methyldiphenyl ether (V) as reacting with pyridine to give N-(2,6-dinitro-4-methylphenyl)pyridinium 2,4-dinitrophenoxide (VI), and we felt it important to repeat this part of their work.

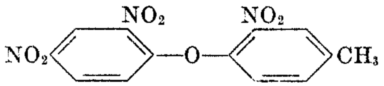

V


VI

Being unable to repeat their synthesis described for V, we tried an application of a standard method, *viz.* reacting 1-chloro- or better 1-fluoro-2,4-dinitrobenzene (8) with 2,6-dinitro-4-methylphenoxide ion, but obtained tars only. Nitration of 2,4-dinitro-4′-methyldiphenyl ether (VII) produced 2,2′,3′,4-tetranitro-4′-methyldiphenyl ether (VIII). The latter compound melted 17° higher than reported by Fox and Turner (9), but the identity was proved by fission with methanolic sodium methoxide to give 2,4-dinitroanisole and 2,3-dinitro-*p*-cresol.


VII

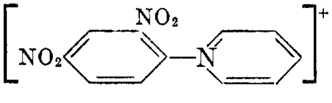

VIII

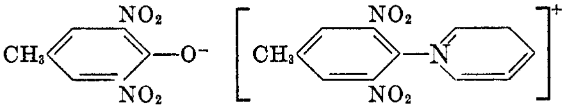

IX

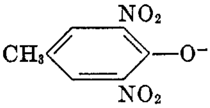
Attempts to nitrate 2,2′,4-trinitro-4′-methyldiphenyl ether (IX) resulted in a concurrent fission giving an oily mixture of phenols, from which after acetylation 2,6-dinitro-*p*-cresyl acetate was isolated. The nitration experiments confirm the very low activating power of the 2,4-dinitrophenoxy group in aromatic S_E reactions, and suggest also that in compound VII the most activated point for electrophilic attack is *ortho* to the methyl group.

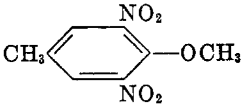
The ether V was eventually prepared by us by utilizing the facile replacement of cationic groups in aromatic S_N reactions—Part I (1).

N-(2,4-Dinitrophenyl)pyridinium 2,6-dinitro-4-methylphenoxide (X) was heated in anisole as a solvent and a good yield of V obtained. This compound is not a heavy yellow oil as reported by Borrows, *et al.* (7) but a crystalline solid, m.p. 160°. When heated with pyridine in acetonitrile as the solvent a red crystalline salt, m.p. 231°, was obtained. Borrows, *et al.* (7) assigned to this the structure VI, but we have proved it to be N-(2,6-dinitro-4-methylphenyl)pyridinium 2,6-dinitro-4-methylphenoxide (XI) by comparison with a sample synthesized by an alternative route. The true compound VI was synthesized from N-(2,6-dinitro-4-methylphenyl)pyridinium *p*-toluenesulphonate (the cation is the same as XI) by reacting it with potassium 2,4-dinitrophenoxide, and was found to have m.p. 186°.


X

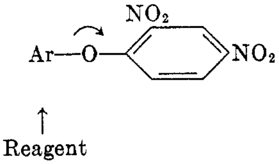

XI



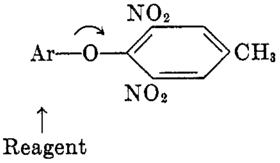

XII

The production of XI by pyridine fission of the ether V does show that the latter is attacked in both rings at a similar rate. Using the more powerfully nucleophilic methoxide ion as reagent gave as products 2,4-dinitrophenol and 2,6-dinitro-*p*-cresylmethyl ether (XII) corresponding to attack in the ring which has less activating substituents [*c.f.* Part II (2)].

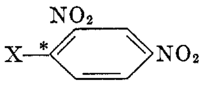
As pointed out in Part I (1), in discussion of nucleophilic attack on a compound Ar-X; when the group X is able by a time variable mechanism to remove electrons from the seat of attack, then reaction will be facilitated over and above the effect due to its electronegativity. This is shown for example by the high reactivity of 2,4-dinitrodiphenyl ether with nucleophilic reagents [Ogata and Okano (10); Beckwith and Miller (11)]. Thus comparing two compounds A and B, A will react faster when ring Ar is attacked by a nucleophilic reagent, owing to the more facile redistribution of Ar—O bond electrons in that case. Comparing attack at * by a nucleophilic reagent on the compounds C and D, we know (2) that C is the more reactive.

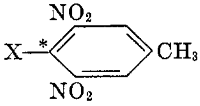


A

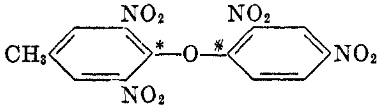


B


C

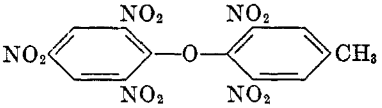

D

The above considerations enable us to explain the apparently anomalous reactions of the ether V. In this compound the lower initial reactivity at the point * is counterbalanced by the greater polarizability of the Ar*—O bond electrons. Correspondingly the higher initial reactivity at the point ⋕ is counterbalanced by the lower polarizability of the Ar ⋕—O bond electrons. With pyridine as reagent the opposing factors lead to similar rates of attack at the points * and ⋕. However when attack is by the more powerfully nucleophilic methoxide ion the polarizability of the Ar—O bond electrons assumes greater importance, and thus leads to the apparently anomalous mode of cleavage.

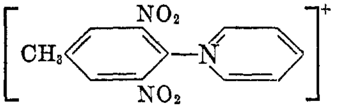


V

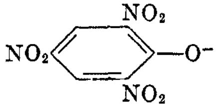
When the two rings are markedly dissimilarly activated by substituents, then the polarizability factor will be unable to cause anomalous effects. However Borrows, *et al.* (7) assumed that 2,2′,4,6,6′-pentanitro-4′-methyldiphenyl ether (XIII) was an intermediate in the reported production of N-(2,6-dinitro-4-methylphenyl)pyridinium picrate (XIV) from picryl chloride, 3,5-dinitro-*p*-cresol, and pyridine, and this implies that even in this case an apparently anomalous fission occurred, though the rings are very dissimilarly activated.

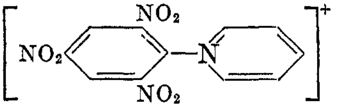


XIII

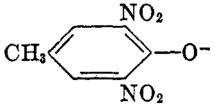


XIV





XV



We therefore synthesized the ether XIII by reacting picryl chloride with sodium 2,6-dinitro-*p*-cresoxide, and also by decomposition of N-picrylpyridinium 2,6-dinitro-*p*-cresoxide (XV). The latter salt differs from the compound so described by Borrows, *et al.* (7), which we believe to be the ether XIII formed by the decomposition of XV during its attempted preparation. We find the ether XIII to react normally with both pyridine and sodium methoxide to give the salt XV and picryl methyl ether respectively. Finally we have also prepared the salt XIV and find it to be different from that described by Borrows, *et al.* (7).

EXPERIMENTAL[3]

2,4-Dinitro-4′-hydroxydiphenylamine (III). 1-Chloro-2,4-dinitrobenzene (1.2 g.) and *p*-aminophenol (1.35 g.) were refluxed in absolute ethanol (15 ml.) for 1.5 hours. After

---

[3] Microanalyses by Dr. Zimmerman, Melbourne, Australia, and Drs. Weiler and Strauss, Oxford. Melting points are corrected.

cooling, the mixture was acidified with hydrochloric acid and poured into water. The ppt. was collected, washed, and crystallized from methanol as gleaming red plates (1.54 g.; 94%), m.p. 196°.

Anal. Calc'd for $C_{12}H_9N_3O_5$: C, 52.4; H, 3.3.
Found: C, 52.2; H, 3.6.

When this substance was refluxed for 20 minutes with acetic anhydride there was obtained in 80% yield 2,4-dinitro-4′-acetoxydiphenylamine as yellow plates, m.p. 140.5°. Reverdin and Crépieux (12) gave m.p. 137°.

2,4-Dinitro-4′-(2,4-dinitrophenoxy)diphenylamine (II). 1-Chloro-2,4-dinitrobenzene (1.0 g.) and 2,4-dinitro-4′-hydroxydiphenylamine (III) (1.2 g.) were dissolved in 20 ml. of hot absolute methanol and 1.40 ml. of 3.35 *N* methanolic sodium methoxide was added. The mixture was boiled gently for 5 minutes, then allowed to stand for 1 hour. After cooling in ice, the ppt. was collected and washed with methanol. The product had m.p. 226° and could be used without further purification. The filtrate on dilution with water gave 0.36 g. of the unchanged phenol. The yield of product was 1.35 g. (80% based on phenol used). The sample for analysis crystallized from acetone as orange needles, m.p. 228°.

Anal. Calc'd for $C_{18}H_{13}N_5O_9$: C, 49.0; H, 2.5; N, 15.9.
Found: C, 49.15; H, 2.6; N, 15.7.

The reaction between 2,4-dinitro-4′-(2,4-dinitrophenoxy)diphenylamine (II) *and sodium methoxide.* Compound II (0.70 g.) and 2.0 ml. of 3.35 *N* methanolic methoxide were refluxed with a further 15 ml. of absolute methanol for 20 minutes, by which time all of the insoluble material had disappeared. The mixture was cooled and poured into 70 ml. of iced-water. The crystalline ppt. was collected, washed with water, and crystallized from ethanol as colorless needles of 2,4-dinitroanisole (205 mg.; 65%), m.p. and mixture m.p. with an authentic sample 94°. The combined filtrates and washings were acidified with hydrochloric acid and the red ppt. was collected. Crystallization from aqueous ethanol gave 2,4-dinitro-4′-hydroxydiphenylamine (III) (425 mg.; 98%), m.p. and mixture m.p. 196°.

The reaction between 2,4-dinitro-4′-aminodiphenyl ether (I) *and sodium methoxide.* The diphenyl ether (1.7 g.), prepared according to the method of Reverdin and Dresel (4) was refluxed for 70 minutes in 60 ml. of 0.29 *N* methanolic sodium methoxide, then cooled, and poured with stirring into 150 ml. of 10% hydrochloric acid. On standing, a red crystalline ppt. (1.25 g.; 74%) was deposited. After washing with water, it was crystallized from methanol as red plates of 2,4-dinitro-4′-hydroxydiphenylamine (II), m.p. and mixture m.p. 196°. The same compound was also obtained when 2,4-dinitroanisole (1.0 g.) and *p*-aminophenol(0.55 g.) were refluxed for 1.5 hours in 40 ml. of 0.29 *N* methanolic sodium methoxide. Yield 0.75 g. (54%), m.p. and mixture m.p. 196°.

2,4-Dinitro-4′-methyldiphenyl ether (VII). 1-Chloro-2,4-dinitrobenzene (6.1 g.) and *p*-cresol (4.0 g.) were dissolved in 15 ml. of absolute methanol and 10.5 ml. of 2.9 *N* sodium methoxide was added. After standing at 45° for 15 minutes the mixture was acidified and diluted with water. The product was crystallized from ethanol as needles (7.4 g.; 90%), m.p. 93°.

2,2′,3′,4-Tetranitro-4′-methyldiphenyl ether (VIII). 2,4-Dinitro-4′-methyldiphenyl ether (VII) (2.5 g.) was added in small quantities and with stirring to 10 ml. of nitric acid (*d.* 1.5) at −5°. After the addition the mixture was kept below 0° for 45 minutes and then poured on to chipped ice. The product was washed with water and dilute aqueous sodium carbonate and crystallized from acetic acid or chloroform as colorless prisms (1.6 g., 48%), m.p. 201°.

Anal. Calc'd for $C_{13}H_8N_4O_9$: C, 42.9; H, 2.2.
Found: C, 43.3; H, 2.2.

The reaction between 2,2′,3′,4-tetranitro-4′-methyldiphenyl ether (VIII) *and sodium methoxide.* The ether VII (0.8 g.) was refluxed in 16 ml. of absolute methanol with 2 ml. of 2.9 *N* methanolic sodium methoxide for 15 minutes. After cooling, the mixture was poured into iced-water, and the ppt. was collected. After washing with water, crystallization from aqueous ethanol gave 0.35 g. (80%) of 2,4-dinitroanisole, m.p. and mixture m.p.

95°. The combined filtrate and washings were acidified with hydrochloric acid, and the ppt. obtained was crystallized from acetic acid as yellow needles (0.38 g.; 87%), m.p. 156°. The substance was confirmed as 2,3-dinitro-*p*-cresol by methylation with methyl sulphate and alkali to give the methyl ether of m.p. 133°. Dodswell and Kenner (13) give m.p. 132–133°. Also when the dinitro-*p*-cresol (100 mg.) was refluxed for 2 minutes with 2 ml. of acetic anhydride and 2 drops of pyridine, there was obtained 110 mg. (91%) of 2,3-dinitro-*p*-cresol acetate as plates from light petroleum. The acetate had m.p. 106°.

Anal. Calc'd for $C_9H_8N_2O_6$: C, 45.0; H, 3.35.
Found: C, 45.3; H, 3.3.

2,2′,4-Trinitro-4′-methyldiphenyl ether (IX). Freshly recrystallized potassium 2-nitro-4-methylphenoxide (2.8 g.) and 1-chloro-2,4-dinitrobenzene (3.5 g.) were heated on an oil-bath at 130° for 1 hour. The melt was cooled and the crushed solid repeatedly was extracted with hot acetone acidified with hydrochloric acid. Concentration of the extract and dilution with ethanol gave the product (4.02 g.; 86%) as colorless narrow plates of m.p. 186.5°.

Anal. Calc'd for $C_{13}H_9N_3O_7$: C, 48.9; H, 2.85.
Found: C, 49.35; H, 2.9.

2,6-Dinitro-p-cresyl acetate. 2,6-Dinitro-*p*-cresol (200 mg.) was refluxed with acetic anhydride (6 ml.) and 3 drops of sulfuric acid for 4 minutes. The ester was worked up by the usual procedures and was crystallized from benzene-light petroleum as colorless needles, m.p. 152°; 190 mg.; 78%.

Anal. Calc'd for $C_9H_8N_2O_6$: C, 45.0; H, 3.35.
Found: C, 45.1; H, 3.45.

Nitration of 2,2′,4-trinitro-4′-methyldiphenyl ether (IX). The ether (2.9 g.) was added in small portions and with stirring to 12 ml. of nitric acid (*d.* 1.5) at −15°. After the addition (10 minutes) the mixture was maintained at that temperature for a further 5 minutes and then poured on to ice. The product was extracted with chloroform, washed, and evaporated to dryness under a vacuum. The oily residue was refluxed with acetic anhydride (15 ml.) and sulfuric acid (0.5 ml.) for 4 minutes, cooled, and poured into water. The product was extracted with chloroform, washed with sodium bicarbonate sol'n and with water, and dried under a vacuum. Crystallization from alcohol gave as the first crop, colorless needles of 2,6-dinitro-*p*-cresyl acetate; m.p. and mixture m.p. 152°. The mother liquors on concentration yielded oils only, which could not be crystallized.

N-(2,4-Dinitrophenyl)pyridinium 2,6-dinitro-4-methylphenoxide (X). When a solution of sodium 2,6-dinitro-4-methylphenoxide (1.1 g.) in water (50 ml.) was added to N-(2,4-dinitrophenyl)pyridinium chloride (1.5 g.) in water (10 ml.) a ppt. was immediately formed. The product was washed with ethanol and ether and crystallized from acetonitrile. The salt formed red needles, m.p. 183° (2.25 g.; quant.).

Anal. Calc'd for $C_{18}H_{13}N_5O_9$: N, 15.8. Found: N, 15.4.

N-Picrylpyridinium 2,6-dinitro-4-methylphenoxide (XV). Potassium 2,6-dinitro-4-methylphenoxide (0.95 g.) in warm water (50 ml.) was added to a warm solution of N-picrylpyridinium *p*-toluenesulfonate (1.9 g.) in 1:1 aqueous methanol (50 ml.). The precipitate was washed with ether and crystallized from acetone as brown plates, m.p. 180° (1.85 g., 94%).

Anal. Calc'd for $C_{18}H_{12}N_6O_{11}$: C, 44.3; H, 2.45; N, 17.2.
Found: C, 44.45; H, 2.4; N, 17.0.

The same compound was obtained on mixing aqueous solutions of N-picrylpyridinium chloride and the phenoxide.

N-(2,6-Dinitro-4-methylphenyl)pyridinium p-toluenesulfonate (*cation as in* XI). 2,6-Dinitro-*p*-cresol (4 g.) and *p*-toluenesulfonyl chloride (4 g.) in diethylaniline (10 ml.) were heated on the water-bath for 30 minutes. After pouring into dilute hydrochloric acid the solid was collected, washed, and crystallized from acetone-ethanol. This gave 6.33 g. (89%) of 2,6-dinitro-*p*-cresyl *p*-toluenesulfonate, m.p. 154°. Then 1.57 g. of this ester was refluxed with 3 ml. of pyridine in 15 ml. of dry benzene for 30 minutes. The mixture was cooled in ice, and diluted with ether, and the product was collected as colorless needles, m.p. 182° (1.79 g., 94%).

N-(2,6-Dinitro-4-methylphenyl)pyridinium 2,6-dinitro-4-methylphenoxide (XI). A solution of potassium 2,6-dinitro-4-methylphenoxide (240 gm.) in 10 ml. of warm water was added to 450 mg. of N-(2,6-dinitro-4-methylphenyl)pyridinium *p*-toluenesulfonate in 15 ml. of water. After cooling, the precipitated salt was collected, washed with ethanol and ether, and crystallized from acetonitrile as orange plates, m.p. 231° (440 mg., 95%).

Anal. Calc'd for $C_{19}H_{15}N_5O_9$: C, 49.9; H, 3.3; N, 15.3.
Found: C, 50.35; H, 3.2; N, 14.8.

N-(2,6-Dinitro-4-methylphenyl)pyridinium 2,4-dinitrophenoxide (VI). Warm aqueous solutions of N-(2,6-dinitro-4-methylphenyl)pyridinium *p*-toluenesulfonate (420 mg.) and potassium 2,4-dinitrophenoxide (210 mg.) were mixed as above. The product crystallized from ethanol-benzene as yellow plates, m.p. 186° (380 mg.; 90%).

Anal. Calc'd for $C_{18}H_{13}N_5O_9$: C, 48.8; H, 2.95; N, 15.8.
Found: C, 49.3; H, 2.95; N, 15.6.

N-(2,6-Dinitro-4-methylphenyl)pyridinium picrate (XIV). Warm aqueous solutions of N-(2,6-dinitro-4-methylphenyl)pyridinium *p*-toluenesulfonate (500 mg.) and picric acid (300 mg.) were mixed as above. The product crystallized from acetonitrile as yellow plates, m.p. 213° (560 mg.; quant.).

Anal. Calc'd for $C_{18}H_{12}N_6O_{11}$: C, 44.3; H, 2.5; N, 17.2.
Found: C, 44.75; H, 2.5; N, 17.05.

2,2',4',6-Tetranitro-4-methyldiphenyl ether (V). N-(2,4-Dinitrophenyl)pyridinium 2,6-dinitro-4-methylphenoxide (X) (5 g.) was added in small portions to gently boiling anisole (15 ml.) in an open beaker. After the addition was complete (5 minutes), the mixture was boiled vigorously for 2 minutes to remove pyridine. The cooled solution was diluted with light petroleum and the resultant dark oil was scratched to induce crystallization. The ether was washed with dilute hydrochloric acid, and ethanol, and crystallized from acetone-ethanol (charcoal) as colorless needles, m.p. 160° (3.6 g.; 85%).

Anal. Calc'd for $C_{13}H_8N_4O_9$: C, 42.9; H, 2.2; N, 15.4.
Found: C, 43.3; H, 2.5; N, 15.35.

Fission of 2,2',4',6-tetranitro-4-methyldiphenyl ether (V). (*a*) *With methanolic sodium methoxide.* The ether (1.0 g.) was refluxed with 5 ml. of 3.35 *N* sodium methoxide and 25 ml. of absolute methanol until no solid remained (15 minutes). The red solution was poured into iced-water and the ppt. of 2,6-dinitro-*p*-cresyl methyl ether was collected, washed, and dried. It crystallized as colorless needles from aqueous ethanol, m.p. 122° (0.55 g.; 94%). The combined filtrate and washings were acidified with hydrochloric acid. After concentration of the liquors, fine crystals of 2,4-dinitrophenol (420 mg.; 83%) of m.p. 113° were deposited.

(*b*) *With pyridine.* The ether (300 mg.) was refluxed with 0.6 ml. of pyridine in 5 ml. of acetonitrile for 1.5 hours. On cooling, a crystalline ppt. was deposited from the dark solution. Recrystallization from acetonitrile yielded N-(2,6-dinitro-4-methylphenyl)pyridinium 2,6-dinitro-4-methylphenoxide (XI) (110 mg.; 58%), m.p. and mixture m.p. 231°.

2,2',4,6,6'-Pentanitro-4'-methyldiphenyl ether (XIII). Picryl chloride (1 g.) and potassium 2,6-dinitro-4-methylphenoxide(1 g.) were refluxed with 1:1 aqueous acetonitrile (10 ml.) for 5 minutes. After dilution with water, the ppt. was collected and washed with water, ethanol, and dilute hydrochloric acid. Crystallization from acetone-ethanol gave colorless needles, m.p. 222° (1.43 g.; 87%).

Anal. Calc'd for $C_{13}H_7N_5O_{11}$: C, 38.15; H, 1.7; N, 17.1.
Found: C, 38.3; H, 2.0; N, 16.75.

When the starting materials were heated together for 30 minutes at 160° without a solvent the yield of ether was 0.35 g. (21%).

When N-picrylpyridinium 2,6-dinitro-4-methylphenoxide (XV) (1.1 g.) was decomposed by boiling with anisole (20 ml.) for 5 minutes and was worked up in the usual way, 0.45 g. (49%) of ether was obtained.

Fission of 2,2′,4,6,6′-pentanitro-4′-methyldiphenyl ether (XIII). (*a*) *With sodium methoxide.* The ether (1.0 g.) and 0.85 ml. of 3.35 *N* sodium methoxide were refluxed with 20 ml. of methanol and 10 ml. of acetone for 15 minutes. After cooling, the mixture was acidified with hydrochloric acid and poured into iced-water. The oily suspension was extracted with ether and the extract repeatedly was washed with sodium carbonate solution. The washings were acidified with hydrochloric acid and the ppt. of 3,5-dinitro-*p*-cresol was crystallized from water as yellow needles, m.p. and mixture m.p. 83°. Yield, 0.43 g., 89%.

The ethereal extract was washed with dilute acid and with water, dried, and evaporated under a vacuum. The oily residue separated from ether-light petroleum as colorless crystals of picryl methyl ether, m.p. and mixture m.p. 63°; yield, 0.46 g.; 78%.

(*b*) *With pyridine.* Pyridine (10 drops) was added to a solution of the ether (110 mg.) in dry acetone (10 ml.) at room temperature. A crystalline ppt. was formed at once. After 30 minutes, the mixture was diluted with light petroleum and the ppt. was collected. The N-picrylpyridinium 2,6-dinitro-4-methylphenoxide (XV) was crystallized from acetone and had m.p. and mixture m.p. 180°; yield, 125 mg., 95%.

Acknowledgement. Assistance from the Research Grant to Australian Universities is gratefully acknowledged.

SUMMARY

1. Some doubtful points in the chemistry of the polynitrodiaryl ethers have been cleared up.

2. Explanations are given for some apparently anomalous effects in the nucleophilic attack on these compounds.

NEDLANDS, WESTERN AUSTRALIA

REFERENCES

(1) MILLER, *Revs. Pure and Appl. Chem.* (*Australia*), **1,** 171 (1951).
(2) MILLER, *J. Chem. Soc.*, 3550 (1952).
(3) MILLER AND WILLIAMS, *J. Chem. Soc.*, 1475 (1953).
(4) REVERDIN AND DRESEL, *Ber.*, **37,** 1516 (1904).
(5) ROBERTS, DE WORMS, AND CLARK, *J. Chem. Soc.*, 196 (1935).
(6) BUNNETT AND ZAHLER, *Chem. Revs.*, **49,** 273 (1951).
(7) BORROWS, CLAYTON, HEMS, AND LONG, *J. Chem. Soc.*, S 190 (1949).
(8) BECKWITH, MILLER, AND (in part) LEAHY, *J. Chem. Soc.*, 3552 (1952).
(9) FOX AND TURNER, *J. Chem. Soc.*, 1853 (1930).
(10) OGATA AND OKANO, *J. Am. Chem. Soc.*, **71,** 3212 (1949).
(11) BECKWITH AND MILLER, not yet published.
(12) REVERDIN AND CREPIEUX, *Ber.*, **36,** 3262 (1903).
(13) DODSWELL AND KENNER, *J. Chem. Soc.*, 580 (1927).