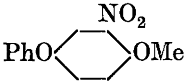
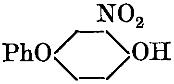
LIII.—*The Relative Directive Powers of Groups of the Form* RO *and* RR′N *in Aromatic Substitution. Part V. The Nitration of* p-*Methoxydiphenyl Ether.*

By Thomas Russell Lea and Robert Robinson.

The three methoxydiphenyl ethers were prepared with the object of examining quantitatively the products of their fission by potassium, but the reaction proved to be a complex one and its study was deemed unlikely to furnish the desired information. In the course of our experiments, however, an observation was made which has a direct bearing on the subject of the present series. *p*-Methoxydiphenyl ether yields a single nitro-derivative (I) the constitution of which follows from its hydrolysis to *o*-nitro-*p*-phenoxyphenol (II).

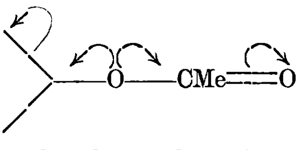
(I.)

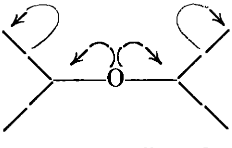




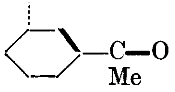
(II.)

This proves that the directive powers of phenoxyl and *p*-methoxyphenoxyl are small compared with that of the methoxyl group and the result is in harmony with the theoretical conceptions outlined in the preceding memoir. The weak directive powers of the acyloxyl and phenoxyl groups are undoubtedly due to the same cause, namely, that the oxygen atom is conjugated on both sides.

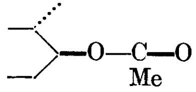




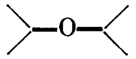
Using the electrical conductivity analogy, the effect has been described as a " side tracking by a neighbouring system of high capacity " (*Chemistry and Industry*, 1925, **44**, 118). On Flürscheim's theory of alternating affinity demand, a similar explanation of the weakness of the phenoxyl group could be elaborated, but a consistent application of this hypothesis would appear to suggest that the acetoxyl group should have a strong directing influence. Yet *o*-methoxyphenyl acetate is nitrated exclusively in the para-position with respect to the methoxyl group. The following scheme illustrates this contrast:



Effect of COMe on nucleus.



Effect of COMe on O attached to nucleus.



Effect of Ph on O attached to nucleus.

EXPERIMENTAL.

m-*Methoxydiphenyl Ether*.—A mixture of *m*-methoxyphenol (15·5 g.), bromobenzene (15·5 g.), potassium hydroxide (6·2 g.), and copper bronze (0·1 g.) was heated under reflux (oil-bath at 240°) for 2·5 hours. The product was isolated by steam distillation, the excess of bromobenzene being first collected. The benzene extract of the distillate was washed with aqueous sodium hydroxide and water, dried, and distilled finally in a vacuum. The substance, b. p. 175°/20 mm., could not be crystallised (Found: C, 77·9; H, 6·2. $C_{13}H_{12}O_2$ requires C, 78·0; H, 6·0%). The yield was 19·0 g.

p-*Methoxydiphenyl Ether*.—This compound was prepared by the method described above for the resorcinol derivative and the yield was the same. The substance, b. p. 186°/32 mm., crystallised at −10°, but melted again at room temperature (Found: C, 77·8; H, 6·1%).

3-*Nitro*-4-*methoxydiphenyl Ether* (I).—A mixture of nitric acid (15 c.c.; *d* 1·42) and acetic acid (15 c.c.) was gradually added to a solution of *p*-methoxydiphenyl ether (5 g.) in acetic acid (20 c.c.) maintained at about 15° by cooling. Fifteen minutes after the addition of the nitric acid, water was added and the solid collected, washed, and dried (5·8 g.). The substance crystallised from alcohol in pale yellow prisms, m. p. 73—74° (Found: C, 63·7; H, 5·2. $C_{13}H_{11}O_4N$ requires C, 63·7; H, 4·9%). No other product of the reaction could be isolated. In a similar manner, *o*-methoxydiphenyl ether (Ullmann and Sponagel, *Ber.*, 1905, **38**, 2211) (5 g.) gave 4·9 g. of a solid product which crystallised from alcohol in long, colourless needles, m. p. 70—71° (Found: C, 63·5; H, 4·7%). In this case, however, only 2·8 g. crystallised from alcohol and an oil was precipitated by the addition of water to the alcoholic mother-liquor. It is probable that the product analysed is 3-*nitro*-6-*methoxydiphenyl ether*.

2-*Nitro*-4-*phenoxyphenol* (II).—3-Nitro-4-methoxydiphenyl ether (4 g.) was hydrolysed by a boiling solution of potassium hydroxide (30 g.) in water (200 c.c.) in a copper flask for 60 hours. The red solution with some red needles in suspension was acidified with hydrochloric acid and the yellow solid, which separated from an emulsion, was collected, washed, and dried (1·0 g.). The substance crystallises from light petroleum in long, yellow needles, m. p. 51—52° (Found: C, 62·3; H, 4·0. $C_{12}H_9O_4N$ requires C, 62·4; H, 3·9%). The substance gives a bright red potassium salt and when boiled in xylene with potassium carbonate and methyl sulphate yields 3-nitro-4-methoxydiphenyl ether, m. p. 73—74°. Since Borsche (*Ber.*, 1923, **56**, [*B*], 1488) has shown that phenoxy groups in the *o*- or *p*-positions to nitro-groups are more reactive than similarly situated alkyloxy-groups, there can be no doubt in regard to the constitution of the product of nitration of *p*-methoxydiphenyl ether.

THE UNIVERSITY, MANCHESTER.

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