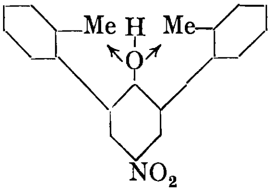
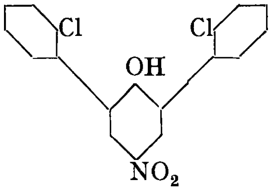
143. *An Instance of the Reversed Field Effect of the Methyl Group.*

By J. Kenner and Frank Morton.

In their examination of the reaction by which 2 : 6-disubstituted-4-nitrophenols are converted into quinones by thermal decomposition (J., 1931, 1842), Jones and Kenner found that 4-nitro-2 : 6-di-*o*-tolylphenol (I) was an exception to the general rule, and only furnished the corresponding quinone when it was oxidised by lead tetra-acetate. That this anomalous behaviour arose from the disinclination of the phenol to pass into the quinonoid condition was clear, because its sodium salt, unlike those of the nitrophenols which conform to the general behaviour, was colourless and remained so even when its aqueous suspension was heated. It appeared, therefore, that in this case the methyl groups of the *o*-tolyl substituents prevent the increased co-ordination of the phenoxide ion with the benzene nucleus, on which the quinonoid condition depends, and this can hardly be otherwise than by a spatial co-ordination effect of the methyl groups. In other words, the behaviour in question is a clear case of the reversed field effect of the methyl group postulated by Bennett and Mosses (J., 1930, 2367; compare Bennett and Baddeley, J., 1933, 263).

(I.)





(II.)

In order to illustrate this point, we have prepared the three 2 : 6-*bischlorophenyl*-4-*nitrophenols* (II) and found, as anticipated from the opposite character of the field effect of the halogen, that the *o*-, like its *m*- and *p*-isomerides, exhibits the normal behaviour in respect both of the colour of its sodium salt and of thermal decomposition.

EXPERIMENTAL.

m-*Chlorophenylacetonitrile*, prepared from the chloride, was obtained in hexagonal plates, m. p. 11·5°, b. p. 261°/757 mm. (Found : N, 9·3. C_8H_6NCl requires N, 9·2%). By hydrolysis with its own weight of sulphuric acid, glacial acetic acid, and water, it furnished m-*chlorophenylacetic acid*, needles, m. p. 76° (compare Muenzen, Cerecedo, and Sherwin, *J. Biol. Chem.*, 1926, **68**, 503) (Found : C, 56·5; H, 4·1. $C_8H_7O_2Cl$ requires C, 56·3; H, 4·1%).

Dichlorodibenzyl Ketones.—These were prepared by distillation of the lead salts (dried at 110°) of the corresponding acids. 2 : 2′-*Dichlorodibenzyl ketone* crystallised from alcohol in needles, m. p. 102° (Found : C, 64·5; H, 4·2; Cl, 25·7. $C_{15}H_{12}OCl_2$ requires C, 64·5; H, 4·3; Cl, 25·5%). The *oxime*, m. p. 112° (Found : N, 4·7. $C_{15}H_{13}ONCl_2$ requires N, 4·8%), and the *semicarbazone*, m. p. 149° (Found : N, 12·4. $C_{16}H_{15}ON_3Cl_2$ requires N, 12·5%), both formed needles. 3 : 3′-*Dichlorodibenzyl ketone*, m. p. 89° (Found : C, 64·5; H, 4·2%), and its *oxime*, m. p. 73° (Found : N, 4·5%), and *semicarbazone*, m. p. 121° (Found : N, 12·5%), all crystallised in needles. 4 : 4′-*Dichlorodibenzyl ketone*, m. p. 93° (Found : C, 64·6; H, 4·2%), and its *oxime*, m. p. 135—136° (Found : N, 4·7%), formed needles, but the *semicarbazone* crystallised in hexagonal plates, m. p. 118° (Found : N, 12·3%).

2 : 6-*Bischlorophenyl*-4-*nitrophenols.*—These were prepared by condensation at 40° of the foregoing ketones with nitromalonaldehyde (compare Jones and Kenner, *loc. cit.*). 2 : 6-*Bis*-o-*chlorophenyl*-4-*nitrophenol*, yellow needles, m. p. 140° (Found : C, 59·9; H, 3·0; N, 3·9. $C_{18}H_{11}O_3NCl_2$ requires C, 60·0; H, 3·0; N, 3·9%), yielded a sodium salt in yellow cubic crystals, from which the *methyl* ether was obtained in faintly yellow needles, m. p. 107° (Found : N, 3·9. $C_{19}H_{13}O_3NCl_2$ requires N, 3·9%). The phenol decomposed in boiling concentrated glacial acetic acid solution with evolution of nitric oxide, but 2 : 6-*bis*-o-*chlorophenyl*-1 : 4-*benzoquinone* was best prepared by oxidation of the phenol (1·8 g.) in glacial acetic acid solution (10 c.c.) at 40° with lead tetra-acetate (2·2 g.). Dark yellow needles, m. p. 103°, were obtained by crystallising the product from light petroleum (Found : C, 65·1; H, 3·0. $C_{18}H_{10}O_2Cl_2$ requires C, 65·5; H, 3·0%). 2 : 6-Bis-*o*-chlorophenyl-4-aminophenol, obtained from the nitrophenol by reduction in boiling glacial acetic acid solution with stannous chloride and hydrochloric acid, was analysed in the form of its *hydrochloride*, needles, m. p. 231° (Found : N, 3·8. $C_{18}H_{13}ONCl_2,HCl$ requires N, 3·8%). Oxidation by dilute chromic acid solution on the steam-bath for 24 hours converted the base into the quinone, m. p. 103° (alone or mixed with a sample prepared in the above manner).

The following were also prepared : 2 : 6-*Bis*-m-*chlorophenyl*-4-*nitrophenol*, faintly yellow needles, m. p. 177—178° (Found : C, 60·0; H, 3·0; N, 3·9; Cl, 20·0%); sodium salt, yellow; *methyl* ether, needles, m. p. 131° (Found : N, 4·0%); 2 : 6-*bis*-m-*chlorophenyl*-1 : 4-*benzoquinone*, orange-yellow needles, m. p. 183° (Found : C, 65·5; H, 2·9%); 2-6-*bis*-m-*chlorophenyl*-4-*aminophenol hydrochloride*, needles, m. p. 254° (Found : N, 3·8%). 2 : 6-*Bis*-p-*chlorophenyl*-4-*nitrophenol*, yellow needles, m. p. 202° (Found : C, 59·9; H, 3·1; N, 3·9; Cl, 19·8%); sodium salt, yellow; *methyl* ether, colourless needles, m. p. 190° (Found : N, 3·9%); 2 : 6-*bis*-p-*chlorophenyl*-1 : 4-*benzoquinone*, dark red needles, m. p. 263° (Found : C, 65·0; H, 3·0%); 2 : 6-*bis*-p-*chlorophenyl*-4-*aminophenol hydrochloride*, needles, m. p. 247° (Found : N, 3·8%).

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