188. *Substitution Products of 2'-Nitro- and 2' : 4'-Dinitro-2-methoxydiphenyl Ethers.*

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IN a previous communication (this vol., p. 705) on substitution in 3'-nitro- and 4'-nitro-2-methoxydiphenyl ethers it was shown that the first-entering substituent occupied the 5-position. The orientation of the second-entering substituent appeared to depend upon the nature of the first, for while two halogen atoms entered successively the 5- and the 4-position, this did not appear to be the case for two nitro-groups or for a halogen atom and a nitro-group.

It was found necessary to investigate the behaviour of *2'-nitro-* and *2' : 4'-dinitro-2-methoxydiphenyl ethers* in order to determine the orientation of two or more nitro-groups.

The results show that on halogenation 2'-nitro-2-methoxydiphenyl ether behaves in the same manner as its isomerides, yielding dihalogeno-derivatives substituted in the 4 : 5-positions, but differs from them in that a trisubstituted product was readily obtained. 2' : 4'-Dinitro-2-methoxydiphenyl ether also yielded a halogenation product substituted in the 5-position, further substitution was difficult with chlorine, and a dibromo-product could not be obtained.

On nitration each of the 2-methoxy-mononitrodiphenyl ethers and 2' : 4'-dinitro-2-methoxydiphenyl ether readily yielded a product substituted in the 5-position. The further nitration of these compounds led in each case to the formation of *2' : 4' : 3 : 5-tetranitro-2-methoxydiphenyl ether* as the main product. Attempts to obtain 2-methoxy-trinitrodiphenyl ethers by the direct nitration of the mononitro-ethers were unsuccessful.

The structures of the various compounds were established by the condensation of the potassium salt of guaiacol or an appropriately substituted guaiacol with *o*-chloronitrobenzene or with 2 : 4-dinitrochlorobenzene.

Consideration of these results would seem to show that the relatively feeble activation due to a phenoxy-group can be so diminished by the introduction of two nitro-groups that even such a facile process as bromination cannot occur. It is not surprising, therefore, that such a process as nitration is dependent upon the activation caused by the methoxy-group.

Experimental.

2'-Nitro-2-methoxydiphenyl Ether.—To 28 g. of molten potassium hydroxide were added 63 g. of guaiacol and 90 g. of *o*-chloronitrobenzene; the mixture was heated at 150° for 6 hours, distilled in steam, and the residue taken into chloroform. The *ether* distilled at 228°/14 mm., solidified, and then crystallised from alcohol in pale yellow needles, m. p. 69° (Found : N, 5·75. $C_{13}H_{11}O_4N$ requires N, 5·7%).

4-Chloro-2'-nitro-2-methoxydiphenyl ether, prepared by the condensation of *o*-chloronitrobenzene and the potassium salt of 4-chloroguaiacol at 200° for 6 hours, separated from methyl alcohol in needles, m. p. 79° (Found : Cl, 12·7. $C_{13}H_{10}O_4NCl$ requires Cl, 12·8%).

5-Chloro-2'-nitro-2-methoxydiphenyl ether, obtained from the nitro-compound and sulphuryl chloride, crystallised from alcohol in needles, m. p. 91° (Found : Cl, 12·75. $C_{13}H_{10}O_4NCl$ requires Cl, 12·8%).

4 : 5-Dichloro-2'-nitro-2-methoxydiphenyl ether was prepared (a) by the action of chlorine, in acetic acid, on 2-methoxy-, 2-methoxy-4-chloro-, and 2-methoxy-5-chloro-2'-nitrodiphenyl ether, (b) by the condensation of *o*-chloronitrobenzene and the potassium salt of 4 : 5-dichloroguaiacol. The product separated from light petroleum (b. p. 60—80°) in plates, m. p. 98° (Found : Cl, 22·6. $C_{13}H_9O_4NCl_2$ requires Cl, 22·6%).

x : 4 : 5-Trichloro-2'-nitro-2-methoxydiphenyl ether, obtained by leading an excess of chlorine into 4 : 5-dichloro-2'-nitro-2-methoxydiphenyl ether in acetic acid in sunlight, crystallised from alcohol in needles, m. p. 107° (Found : Cl, 30·7. $C_{13}H_8O_4NCl_3$ requires Cl, 30·6%).

4-Bromo-2'-nitro-2-methoxydiphenyl ether, obtained by the condensation of *o*-chloronitrobenzene and the potassium salt of 4-bromoguaiacol, separated from methyl alcohol in needles, m. p. 77° (Found : Br, 24·9. $C_{13}H_{10}O_4NBr$ requires Br, 24·7%).

5-Bromo-2'-nitro-2-methoxydiphenyl ether, prepared (a) by the action of bromine on the nitro-compound in acetic acid and keeping for 12 hours or (b) by the condensation of *o*-chloronitrobenzene and the potassium salt of 5-bromoguaiacol, separated from alcohol in prisms, m. p. 90° (Found : Br, 24·8. $C_{13}H_{10}O_4NBr$ requires Br, 24·7%).

4 : 5-Dibromo-2'-nitro-2-methoxydiphenyl ether was obtained by the action of excess of bromine on 2-methoxy-, 2-methoxy-4-bromo-, or 2-methoxy-5-bromo-2'-nitrodiphenyl ether in acetic acid for 4 hours at 90°; and by the condensation of *o*-chloronitrobenzene and the potassium salt of 4 : 5-dibromoguaiacol. The ether crystallised from alcohol or acetic acid in heavy prisms, m. p. 112° (Found : Br, 39·8. $C_{13}H_9O_4NBr_2$ requires Br, 39·7%).

2' : 4-Dinitro-2-methoxydiphenyl ether, prepared by the condensation of *o*-chloronitrobenzene and the potassium salt of 4-nitroguaiacol for 6 hours at 200° in the presence of copper powder, crystallised from alcohol in yellow needles, m. p. 105° (Found : N, 9·6. $C_{13}H_{10}O_6N_2$ requires N, 9·65%).

2' : 4'-Dinitro-2-methoxydiphenyl ether, prepared by the condensation of 2 : 4-dinitrochlorobenzene with guaiacol in alcoholic potash solution for 6 hours at the temperature of the water-bath, crystallised from alcohol in pale yellow needles, m. p. 92° (Found : N, 9·6. $C_{13}H_{10}O_6N_2$ requires N, 9·65%).

4-Chloro-2' : 4'-dinitro-2-methoxydiphenyl ether, obtained by the condensation of 2 : 4-dinitrochlorobenzene with the potassium salt of 4-chloroguaiacol in alcohol for 6 hours on the water-bath, separated from alcohol in needles, m. p. 116° (Found : Cl, 10·95. $C_{13}H_9O_6N_2Cl$ requires Cl, 10·95%).

5-Chloro-2' : 4'-dinitro-2-methoxydiphenyl ether, prepared by the action of sulphuryl chloride on the nitro-compound, crystallised from alcohol or acetic acid in pale yellow needles, m. p. 117° (Found : Cl, 11·05. $C_{13}H_9O_6N_2Cl$ requires Cl, 10·95%).

4 : 5-Dichloro-2' : 4'-dinitro-2-methoxydiphenyl ether, prepared (a) by the condensation of 2 : 4-dinitrochlorobenzene and the potassium salt of 4 : 5-dichloroguaiacol in alcohol at 90° for 6 hours or (b) by the action of excess of chlorine on 2-methoxy-4-chloro- or 2-methoxy-5-chloro-2' : 4'-dinitrodiphenyl ether in warm acetic acid, crystallised from acetic acid in pale yellow leaves, m. p. 144° (Found : Cl, 19·75. $C_{13}H_8O_6N_2Cl_2$ requires Cl, 19·75%).

4-Bromo-2' : 4'-dinitro-2-methoxydiphenyl ether, obtained by the condensation of 2 : 4-dinitro-

chlorobenzene and the potassium salt of 4-bromoguaiacol in alcohol at 90°, separated from alcohol in pale yellow needles, m. p. 132° (Found : Br, 21·65. $C_{13}H_9O_6N_2Br$ requires Br, 21·7%).

5-*Bromo*-2′ : 4′-*dinitro*-2-*methoxydiphenyl ether*, prepared (a) by the action of bromine on the nitro-compound in acetic acid or (b) by the condensation of 2 : 4-dinitrochlorobenzene and the potassium salt of 5-bromoguaiacol in alcohol at 90°, crystallised from alcohol or acetic acid in pale yellow needles, m. p. 140° (Found : Br, 21·55. $C_{13}H_9O_6N_2Br$ requires Br, 21·7%).

4 : 5-*Dibromo*-2′ : 4′-*dinitro*-2-*methoxydiphenyl ether*, obtained by the condensation of 2 : 4-dinitrochlorobenzene and the potassium salt of 4 : 5-dibromoguaiacol in alcohol at 90°, separated from acetic acid in yellow leaves, m. p. 165° (Found : Br, 35·75. $C_{13}H_8O_6N_2Br_2$ requires Br, 35·7%).

2′ : 5-*Dinitro*-2-*methoxydiphenyl ether*, obtained (a) by dissolving 10 g. of 2′-nitro-2-methoxydiphenyl ether in 100 c.c. of nitric acid (*d* 1·4) below 30° and keeping the solution over-night or (b) by the condensation of *o*-chloronitrobenzene and the potassium salt of 5-nitroguaiacol at 180°, crystallised from alcohol in pale yellow needles, m. p. 115° (Found : N, 9·7. $C_{13}H_{10}O_6N_2$ requires N, 9·65%).

2′ : 4 : 4′-*Trinitro*-2-*methoxydiphenyl ether*, prepared by the condensation of 2 : 4-dinitrochlorobenzene with the potassium salt of 4-nitroguaiacol in alcohol at 90° until the scarlet colour of the potassium salt had disappeared, separated from alcohol in yellow needles, m. p. 138° (Found : N, 12·5. $C_{13}H_9O_8N_3$ requires N, 12·55%).

2′ : 4 : 4′ : x-*Tetranitro*-2-*methoxydiphenyl ether*, prepared by dissolving 2′ : 4-dinitro- or 2′ : 4 : 4′-trinitro-diphenyl ether in nitric acid (*d* 1·5) and keeping the solution for 24 hours, crystallised from acetic acid in yellow needles, m. p. 159° (Found : N, 14·7. $C_{13}H_8O_{10}N_4$ requires N, 14·75%).

2′ : 4′ : 5-*Trinitro*-2-*methoxydiphenyl ether*, obtained (a) by dissolving 2′ : 4′-dinitro-2-methoxydiphenyl ether in nitric acid (*d* 1·4) and keeping the solution over-night, or (b) by refluxing the potassium salt of 5-nitroguaiacol with 2 : 4-dinitrochlorobenzene in alcohol, crystallised from acetic acid in needles, m. p. 161° (Found : N, 12·55. $C_{13}H_9O_8N_3$ requires N, 12·55%).

2′ : 3 : 4′ : 5-*Tetranitro*-2-*methoxydiphenyl ether*.—To 100 c.c. of nitric acid (*d* 1·5) were added 10 g. of finely powdered 2′-nitro-, 4′-nitro-, 2′ : 5-dinitro-, 4′ : 5-dinitro-, 2′ : 4′-dinitro-, or 2′ : 4′ : 5-trinitro-2-methoxydiphenyl ether below 30°; the solution was kept over-night and finally warmed for 30 minutes on the water-bath. The potassium salt of 3 : 5-dinitroguaiacol and 2 : 4-dinitrochlorobenzene were refluxed in alcoholic solution until the bright red colour of the potassium salt disappeared (16—20 hours). The product crystallised from acetic acid in pale greenish-yellow plates, m. p. 174°. The m. p.'s of the various specimens were between 172° and 174° and the lowest mixed m. p. was 172° (Found : N, 14·75. $C_{13}H_8O_{10}N_4$ requires N, 14·75%).

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