16. *Substitution in the Methyl-4′-nitro- and -4′-acetamido-diphenyl Ethers.*

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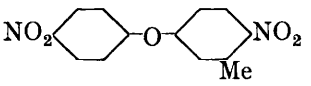
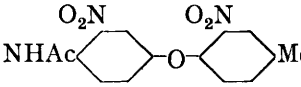
Cook and his collaborators (*Amer. Chem. J.*, 1902, **28**, 486; *J. Amer. Chem. Soc.*, 1902, **24**, 1200) have described the methylnitrodiphenyl ethers obtained by the condensation of *o*- and *p*-chloronitrobenzene with the isomeric cresols. They nitrated and sulphonated the ethers, but did not determine the positions of the substituents. Further, they found that a carboxylic acid could not be obtained by the oxidation of the methyl group.

Our results show that on further substitution 2-methyl- and 3-methyl-4′-nitrodiphenyl ethers yield each a product in which the 4-position is occupied. Halogenation proceeded smoothly, but nitration was a violent reaction in which considerable amounts of nitrophenols were formed as well as 2-*methyl*- or 3-*methyl*-4 : 4′-*dinitrodiphenyl ether* (I). The introduction of a second substituent into these molecules could not be effected.

On treatment with the usual oxidising agents under various conditions, 4′-nitro-2-methyldiphenyl ether was mainly recovered unchanged, but 4′-nitro-3-methyldiphenyl ether and its substitution products were slowly converted into the corresponding carboxylic acids; the yield was under 20% and but little of the initial ether was destroyed.

The halogenation of 2-methyl- or 3-methyl-4′-acetamidodiphenyl ether resulted in products substituted in the 4-position; on nitration, however, the entering group occupied the 3′-position. 4-*Bromo*-3′-*nitro*-4′-*acetamido*-2-*methyldiphenyl ether* could be obtained by bromination and nitration or by the introduction of the substituents in the reverse order.

(I.) 

 (II.)

A dichlorination product of 4′-acetamido-3-methyldiphenyl ether was obtained in a yield too small to allow of the determination of its structure. Both 2-methyl- and 3-methyl-4′-acetamidodiphenyl ether yielded 3′ : 4-dinitro-derivatives.

Chlorination of 4′-nitro-4-methyldiphenyl ether yielded an inseparable mixture of chlorinated products; whereas bromination under similar conditions gave 2-*bromo*-4′-*nitro*-4-*methyldiphenyl ether* in theoretical yield. Nitration also gave a product substituted in the 2-position.

Halogenation of 4′-acetamido-4-methyldiphenyl ether yielded intractable oils. Nitration, however, proceeded smoothly in two stages with the formation of 3′-*nitro*- and 2 : 3′-*dinitro*-4′-*acetamido*-4-*methyldiphenyl ethers* (II).

Oxidation of 4′-nitro-4-methyldiphenyl ether and its substitution products, to the corresponding carboxylic acids, proceeded more smoothly than that of the other isomerides, but the yield was still small.

The structures assigned to the substitution products depend on condensation of *p*-chloronitrobenzene and the appropriately substituted cresol; confirmation was obtained

by reduction of the nitro-compound, nitration, and deamination, the product being synthesised from the *m*-halogenonitrobenzene and the substituted cresol.

Consideration of these results shows that the ethereal oxygen atom exercises complete control of the orientation of the substituents, except for the introduction of a nitro-group when one nucleus contains an acetamido-group; by comparison with nitrodiphenyl ether the only effect which can be ascribed to the methyl group is a more controlled nitration.

Experimental.

4′-Nitro-2-methyldiphenyl Ether.—To 28 g. of molten potassium hydroxide were slowly added 54 g. of *o*-cresol, and 90 g. of *p*-chloronitrobenzene; the mixture was heated at 160° for 6 hours. The ether distilled at 225—230°/14 mm., solidified, and then separated from light petroleum in pale yellow octahedra, m. p. 35°.

4′-Acetamido-2-methyldiphenyl ether, obtained by reduction of the nitro-compound with stannous chloride in ethereal hydrogen chloride, and refluxing of the crude base with acetic anhydride–acetic acid (1 : 8) for 12 hours, crystallised from benzene–light petroleum in needles, m. p. 110° (Found : N, 5·65. $C_{15}H_{15}O_2N$ requires N, 5·8%).

4-Chloro-4′-nitro-2-methyldiphenyl ether, prepared from the nitro-compound and sulphuryl chloride (2 mols.) (kept for 2 days), had b. p. 235—240°/12 mm. and formed needles, m. p. 65°, from methyl alcohol (Found : Cl, 13·6. $C_{13}H_{10}O_3NCl$ requires Cl, 13·5%).

4-Chloro-4′-acetamido-2-methyldiphenyl ether, obtained from the preceding nitro-compound by reduction and acetylation, crystallised from dilute methyl alcohol or light petroleum–benzene in needles, m. p. 122° (Found : Cl, 12·9. $C_{15}H_{14}O_2NCl$ requires Cl, 12·9%).

4-Chloro-3′-nitro-4′-acetamido-2-methyldiphenyl ether was prepared (1) by the nitration of 4-chloro-4′-acetamido-2-methyldiphenyl ether with nitric acid (*d* 1·5) in acetic acid at 80°, (2) by the action of a small excess of chlorine on 3′-nitro-4′-acetamido-2-methyldiphenyl ether in acetic acid in presence of fused sodium acetate, at 80°. The product separated from dilute methyl alcohol in pale brown needles, m. p. 128°, in yellow needles, m. p. 133°, or as a mixture of both forms. The needles, m. p. 128°, change into the higher-melting product above 124° (Found : Cl, 11·2. $C_{15}H_{13}O_4N_2Cl$ requires Cl, 11·1%). The corresponding *4′-amino*-compound crystallised from dilute methyl alcohol in bright red needles, m. p. 104° (Found : Cl, 12·65. $C_{13}H_{11}O_3N_2Cl$ requires Cl, 12·75%).

4-Chloro-3′-nitro-2-methyldiphenyl ether, prepared by deamination of the above base, or by condensation of *m*-iodonitrobenzene and the potassium salt of 5-chloro-2-hydroxy-1-methylbenzene at 220° in the presence of copper powder, crystallised from light petroleum in faintly orange needles, m. p. 52° (Found : Cl, 13·5. $C_{13}H_{10}O_3NCl$ requires Cl, 13·5%).

4-Bromo-4′-nitro-2-methyldiphenyl ether, obtained by the action of bromine in acetic acid solution, or by condensation of *p*-chloronitrobenzene with potassium 5-bromo-*o*-tolyloxide for 6 hours at 160°, separated from methyl alcohol in plates, and from light petroleum in prisms, m. p. 73° (Found : Br, 26·2. $C_{13}H_{10}O_3NBr$ requires Br, 26·0%).

4-Bromo-4′-acetamido-2-methyldiphenyl ether, prepared by reduction of the nitro-compound and acetylation, or by bromination of 4′-acetamido-2-methyldiphenyl ether in acetic acid in presence of fused sodium acetate, crystallised from methyl alcohol in needles, m. p. 144° (Found : Br, 25·0. $C_{15}H_{14}O_2NBr$ requires Br, 25·0%).

4-Bromo-3′-nitro-4′-acetamido-2-methyldiphenyl ether was obtained when 4-bromo-4′-acetamido-2-methyldiphenyl ether was treated with nitric acid (*d* 1·5) in acetic acid at 80°, and when 3′-nitro-4′-acetamido-2-methyldiphenyl ether was brominated in acetic acid at 80°. It separated from methyl alcohol or benzene–light petroleum in lemon-yellow needles, m. p. 147° (Found : Br, 21·95. $C_{15}H_{13}O_4N_2Br$ requires Br, 21·85%). The *base* crystallised from methyl alcohol in red needles, m. p. 92° (Found : Br, 24·85. $C_{13}H_{11}O_3N_2Br$ requires Br, 24·75%).

4-Bromo-3′-nitro-2-methyldiphenyl ether, prepared by deamination of the base or by bromination of 3′-nitro-2-methyldiphenyl ether in acetic acid, separated from light petroleum in pale orange needles, m. p. 50° (Found : Br, 26·15. $C_{13}H_{10}O_3NBr$ requires Br, 26·0%).

3′-Nitro-4′-acetamido-2-methyldiphenyl ether, obtained when 4′-acetamido-2-methyldiphenyl ether was nitrated in acetic acid at 80°, crystallised from light petroleum in yellow needles, m. p. 83° (Found : N, 9·85. $C_{15}H_{14}O_4N_2$ requires N, 9·8%). The *base* separated from methyl alcohol in deep red prisms, m. p. 94° (Found : N, 11·5. $C_{13}H_{12}O_3N_2$ requires N, 11·5%).

3′-Nitro-2-methyldiphenyl ether was obtained by deamination of the preceding base, or by condensation of *m*-iodonitrobenzene with potassium *o*-tolyloxide at 200° for 8 hours in

presence of copper powder. The product was a yellow oil, b. p. 235°/14 mm. Each specimen yielded the same bromination product, m. p. 50°.

3′ : 4-*Dinitro*-4′-*acetamido*-2-*methyldiphenyl Ether*.—4′-Acetamido-2-methyldiphenyl ether was added slowly to nitric acid (*d* 1·4), and after 10 minutes the mixture was poured on ice. The *product*, collected at once and crystallised from alcohol and then acetic acid, formed dull yellow needles, m. p. 137° (Found: N, 12·55. $C_{15}H_{13}O_6N_3$ requires N, 12·7%). The *base* separated from methyl alcohol in flat golden-brown needles, m. p. 170° (Found: N, 14·5. $C_{13}H_{11}O_5N_3$ requires N, 14·55%).

3′ : 4-*Dinitro*-2-*methyldiphenyl ether*, obtained by deamination of the base, or by condensation of potassium *m*-nitrophenoxide with 2-bromo-5-nitrotoluene at 220° for 12 hours, crystallised from methyl alcohol in light brown needles, m. p. 110° (Found: N, 10·2. $C_{13}H_{10}O_5N_2$ requires N, 10·2%).

4 : 4′-*Dinitro*-2-*methyldiphenyl Ether*.—(1) 4′-Nitro-2-methyldiphenyl ether was added to a large excess of nitric acid (*d* 1·4) and carefully warmed till the violent reaction ceased and the product solidified. (2) *p*-Chloronitrobenzene was heated with potassium 5-nitro-*o*-tolyloxide at 180° for 15 hours. The ether crystallised from dilute acetic acid in plates, m. p. 132°.

3-*Carboxy*-4′-*nitrodiphenyl ether*, obtained in poor yield when an excess of chromic acid was added to 4′-nitro-3-methyldiphenyl ether in boiling acetic acid, crystallised from dilute acetic acid in small prisms, m. p. 183° (Found: C, 60·4; H, 3·8. $C_{13}H_9O_5N$ requires C, 60·25; H, 3·5%).

4′-*Amino*-3-*methyldiphenyl ether*, obtained by reduction of the nitro-compound and purified through the sulphate, formed needles, m. p. 82°, from dilute methyl alcohol or light petroleum (Found: N, 7·1. $C_{13}H_{13}ON$ requires N, 7·05%). The nitrate crystallised from dilute nitric acid in flat needles, m. p. 158° (decomp.), and the *acetyl* derivative from alcohol in needles, m. p. 140° (Found: N, 5·8. $C_{15}H_{15}O_2N$ requires N, 5·8%).

4-*Chloro*-4′-*nitro*-3-*methyldiphenyl ether*, prepared (1) by adding an excess of chlorine to 4′-nitro-3-methyldiphenyl ether in carbon tetrachloride, (2) by condensation of *p*-chloronitrobenzene with potassium 6-chloro-*m*-tolyloxide for 8 hours at 180°, crystallised from methyl alcohol in plates, m. p. 114° (Found: Cl, 13·35. $C_{13}H_{10}O_3NCl$ requires Cl, 13·45%).

4-Chloro-4′-acetamido-3-methyldiphenyl ether was prepared by reduction of the nitro-compound and subsequent acetylation and isolated as the hydrochloride in needles, m. p. 200° (decomp.), from dilute hydrochloric acid. The *acetyl* derivative crystallised from methyl alcohol in fine needles, m. p. 115° (Found: Cl, 13·05. $C_{15}H_{14}O_2NCl$ requires Cl, 12·9%), and was also obtained by the action of excess of chlorine on 4′-acetamido-3-methyldiphenyl ether in carbon tetrachloride in presence of fused sodium acetate.

4-*Chloro*-3′-*nitro*-4′-*acetamido*-3-*methyldiphenyl ether*, obtained by chlorination of the nitro-compound, or by nitration of the chloro-compound in acetic acid at 80°, crystallised in lemon-yellow needles, m. p. 101°, from alcohol (Found: N, 8·7. $C_{15}H_{13}O_4N_2Cl$ requires N, 8·75%). The *base* separated from methyl alcohol in bright red plates, m. p. 95° (Found: Cl, 12·75. $C_{13}H_{11}O_3N_2Cl$ requires Cl, 12·75%).

4-*Chloro*-3′-*nitro*-3-*methyldiphenyl ether*, obtained on deamination of the base, crystallised from light petroleum in pale orange needles, m. p. 57° (Found: Cl, 13·5. $C_{13}H_{10}O_3NCl$ requires Cl, 13·45%).

4-*Bromo*-4′-*nitro*-3-*methyldiphenyl ether*, prepared by bromination of the nitro-compound in acetic acid, or by condensation of *p*-chloronitrobenzene and potassium 6-bromo-*m*-tolyloxide for 8 hours at 170°, formed flat prisms, m. p. 96°, from dilute acetic acid (Found: Br, 25·95. $C_{13}H_{10}O_3NBr$ requires Br, 25·95%).

4-*Bromo*-4′-*nitro*-3-*carboxydiphenyl ether*, prepared by oxidation of the nitro-compound with chromic acid in boiling acetic acid, crystallised in needles, m. p. 157°, from dilute acetic acid (Found: equiv., 335. $C_{13}H_8O_5NBr$ requires equiv., 338). The *ethyl* ester separated from methyl alcohol in needles, m. p. 76° (Found: Br, 21·7. $C_{15}H_{12}O_5NBr$ requires Br, 21·8%).

4-*Bromo*-4′-*acetamido*-3-*methyldiphenyl ether*, obtained by reduction of the nitro-compound and subsequent acetylation, or by bromination of 4′-acetamido-3-methyldiphenyl ether in acetic acid in presence of fused sodium acetate, crystallised from methyl alcohol or dilute acetic acid in needles, m. p. 130° (Found: Br, 24·9. $C_{15}H_{14}O_2NBr$ requires Br, 25·0%).

4-*Bromo*-3′-*nitro*-4′-*acetamido*-3-*methyldiphenyl ether*, prepared by the nitration of the bromo-compound in acetic acid at 80°, or by bromination of the nitro-compound in acetic acid at 15°, separated from methyl alcohol in lemon-yellow needles, m. p. 102° (Found: N, 7·8. $C_{15}H_{13}O_4N_2Br$ requires N, 7·8%). The *base* formed deep red prisms, m. p. 111°, from methyl alcohol (Found: Br, 24·5. $C_{13}H_{11}O_3N_2Br$ requires Br, 24·7%).

4-*Bromo*-3′-*nitro*-3-*methyldiphenyl ether*, obtained on deamination of the base, or by bromination of 3′-nitro-3-methyldiphenyl ether, separated from light petroleum in yellow prisms, m. p. 59° (Found : Br, 26·1. $C_{13}H_{10}O_3NBr$ requires Br, 26·0%).

3′-*Nitro*-4′-*acetamido*-3-*methyldiphenyl ether*, prepared by nitration of the acetyl derivative in acetic acid at 80°, crystallised from light petroleum in golden needles, m. p. 81° (Found : N, 9·8. $C_{15}H_{14}O_4N_2$ requires N, 9·8%). The *base* separated from methyl alcohol in red prisms, m. p. 52° (Found : N, 11·4. $C_{13}H_{12}O_3N_2$ requires N, 11·5%).

3′-*Nitro*-3-*methyldiphenyl ether*, obtained by deamination of the base, or by condensation of *m*-iodonitrobenzene and potassium *m*-tolyloxide in presence of copper powder at 200° for 8 hours, solidified after distillation under diminished pressure and long standing, and then separated from benzene–light petroleum in faintly yellow prisms, m. p. 47° (Found : C, 67·9; H, 5·0. $C_{13}H_{11}O_3N$ requires C, 68·1; H, 4·85%).

3′ : 4-*Dinitro*-4′-*acetamido*-3-*methyldiphenyl Ether*.—4′-Acetamido-3-methyldiphenyl ether or its mononitration product was dissolved in nitric acid (*d* 1·4) and kept for 15 minutes at 15°. The *product* crystallised from alcohol or dilute acetic acid in olive-yellow needles, m. p. 144° (Found : N, 12·7. $C_{15}H_{13}O_6N_3$ requires N, 12·7%). The *base* separated from methyl alcohol in orange needles, m. p. 140° (Found : N, 14·55. $C_{13}H_{11}O_5N_3$ requires N, 14·6%).

3′ : 4-*Dinitro*-3-*methyldiphenyl ether*, prepared by deamination of the base, or by condensation of potassium *m*-nitrophenoxide and 5-bromo-2-nitrotoluene for 5 hours at 170°, crystallised from light petroleum in orange needles, m. p. 87° (Found : N, 10·15. $C_{13}H_{10}O_5N_2$ requires N, 10·2%).

4 : 4′-*Dinitro*-3-*methyldiphenyl ether*, obtained when the mononitro-compound was gently warmed with nitric acid (*d* 1·4), or *p*-chloronitrobenzene and potassium 4-nitro-*m*-tolyloxide were condensed for 8 hours at 180°, formed yellow rhombs, m. p. 120°, from acetic acid (Found : N, 12·2. $C_{13}H_{10}O_5N_2$ requires N, 12·2%).

4 : 4′-*Dinitro*-3-*carboxydiphenyl ether*, prepared by oxidation of the preceding ether, separated from dilute acetic acid in small prisms, m. p. 185° (Found : N, 9·2. $C_{13}H_8O_7N_2$ requires N, 9·2%).

4′-*Nitro*-4-*acetyl*-3-*methyldiphenyl ether* was obtained when a carbon disulphide solution of 4′-nitro-3-methyldiphenyl ether and acetyl chloride was dropped on aluminium chloride under the same solvent, and the reaction completed by warming. It separated from dilute acetic acid in needles, m. p. 88° (Found : N, 5·2. $C_{15}H_{13}O_4N$ requires N, 5·15%).

4′-*Nitro*-4-*carboxy*-3-*methyldiphenyl ether*, prepared by oxidation of the acetyl compound, crystallised from dilute acetic acid in rosetted needles, m. p. 204° (Found : C, 61·55; H, 4·2. $C_{14}H_{11}O_5N$ requires C, 61·55; H, 4·05%).

4′-Nitro-4-methyldiphenyl ether, prepared by condensation of *p*-chloronitrobenzene and potassium *p*-tolyloxide for 8 hours at 180°, separated from alcohol in yellow rhombs, m. p. 68°.

4-*Nitro*-4′-*carboxydiphenyl ether*, prepared by oxidation of the nitro-compound, crystallised from acetic acid in flat plates, m. p. 245° (Found : C, 60·1; H, 3·65. $C_{13}H_9O_5N$ requires C, 60·25; H, 3·5%). The *ethyl* ester separated from methyl alcohol in needles, m. p. 78° (Found : N, 4·85. $C_{15}H_{13}O_5N$ requires N, 4·85%).

4′-Amino-4-methyldiphenyl ether, obtained by reduction of the nitro-compound, separated from alcohol in needles, m. p. 125°. The *acetyl* derivative crystallised from alcohol or benzene–light petroleum in needles, m. p. 135° (Found : C, 74·65; H, 6·4. $C_{15}H_{15}O_2N$ requires C, 74·7; H, 6·25%).

2-*Bromo*-4′-*nitro*-4-*methyldiphenyl ether*, obtained by bromination of the nitro-compound in acetic acid at 15°, or by condensation of *p*-chloronitrobenzene and potassium 3-bromo-*p*-tolyloxide at 220° for 8 hours, separated from methyl alcohol in prisms, m. p. 82° (Found : Br, 25·9. $C_{13}H_{10}O_3NBr$ requires Br, 25·95%).

2-*Bromo*-4′-*nitro*-4-*carboxydiphenyl ether*, obtained on oxidation of the preceding ether, crystallised from dilute acetic acid in plates, m. p. 168° (Found : Br, 23·55. $C_{13}H_8O_5NBr$ requires Br, 23·65%). The ethyl ester crystallised from methyl alcohol in needles, m. p. 119°.

2-*Bromo*-4′-*acetamido*-4-*methyldiphenyl ether*, prepared by reduction of the nitro-compound and acetylation, separated from alcohol in needles, m. p. 142° (Found : Br, 25·1. $C_{15}H_{14}O_2NBr$ requires Br, 25·0%).

2-*Bromo*-3′-*nitro*-4′-*acetamido*-4-*methyldiphenyl ether*, obtained by nitration of the preceding ether in acetic acid at 80°, separated from methyl alcohol in yellow needles, m. p. 98° (Found : Br, 22·05. $C_{15}H_{13}O_4N_2Br$ requires Br, 21·95%). The *base* crystallised from methyl alcohol in red needles, m. p. 101° (Found : Br, 24·8. $C_{13}H_{11}O_3N_2Br$ requires Br, 24·7%).

2-*Bromo*-3′-*nitro*-4-*methyldiphenyl ether*, obtained on deamination of the base, or by condensation of *m*-chloronitrobenzene and potassium 3-bromo-*p*-tolyloxide for 8 hours at 220°, separated from methyl alcohol in pale orange prisms, m. p. 47° (Found: Br, 26·1. $C_{13}H_{10}O_3NBr$ requires Br, 26·0%).

3-*Bromo*-3′-*nitro*-4-*methyldiphenyl ether*, formed by condensation of *m*-iodonitrobenzene and potassium 2-bromo-*p*-tolyloxide for 8 hours at 200°, separated from methyl alcohol in pale yellow prisms, m. p. 68° (Found: Br, 26·05. $C_{13}H_{10}O_3NBr$ requires Br, 26·0%).

3′-*Nitro*-4′-*acetamido*-4-*methyldiphenyl ether*, prepared by nitration of the acetyl derivative in acetic acid at 80°, crystallised from dilute methyl alcohol or light petroleum in flat golden needles, m. p. 95° (Found: N, 9·85. $C_{15}H_{14}O_4N_2$ requires N, 9·8%). The *base* separated from dilute methyl alcohol in red leaflets, m. p. 91° (Found: N, 11·5. $C_{13}H_{12}O_3N_2$ requires N, 11·5%).

3′-Nitro-4-methyldiphenyl ether was obtained, by condensation of *m*-iodonitrobenzene with potassium *p*-tolyloxide in presence of copper powder at 170° for 12 hours, as a faintly yellow oil, b. p. 220°/23 mm. On treatment with nitric acid (*d* 1·4) at 80°, it yielded a dinitro-compound, which crystallised from methyl alcohol or light petroleum in prisms, m. p. 86°. The same dinitro-compound was obtained by deamination of 3′-nitro-4′-amino-4-methyldiphenyl ether and nitration of the resulting oil.

2 : 3′-*Dinitro*-4′-*acetamido*-4-*methyldiphenyl ether* was obtained when finely powdered 4′-acetamido-4-methyldiphenyl ether was added to nitric acid (*d* 1·4) and kept for 15 minutes. The product, after extraction with boiling alcohol, crystallised from dilute acetic acid in pale brown needles, m. p. 134° (Found: N, 12·8. $C_{15}H_{13}O_6N_3$ requires N, 12·7%). The *base* crystallised from methyl alcohol in heavy red-brown prisms, m. p. 119° (Found: N, 14·5. $C_{13}H_{11}O_5N_3$ requires N, 14·55%).

2 : 3′-*Dinitro*-4-*methyldiphenyl ether*, obtained by deamination of the base, or by condensation of 4-chloro-3-nitrotoluene with potassium *m*-nitrophenoxide at 200° for 12 hours in presence of copper powder, crystallised, after distillation under diminished pressure, from methyl alcohol in flat prisms, m. p. 87° (Found: N, 10·25. $C_{13}H_{10}O_5N_2$ requires N, 10·2%).

2 : 4′-*Dinitro*-4-*methyldiphenyl ether*, prepared by cautiously warming 4′-nitro-4-methyldiphenyl ether with nitric acid (*d* 1·4), separated from alcohol in pale brown needles, m. p. 104° (Found: N, 10·25. $C_{13}H_{10}O_5N_2$ requires N, 10·2%). The same compound resulted when 4-chloro-3-nitrotoluene was condensed with potassium *p*-nitrophenoxide at 220° for 12 hours, and when 2-nitro-4-methyldiphenyl ether was further nitrated in nitric acid (*d* 1·4).

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