Preparation of Nitroquinols and their Methyl Ethers and Benzenesulphonyl Derivatives

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Step-wise nitration of quinol monobenzenesulphonate gave 2-nitro- and 2,6-dinitro-derivatives from which the corresponding quinols were prepared. Similar treatment of 2-nitroquinol 1-benzenesulphonate led to 2,3- and 2,5-dinitro- and 2,3,5-trinitro-quinol. Methyl ethers of all these compounds and of tetranitroquinol were prepared.

THE partially benzenesulphonated polyhydric phenols can be useful in synthesis.[1] These compounds are stable to acid hydrolysis and can successfully be used as starting materials in reactions in strongly acidic media (*e.g.*, in nitration). They may therefore be used in improved methods for the preparation of nitro-derivatives of phenols such as quinol, which are sensitive to the conditions of nitration. Orientation of the nitro-groups can in this case be directed only by the free hydroxy-group, and the reaction can be made by temperature control to proceed in separate steps. Thus it is possible to obtain a desired nitro-compound in good yield without by-products, except when the orientation control leads to two or more equally possible isomers. After the first nitration it is possible to block the free hydroxy-group by benzenesulphonylation, to release another one by partial hydrolysis, and to continue the nitration to more highly substituted compounds, with the orientation directed by the new hydroxy-group. Sometimes this process gives the original phenol instead of the desired one; this is common when the last blocked hydroxy-group is *ortho* to a nitro-group, and thus more sensitive to hydrolysis. To overcome this a nitro-compound must be used with the hydroxy-group to be released blocked by an ester group such as acetate, which is more sensitive to hydrolysis than benzenesulphonate. By this method, nitration, followed by a final hydrolysis, can give all the possible nitrophenols, including those which are otherwise difficult to synthesise. This Paper describes a route for the preparation of nitroquinols and of their methyl ethers.

Quinol monobenzenesulphonate [1] on mild nitration gave only 2-nitroquinol 4-benzenesulphonate; under more vigorous conditions, the 2,6-dinitroquinol 4-benzenesulphonate was the only product. The nitro-compounds were hydrolysed, to give the mononitro-quinol and the 2,6-dinitroquinol, respectively. If the compounds were methylated before hydrolysis, the 1-methyl ethers of the nitroquinols were obtained. Benzenesulphonylation of the 2-nitroquinol 4-benzenesulphonate to give the diester, followed by partial hydrolysis, gave not the 1-ester, but the 4-ester as the main hydrolysis product. However, the 1-ester was obtained in a similar way from 2-nitroquinol 4-acetate.[2] Nitration of the 2-nitroquinol 1-benzenesulphonate proceeds in two steps to give dinitro- and trinitro-compounds. When nitration took place in acetic acid solution at 45°, a mixture was obtained which could be separated into dinitro-compound A, less soluble in benzene and nitric acid, and dinitro-compound B. The dinitro-compound A, when benzenesulphonylated to the diester and then reduced with sodium dithionite, gave a diamine which formed a phenazine compound with phenanthraquinone, a characteristic reaction of *o*-diamines. When treated similarly, the dinitro-compound B gave no phenazine compound. Thus the dinitro-compound A was identified as the 2,3-dinitroquinol monobenzenesulphonate, and the dinitro-compound B as the only possible 2,5-dinitroquinol monobenzenesulphonate. Both nitro-compounds were hydrolysed to the dinitroquinols; the 2,3-dinitroquinol was rather unstable.

The second step of the nitration of 2-nitroquinol 1-benzenesulphonate gave 2,3,5-trinitroquinol 1-benzenesulphonate, which can be hydrolysed to a yellow oil consisting of impure trinitroquinol; this gives the known trinitroquinoldimethyl ether on methylation.[3] Methylation of the product of nitration followed by hydrolysis gave the 2,3,5-trinitroquinol 4-methyl ether, from which by further nitration the tetranitroquinol monomethyl ether was obtained.

EXPERIMENTAL

2-Nitroquinol 4-Benzenesulphonate.—Nitric acid (*d* 1·4; 8 ml.) was added dropwise to a stirred solution of anhydrous quinol monobenzenesulphonate [1] (25 g.) in acetic acid (50 ml.) at room temperature. Stirring was continued for 30 min. after the precipitation of yellow crystals. Water (500 ml.) was added, and the mixture was stirred for 2 hr. to assist deposition. The product was filtered off, washed with water, and dried to give *2-nitroquinol 4-benzenesulphonate* (27·3 g., 92%), as yellow prisms, m. p. 89° (from benzene) (Found: N, 4·3; S, 11·1. $C_{12}H_9NO_6S$ requires N, 4·7; S, 10·9%). Acetylation yielded the 1-acetate, m. p. 76° (from methanol). Methylation with dimethyl sulphate gave the *methyl ether* as prisms, m. p. 105—106° (from methanol) (Found: N, 4·2; S, 10·5. $C_{13}H_{11}NO_6S$ requires N, 4·5; S, 10·4%). The same product was obtained (97%) by nitration of the methyl ether of quinol benzenesulphonate [1] (5·3 g.), in a mixture of conc. sulphuric acid (10 ml.) and nitric acid (*d* 1·4; 20 ml.) at 30° for 1 hr. Benzenesulphonylation in pyridine gave the mononitroquinol dibenzenesulphonate, m. p. 122° (from acetic acid).

2-Nitroquinol 1-Benzenesulphonate.—Benzenesulphonyl chloride (16 ml.) was added dropwise to a solution of

[1] E. Kampouris, *J. Chem. Soc.*, 1965, 2651.
[2] F. Kehrmann and W. Klopfenstein, *Helv. Chim. Acta*, 1923, **6**, 952.
[3] J. Habermann, *Ber.*, 1878, **11**, 1034.

2-nitroquinol 4-acetate [2] (19·7 g.) in pyridine (40 ml.), and the mixture was shaken in cold water till crystals appeared. After 4 hr. at room temperature, the mixture was poured into cold 15% hydrochloric acid and stirred to solidify. The solid was filtered off, washed with dilute hydrochloric acid and then with water, and dried to give 1-O-*acetyl*-3-*nitroquinol* 4-*benzenesulphonate* (32·5 g., 97%), as prisms, m. p. 64—65° (from methanol) (Found: N, 3·9; S, 9·7. $C_{14}H_{11}NO_7S$ requires N, 4·1; S, 9·5%). Hydrolysis of the acetate (16·9 g.) dispersed in methanol (100 ml.) with potassium hydroxide solution (20%; 14·5 ml.) at room temperature gave 2-*nitroquinol* 1-*benzenesulphonate* (14 g., 95%), as light yellow leaves, m. p. 115—116° (from benzene) (Found: N, 4·5; S, 10·7. $C_{12}H_9NO_6S$ requires N, 4·7; S, 10·9%). Methylation yielded the *methyl ether*, m. p. 64° (from methanol) (Found: N, 4·3; S, 10·5. $C_{13}H_{11}NO_6S$ requires N, 4·5; S, 10·4%). Benzenesulphonylation in pyridine gave the diester which on partial hydrolysis yielded the 2-nitroquinol 4-benzenesulphonate.

2-*Nitroquinol* 1-*Methyl Ether*.—Potassium hydroxide solution (20%; 34 ml.) was added at 45° to a stirred dispersion of the pulverised methyl ether of 2-nitroquinol 4-benzenesulphonate (9·3 g.) in methanol (40 ml.). The reaction mixture was kept at 50—55° for 15 min. and the resulting red solution was diluted with water and acidified with hydrochloric acid until it became clear yellow. It was extracted with ether, and the ether was evaporated to leave 2-nitroquinol 1-methyl ether (4·7 g., 92%), as yellow crystals, m. p. 85° (from benzene), in agreement with that of the so-called unstable form of the dimorphous compound [4] (Found: C, 50·0; H, 4·1; N, 8·1. Calc. for $C_7H_7NO_4$: C, 49·7; H, 4·2; N, 8·3%). Acetylation yielded the acetate, m. p. 106° (from methanol) (lit.,[5] 106°). Methylation gave mononitroquinol dimethyl ether, m. p. 71—72° (from light petroleum) (lit.,[4,6] 71·5°).

2-*Nitroquinol* 4-*Methyl Ether*.—The methyl ether of 2-nitroquinol 1-benzenesulphonate, when hydrolysed in a similar way with half the amount of the alkaline solution, gave 2-nitroquinol 4-methyl ether (90%), precipitated on acidification as orange crystals, m. p. 79—80° (from methanol) (lit.,[4,5] 79—80, 80°).

Mononitroquinol.—Hydrolysis of 2-nitroquinol 4-benzenesulphonate (5·9 g.) in methanol (30 ml.) at 45° with potassium hydroxide solution (20%; 28 ml.) gave mononitroquinol (2·9 g., 93%), as red-orange prisms, m. p. 132° (from benzene) (lit.,[4,7] 132, 133—134°). Acetylation gave the diacetate, m. p. 81—82° (from methanol) (lit.,[2] 80°).

2,6-*Dinitroquinol* 4-*Benzenesulphonate*.—Anhydrous quinol monobenzenesulphonate [1] (10 g.) was dissolved in warm nitric acid (*d* 1·4; 75 ml.), and the solution kept at 60—65° for 10 min. after the precipitation of yellow crystals. It was then cooled, diluted with water to 1 l., and stirred for 2 hr. It was kept cooled, and the deposited product filtered off next day, washed with cool 0·02N-hydrochloric acid, and dried to give 2,6-*dinitroquinol* 4-*benzenesulphonate* (12 g., 88%), as bright yellow needles, m. p. 110—111° (from benzene) (Found: N, 8·0; S, 9·7. $C_{12}H_8N_2O_8S$ requires N, 8·2; S, 9·4%). Crystallisation from xylene yielded yellow prisms, m. p. 94—95°, containing solvent, which slowly disintegrated in air (Found: C_8H_{10}, 13·9. $2C_{12}H_8N_2O_8S,C_8H_{10}$ requires C_8H_{10}, 13·5%). Acetylation gave the acetate, m. p. 151° (from benzene). Methylation yielded the *methyl ether*, as prisms, m. p. 111° (from benzene) (Found: N, 7·7; S, 9·0. $C_{13}H_{10}N_2O_8S$ requires N, 7·9; S, 9·1%).

2,6-*Dinitroquinol*.—Potassium hydroxide solution (20%; 14 ml.) was added at 50° to a solution of 2,6-dinitroquinol 4-benzenesulphonate (3·4 g.) in methanol (200 ml.), and the mixture was stirred until the separated phenolic salt of the hydroxy-ester had disappeared. After being maintained at this temperature for 10 min., the clear violet solution was diluted with water, acidified with hydrochloric acid, extracted with ether, and the ether was evaporated to leave 2,6-dinitroquinol monohydrate (1·8 g., 82%), as gold-yellow leaves, m. p. 90° (from water) (Found: H_2O, 8·9. Calc. for $C_6H_4N_2O_6,H_2O$: H_2O, 8·3%). Nietzki [8] mentions a hydrate with 1·5 mol. of water (lost at about 100°) melting at 135—136°. The compound was crystallised anhydrous from xylene as yellow crystals, m. p. 135—136° (lit.,[7,9] 134—135, 132—136°) (Found: C, 35·8; H, 1·7; N, 14·4. Calc. for $C_6H_4N_2O_6$: C, 36·0; H, 2·0; N, 14·0%). Acetylation gave the diacetate, m. p. 134—135° (from methanol) (lit.,[2,10] 134, 135—136°). Methylation yielded the dimethyl ether, m. p. 111° (from methanol) (lit.,[9] 109—111°).

2,6-*Dinitroquinol* 1-*Methyl Ether*.—Hydrolysis of the methyl ether of 2,6-dinitroquinol 4-benzenesulphonate (3·5 g.) methanol (50 ml.) by potassium hydroxide solution (20%; 11·2 ml.) gave the 2,6-dinitroquinol 1-methyl ether (2 g., 93%), separated by extraction with ether, as yellow needles, m. p. 152° (from xylene) (lit.,[11] 149°). Acetylation gave the acetate, m. p. 65—66° (from light petroleum–trichloroethylene 3 : 1 v/v) (lit.,[11] 63°). Methylation yielded the dimethyl ether, m. p. 111°.

Nitration of 2-*Nitroquinol* 1-*Benzenesulphonate*.—Nitric acid (*d* 1·4; 10 ml.) was added to a solution of 2-nitroquinol 1-benzenesulphonate (29·5 g.) in acetic acid (100 ml.), at 40°. The mixture was kept at about 45° for 1 hr., then diluted with water to 1 l., stirred for 4 hr., and cooled for 1 day. The solid precipitate was collected, triturated with water, filtered off, washed with water, and dried ($CaCl_2$) to give a mixture of the 2,3- and 2,5-dinitroquinol benzenesulphonates (30·5 g., 90%). This product was crystallised from benzene, the benzene mother-liquor was evaporated, and the residue was crystallised from methanol. The methanolic mother-liquor was evaporated, the residue treated with nitric acid (*d* 1·4) at 50°, and the solution diluted to separate the dissolved product. This process gave 2,3-*dinitroquinol monobenzenesulphonate* (about 18 g., 53%), the compound crystallised from benzene and undissolved in nitric acid, and 2,5-*dinitroquinol monobenzenesulphonate* (about 12 g., 35%) the compound crystallised from methanol and dissolved in nitric acid. The former yielded yellow prisms, m. p. 135—136° (from benzene) (Found: N, 8·1; S, 9·6. $C_{12}H_8N_2O_8S$ requires N, 8·2; S, 9·4%). Its acetate crystallised in prisms, m. p. 109—110° (from benzene). Methylation with diazomethane gave the *methyl ether* as prisms, m. p. 143—144° (from acetic acid) (Found: N, 8·0; S, 8·9. $C_{13}H_{10}N_2O_8S$ requires N, 7·9; S, 9·1%). Benzenesulphonylation in pyridine yielded 2,3-*dinitroquinol di-*

[4] R. Robinson and J. C. Smith, *J. Chem. Soc.*, 1926, 392.
[5] A. Klemenc, *Monatsh.*, 1914, **35**, 85.
[6] O. Mühlhäuser, *Annalen*, 1881, **207**, 235.
[7] F. Kehrmann, M. Sandoz, and R. Monnier, *Helv. Chim. Acta*, 1921, **4**, 94.
[8] R. Nietzki, *Ber.*, 1878, **11**, 469.
[9] A. Burqer and G. T. Fitchett, *J. Amer. Chem. Soc.*, 1953, **75**, 1359.
[10] M. Richter, *Ber.*, 1913, **46**, 3434.
[11] F. Kehrmann and G. Jequier, *Helv. Chim. Acta*, 1923, **6**, 949.

benzenesulphonate, m. p. 172—173° (from benzene) (Found: N, 5·6; S, 13·6. $C_{18}H_{12}N_2O_{10}S_2$ requires N, 5·8; S, 13·3%).

Crystallisation of the 2,5-dinitroquinol monobenzenesulphonate from methanol gave yellow plates, m. p. 98—99° (Found: N, 8·0; S, 9·5. $C_{12}H_8N_2O_8S$ requires N, 8·2; S, 9·4%). Crystallisation from benzene gave needles, m. p. 63—65°, containing solvent (Found: C_6H_6, 10·8. Calc. for $2C_{12}H_8N_2O_8S,C_6H_6$: C_6H_6, 10·3%). The acetate formed needles, m. p. 142—143° (from benzene). The *methyl ether* crystallised from methanol in flattened prisms, m. p. 136—137° (Found: N, 7·7; S, 9·2. $C_{13}H_{10}N_2O_8S$ requires N, 7·9; S, 9·1%). The *dibenzenesulphonate* crystallised as needles, m. p. 207—209° (from acetic acid) (Found: N, 5·7; S, 13·4. $C_{18}H_{12}N_2O_{10}S_2$ requires N, 5·8; S, 13·3%).

2,3-*Diaminoquinol Dibenzenesulphonate*.—Successive quantities of sodium dithionite solution were added to a boiling dispersion of pulverised 2,3-dinitroquinol dibenzenesulphonate (9·6 g.), in methanol (250 ml.) until the solution was completely decolourised. Water (750 ml.) was then added and the mixture cooled for 2 days. The precipitated product was filtered off, washed with cold water, and dried to give 2,3-*diaminoquinol dibenzenesulphonate* (5·4 g., 64%), as crystals, m. p. 135—137° (Found: N, 6·3; S, 15·7. $C_{18}H_{16}N_2O_6S_2$ requires N, 6·6; S, 16·0%). An acetic acid solution of phenanthraquinone was added to a solution of 2,3-diaminoquinol dibenzenesulphonate, in acetic acid, and the *phenazine compound* was precipitated as small yellow needles, m. p. 238—239° (from xylene) (Found: N, 4·4; S, 11·0. $C_{32}H_{20}N_2O_6S_2$ requires N, 4·7; S, 10·8%).

A similar reduction gave 2,5-*diaminoquinol dibenzenesulphonate* from the dinitro-compound, as needles, m. p. 201—202° (decomp.) (from xylene) (Found: N, 6·4; S, 16·2. $C_{18}H_{16}N_2O_6S_2$ requires N, 6·6; S, 16·0%).

2,3-*Dinitroquinol*.—A solution of 2,3-dinitroquinol monobenzenesulphonate (1·7 g.) was added to a solution of potassium hydroxide (2%; 56 ml.), and the mixture stirred at room temperature for 5 min. until it reached a clear red colour. The solution was then diluted with water to 250 ml., acidified with hydrochloric acid, and extracted with ether. The ether was evaporated, leaving 2,3-*dinitroquinol* (0·9 g., 90%), as orange needles (decomp. on standing), m. p. 98—100° (Found: C, 35·9; H, 1·8; N, 13·6. $C_6H_4N_2O_6$ requires C, 36·0; H, 2·0; N, 14·0%). Acetylation gave the *diacetate*, as prisms, m. p. 137° (from methanol) (Found: C, 42·0; H, 2·6; N, 9·8. $C_{10}H_8N_2O_8$ requires C, 42·2; H, 2·8; N, 9·9%). Methylation yielded the dimethyl ether, as bright yellow crystals, m. p. 183° (from methanol) (lit.,[12] 177°) (Found: C, 42·3; H, 3·3; N, 12·0. Calc. for $C_8H_8N_2O_6$: C, 42·1; H, 3·5; N, 12·3%).

2,5-*Dinitroquinol*.—2,5-Dinitroquinol monobenzenesulphonate was similarly hydrolysed to 2,5-*dinitroquinol* (90%) precipitated on acidification, as orange prisms, m. p. 201—203° (from methanol) (Found: C, 36·2; H, 1·9; N, 13·9. $C_6H_4N_2O_6$ requires C, 36·0; H, 2·0; N, 14·0%). Acetylation gave the *diacetate*, m. p. 169—170° (from acetic acid) (Found: C, 42·4; H, 2·9; N, 10·0. $C_{10}H_8N_2O_8$ requires C, 42·2; H, 2·8; N, 9·9%). Methylation yielded the dimethyl ether, m. p. 201—202° (from acetic acid) (lit.,[12,13] 202, 200—202°).

2,3-*Dinitroquinol Monomethyl Ether*.—Hydrolysis of the methyl ether of 2,3-dinitroquinol benzenesulphonate (3·5 g.) dispersed in methanol (50 ml.) with potassium hydroxide solution (20%; 6 ml.) at 35° gave 2,3-*dinitroquinol monomethyl ether* (2 g., 93%), as orange prisms, m. p. 162—163° (decomp.) (Found: C, 39·0; H, 2·7; N, 13·0. $C_7H_6N_2O_6$ requires C, 39·2; H, 2·8; N, 13·1%). Wender[14] gives m. p. 110° for the same product prepared from 2,3-dinitro-4-aminoanisole. Acetylation yielded the acetate, m. p. 96—97° (from light petroleum–benzene 2 : 1 v/v), and methylation gave the dimethyl ether, m. p. 183°.

2,5-*Dinitroquinol Monomethyl Ether*.—By a similar hydrolysis the methyl ether of 2,5-dinitroquinol benzenesulphonate gave the 2,5-*dinitroquinol monomethyl ether* (93%), m. p. 165° (from methanol) (Found: C, 39·3; H, 2·6; N, 13·2. $C_7H_6N_2O_6$ requires C, 39·2; H, 2·8; N, 13·1%). Acetylation yielded the acetate as needles, m. p. 97—98° (from methanol), and methylation gave the dimethyl ether, m. p. 201—202°.

2,3,5-*Trinitroquinol 1-Benzenesulphonate*.—Powdered 2-nitroquinol 1-benzenesulphonate (14·8 g.) was dissolved in nitric acid (*d* 1·4; 70 ml.) at 50°; the temperature was then gradually raised to 80°, and the mixture stirred for 5 min. after the precipitation of a crystalline product. It was then cooled and the precipitate filtered off, washed with water, and dried to give 2,3,5-*trinitroquinol 1-benzenesulphonate* (16 g., 83%). This product was also obtained by a similar nitration from the acetate of 2-nitroquinol 1-benzenesulphonate, and from 2,3- or 2,5-dinitroquinol monobenzenesulphonate. Crystallisation from benzene gave yellow prisms, m. p. 144—145° (Found: C, 37·5; H, 1·7; N, 11·0; S, 8·5. $C_{12}H_7N_3O_{10}S$ requires C, 37·4; H, 1·8; N, 10·9; S, 8·3%). Acetylation yielded the acetate, as needles, m. p. 111—112° (from acetic acid). Methylation gave the *methyl ether*, m. p. 151—152° (from benzene) (Found: C, 39·3; H, 2·1; N, 10·3; S, 8·2. $C_{13}H_9N_3O_{10}S$ requires C, 39·1; H, 2·3; N, 10·5; S, 8·0%).

2,3,5-*Trinitroquinol 4-Methyl Ether*.—Hydrolysis of the methyl ether of 2,3,5-trinitroquinol 1-benzenesulphonate (4 g.) dispersed in methanol (100 ml.) with potassium hydroxide solution (20%; 6 ml.) at room temperature gave 2,3,5-*trinitroquinol 4-methyl ether* (2·4 g., 90%), as a yellow oily product difficult to dry which exploded violently when heated above 180°. The same product was obtained by nitration of 2,6-dinitroquinol 1-methyl ether (10·7 g.) in nitric acid (*d* 1·4; 50 ml.). The solution was maintained at 40° for 5 min. after it became cloudy, and the product (90%) extracted with ether, as yellow prisms containing solvent, slowly disintegrating in air, m. p. 62—63° (from xylene) (Found: C_8H_{10}, 17·3. Calc. for $2C_7H_5N_3O_8,C_8H_{10}$: C_8H_{10}, 17·0%). Crystallisation from trichloroethylene yielded yellow prisms, m. p. 78—79° (Found: C, 32·5; H, 1·7; N, 16·4. $C_7H_5N_3O_8$ requires C, 32·4; H, 1·9; N, 16·2%). Acetylation gave the acetate, m. p. 85—86° (from trichloroethylene). Methylation yielded the dimethyl ether, m. p. 98—99° (from methanol) (lit.,[3] 100—101°).

2,3,5-*Trinitroquinol 1-Methyl Ether*.—Powdered 2-nitroquinol 1-methyl ether (5·1 g.) was stirred into nitric acid (*d* 1·4; 50 ml.). The temperature was raised to 65°, and maintained for 5 min. after the precipitation of a crystalline product. The mixture was then diluted with water to 200 ml., cooled for 4 hr., and the product was filtered off, washed with water, and dried to give 2,3,5-*trinitroquinol 1-methyl ether* (5·4 g., 70%), as yellow crystals, m. p. 111° (from benzene) (Found: C, 32·2; H, 1·8; N, 16·0. $C_7H_5N_3O_8$ requires C, 32·4; H, 1·9; N, 16·2%). Acetylation yielded the acetate as prisms, m. p. 123—124° (from

[12] R. Nietzki and F. Rechberg, *Ber.*, 1890, **23**, 1211.
[13] G. M. Robinson, *J. Chem. Soc.*, 1916, **109**, 1078.
[14] G. Wender, *Gazzetta*, 1889, **19**, 221.

light petroleum–benzene 1 : 1 v/v). Methylation gave the dimethyl ether.

Trinitroquinol.—Potassium hydroxide solution (20%; 8·4 ml.) was added at room temperature to a solution of 2,3,5-trinitroquinol 1-benzenesulphonate (3·8 g.) in methanol (200 ml.). The mixture was stirred for 10 min. after the precipitation of the potassium salt of the trinitroquinol. Ether (500 ml.) was added, and the mixture cooled at 0° and acidified with hydrochloric acid (10 ml.). Cold water (500 ml.) was added and the ethereal layer separated and dried ($CaCl_2$). The ether was evaporated under reduced pressure to leave crude trinitroquinol (about 2·2 g., 90%) as a yellow oil very soluble in methanol and acetone, readily soluble in benzene, xylene, and trichloroethylene, and sparingly soluble in light petroleum. Attempts to crystallise it failed and the unstable product decomposed in a few days to a resinous mass. The potassium salt precipitated during the hydrolysis was hygroscopic and unstable. The more stable *barium salt* was obtained as a brown powder which exploded on heating by treating the ether solution with barium hydroxide solution (Found: Ba, 36·5. Calc. for $C_6HBaN_3O_8$: Ba, 36·1%). Acetylation of the crude trinitroquinol soon after the evaporation of the ether gave the *trinitroquinol diacetate* (75%, based on the benzenesulphonate), m. p. 134° (from methanol) (Found: C, 36·8; H, 2·3; N, 12·5. $C_{10}H_7N_3O_{10}$ requires C, 36·5; H, 2·1; N, 12·8%). Methylation yielded trinitroquinol dimethyl ether (70%), m. p. 98—99° (from methanol) (Found: C, 35·2; H, 2·5; N, 15·5. Calc. for $C_8H_7N_3O_8$: C, 35·2; H, 2·6; N, 15·4%).

Tetranitroquinol Monomethyl Ether.—Powdered 2,3,5-trinitroquinol 4-methyl ether (13 g.) or 2,6-dinitroquinol 1-methyl ether (10·7 g.) was stirred in nitric acid (*d* 1·4; 50 ml.) at 40° for 5 min. The temperature was then raised to 70° and maintained for 5 min. after a crystalline product separated. The mixture was then cooled, and the product was filtered off, washed with cold dilute hydrochloric acid (8%), and dried *in vacuo* to give *tetranitroquinol monomethyl ether* (13 g., 85%), as yellow plates, m. p. 116—117° (from trichloroethylene) (Found: C, 27·9; H, 1·5; N, 18·2. $C_7H_4N_4O_{10}$ requires C, 27·6; H, 1·3; N, 18·4%). Acetylation yielded the acetate, m. p. 129—130° as prisms (from trichloroethylene), which slowly deacetylated. Methylation gave the *dimethyl ether* as prisms, m. p. 179—180° (from methanol) (Found: C, 30·5; H, 2·2; N, 17·3. $C_8H_6N_4O_{10}$ requires C, 30·2; H, 1·9; N, 17·6%).

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