

Oxidative Demethylation of 2,3-Dicyano-1,4-dimethoxynaphthalene and Nitrations of Some 1,4-Naphthoquinones and Phthalic Anhydride by Nitronium Salts

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The nitration of 1,4-naphthoquinone derivatives and phthalic anhydride by nitronium tetrafluoroborate in tetra-methylene sulphone is reported. The reaction of 2,3-dicyano-1,4-dimethoxynaphthalene with nitronium hexa-fluorophosphate in acetonitrile gave 2,3-dicyano-1,4-naphthoquinone and *N*-methylacetamide. On the basis of the above observation the mechanism of oxidative demethylation of methyl naphthyl ethers by nitronium salts is discussed.

It was noted earlier¹ that selective substitution of nitro-groups in an electron-acceptor system increases the overall electron affinity of the acceptor. Thus it seemed worthwhile to explore the possibilities of modification of weak electron acceptors by ready nitration. The use of nitronium salts^{2,3} appeared promising in this case since aqueous acidic conditions of nitration are avoided. During this investigation it was also observed that 2,3-dicyano-1,4-dimethoxynaphthalene (I)⁴ was smoothly

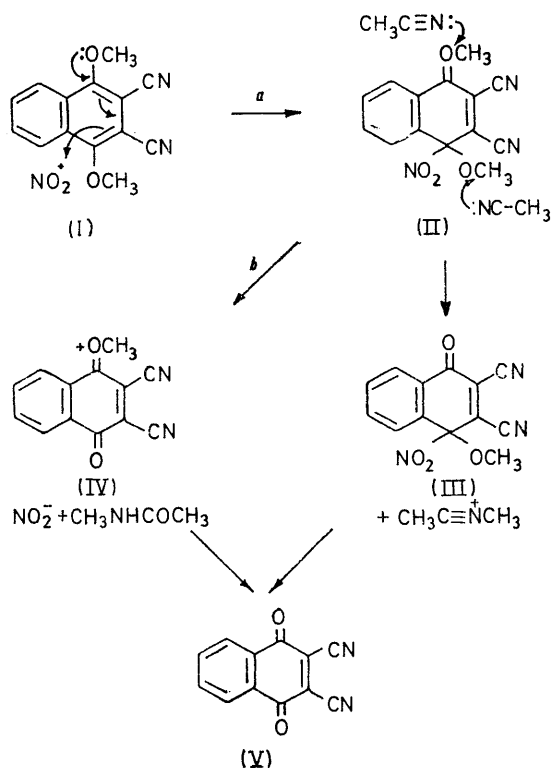
converted into 2,3-dicyano-1,4-naphthoquinone (V) on treatment with nitronium hexafluorophosphate. We now report the study of oxidative demethylation of (I) and the results of nitration of selected 1,4-naphthoquinone derivatives and phthalic anhydride by nitronium salts.

Treatment of 2,3-dicyano-1,4-dimethoxynaphthalene

¹ S. Chatterjee, *J. Chem. Soc. (B)*, 1971, 2194.
² G. A. Olah and S. J. Kuhn, *J. Amer. Chem. Soc.*, 1961, **83**, 5464.

³ G. A. Olah and S. J. Kuhn, in 'Friedel-Crafts and Related Reactions,' ed. G. A. Olah, Interscience, New York, 1964, vol. 2, part 2, ch. 43.
⁴ K. Wallenfels, G. Bachmann, D. Hoffmann, and R. Kern, *Tetrahedron*, 1965, **21**, 2239.

with three mol. equiv. of nitronium hexafluorophosphate in anhydrous acetonitrile at 0° for 2 h gave 2,3-dicyano-1,4-naphthoquinone and 15% *N*-methylacetamide. The presence of acetamide in the mixture was not detected. Control experiments performed with acetonitrile and nitronium hexafluorophosphate yielded only acetamide, *N*-methylacetamide not being detected.



SCHEME

Substituent and steric effects on the course of oxidative demethylation of phenyl and naphthyl ethers in nitric acid have received some attention.⁵ Since the active species in nitration is the nitronium ion NO₂⁺ it is plausible that the demethylation of (I) by NO₂⁺PF₆⁻ in anhydrous acetonitrile would follow a mechanism similar to that suggested by Musgrave⁵ and Barton *et al.*⁶ for the oxidative demethylation of alkyl aryl ethers by nitric and nitrous acids respectively. Apparently, the σ -complex (II) is formed *via* methoxy-directed *ipso*-addition of nitronium ion to (I) (Scheme). Ions analogous to (II) are postulated for the oxidative demethylation of *p*-methoxybenzene derivatives,⁷ and *p*-halogeno-⁸ and 3,4-dimethyl-anisoles⁹ to the corresponding quinones. Isolation of *N*-methylacetamide from the reaction mixture in the present case strongly suggests

⁵ O. C. Musgrave, *Chem. Rev.*, 1969, **69**, 499.

⁶ D. H. R. Barton, P. G. Gordon, and D. G. Hewitt, *J. Chem. Soc. (C)*, 1971, 1206.

⁷ W. F. Gum, jun., M. R. W. Levy, and M. M. Joulie, *J. Chem. Soc.*, 1965, 2282; M. Kohn and L. W. Guttman, *Monatsh.*, 1925, **45**, 573; G. S. K. Rao, K. V. Rao, and T. R. Seshadri, *Proc. Indian Acad. Sci.*, 1948, **27A**, 295.

⁸ C. L. Perrin and G. A. Skinner, *J. Amer. Chem. Soc.*, 1971, **93**, 3389.

abstraction of methyl group from (II) by solvent acetonitrile *via* a Ritter type¹⁰ process followed by hydrolysis of the *N*-methylacetamidinium ion during aqueous work-up. The intermediate (III) thus generated, could decompose to the 1,4-naphthoquinone derivative. Analogous conversion of *ipso*-addition products, such as 1-chloro-1-nitronaphthalen-2(1*H*)-one¹¹ and 4-nitro-3,4,5-trimethoxycyclohexa-2,5-dienone¹² are known to decompose spontaneously in chloroform solution to 1,2-naphthoquinone and 2,6-dimethoxybenzoquinone respectively.

The possibilities of alternative or competitive mechanisms of demethylation of (I) either by the elimination of nitrite ion (Scheme, *b*) or by PF₅ generated *in situ* during the reaction cannot be entirely discounted. However, demethylation by PF₅ preceding oxidation seems unlikely in this case since NO₂⁺PF₆⁻ is stable under our reaction conditions.³ Secondly, as no nitrite ion could be detected in the aqueous extract after quenching the reaction,¹³ it seems that pathway *b* leading to structures (IV) and (V) is not a major contributing factor to the oxidative demethylation of (I).

Nitration of 1,4-naphthoquinones were carried out in anhydrous tetramethylene sulphone under nitrogen with a 1:1 or 2:1 ratio of nitronium tetrafluoroborate to quinone. No improvement in the yield of nitrated products was observed by using an excess of nitrating agent, a longer reaction time, or a higher temperature. Nitration of 2,3-dicyano-1,4-naphthoquinone in tetramethylene sulphone or in acetonitrile, however, resulted in complete recovery of the starting material. Nitration at higher temperature yielded only tars.

EXPERIMENTAL

I.r. spectra were measured with a Perkin-Elmer Infra-cord 137B spectrometer and u.v. and visible spectra were measured in a Cary model 14 spectrophotometer. N.m.r. spectra were measured with a Varian A60 spectrometer.

5-Nitro-1,4-naphthoquinone.—A mixture of sublimed 1,4-naphthoquinone (21.3 g, 135.0 mmol) and pure anhydrous nitronium tetrafluoroborate (21.5 g, 162 mmol; 20% excess) in tetramethylene sulphone (225 ml; distilled over sodium hydride and stored under nitrogen; *ca.* 50 p.p.m. H₂O) was magnetically stirred under dry nitrogen at 0°. After 2 h the ice-bath was removed and the deep red mixture was allowed to warm to room temperature. The yellow precipitate obtained after pouring into ice-water (500 ml) was filtered and air-dried. The crude product was sublimed under vacuum when unchanged 1,4-naphthoquinone (13 g) was recovered. The residue was crystallized from anhydrous ethanol to give the *product* (5.5 g, 45%), m.p. 161–165° (lit.,¹⁴ m.p. for 6-nitro-isomer 130°) (Found: C, 59.25; H, 2.45; N, 6.9. C₁₀H₅NO₄ requires C, 59.05; H, 2.5; N, 9.0).

⁹ A. Fischer and D. R. A. Leonard, *J.C.S. Chem. Comm.*, 1973, 300.

¹⁰ L. I. Krimen and D. J. Cota, *Org. Reactions*, 1969, **17**, 213.

¹¹ C. L. Perrin, *J. Org. Chem.*, 1971, **36**, 420.

¹² B. A. Collins, K. E. Richards, and G. J. Wright, *J.C.S. Chem. Comm.*, 1972, 1216.

¹³ 'Mellor's Modern Inorganic Chemistry,' ed. G. D. Parks, Wiley, New York, 1961, p. 933.

¹⁴ K. Babu Rao and N. V. Subba Rao, *J. Sci. Ind. Res.*, 1958, **17B**, 225.

6.9%), λ_{max} (CH_2Cl_2) 245 (ϵ 20,100), 251 (21,600), 260 (15,300), and 328 (2100) nm, λ_{max} (MeOH) 227 (ϵ 14,300); 247 (18,400), 257 (13,000), and 326 (2100) nm.

2,3-Dichloro-5-nitro-1,4-naphthoquinone.—A mixture of 2,3-dichloro-1,4-naphthoquinone (18.2 g, 80 mmol) and anhydrous nitronium tetrafluoroborate (21.76 g, 164 mmol) in tetramethylene sulphone (50 ml) was heated with stirring under nitrogen at 95° for 23 h. The mixture was poured in ice-water (500 ml) and a yellow solid was isolated after adjustment of the pH to 3.4. Crystallization from chloroform gave the product (8.6 g, 50%), m.p. 150—151°, undepressed on admixture with an authentic sample. The i.r. spectrum (KBr) was identical with that of an authentic sample.¹

3-Nitrophthalic Acid.—Using the above method a 1:1 molar mixture of phthalic anhydride and $\text{NO}_2^+\text{BF}_4^-$ in tetramethylene sulphone (80 ml) at 90° for 7 h gave, after hydrolysis with 0.1N-hydrochloric acid, 3-nitrophthalic acid (37%), m.p. 216—218°, undepressed on admixture with an authentic sample.

Demethylation of 2,3-Dicyano-1,4-dimethoxynaphthalene.—To a solution of nitronium hexafluorophosphate (11.6 g,

60.7 mmol) in acetonitrile (80 ml) at 0° under nitrogen 2,3-dicyano-1,4-dimethoxynaphthalene (4.85 g, 20 mmol) was added with stirring. The deep blue solution was kept at 0° for 1.5 h and then allowed to warm to room temperature. After 2 h the precipitated 2,3-dicyano-1,4-naphthoquinone was filtered off and crystallized from acetonitrile, m.p. 270—271° (lit.,¹ 270—271°), undepressed on admixture with an authentic sample, i.r. spectrum identical with that of an authentic sample.

The mother liquor was diluted to 100 ml with water and extracted with benzene in a liquid-liquid extractor. The benzene was slowly evaporated to give an oil (0.7 g) which was analysed by preparative g.l.c. on a Porapak Q column (36 in \times 3/8 in) at 218° (helium flow 60 ml min⁻¹). *N*-Methylacetamide was isolated (15%; measured using acetamide as standard on the same column) and identified by i.r. and n.m.r. spectroscopy, molecular weight determination, and by coinjection with authentic *N*-methylacetamide.

We thank the National Research Council for a Postdoctoral Fellowship (to W. D. K.).

[3/1863 Received, 7th September, 1973]