ipso-Nitration at an Aromatic Methoxy-group

By B. A. COLLINS, K. E. RICHARDS, and G. J. WRIGHT*

(Department of Chemistry, University of Canterbury, Christchurch, New Zealand)

Summary The major product from reaction of 5-acetoxyor 5-methoxy-1,2,3-trimethoxybenzene with nitric acid in acetic anhydride is 2,6-dimethoxyquinone, via the moderately stable 3,4,5-trimethoxy-4-nitrocyclohexa-2,5dienone as common intermediate.

THE addition-elimination mechanism for aromatic acetoxylation has been established¹ for some alkylbenzenes, which are the only substrates to have yielded the key diene intermediates. We now report a dienone product, from the reaction of the substituted trimethoxybenzenes with nitric acid-acetic anhydride mixtures, for which initial



attack must be electrophilic substitution at an aromatic carbon atom bearing a heteroatom. This removes the possibility that the acetoxylation mechanism relies on special properties of the methyl group.

Reaction of 5-acetoxy-1,2,3-trimethoxybenzene (1a) with nitric acid in acetic anhydride at -70° followed by removal of volatile material under reduced pressure gave a crude product shown (n.m.r.) to be a mixture of 4-nitro-3,4,5trimethoxycyclohexa-2,5-dienone (2) (80%) and the known 2,6-dimethoxyquinone (3) (20%). The nitrodienone (2), extracted with carbon tetrachloride and recrystallised from ether-light petroleum, was a solid, m.p. 101°, identified on the basis of the following spectroscopic evidence: M^+ . $C_9H_{11}NO_6$; λ_{max} (methanol) 244 and 297 nm (ϵ 17,160 and 4650); μ_{max} (liquid) 1670, 1640, 1614, 1578 and 1345 cm⁻¹; δ (60 MHz; CDCl₃) 3.61 (3H, s, 4-OMe), 3.78 (6H, s, 3- and 5-OMe), and 5.68 p.p.m. (2H, s, 2- and 6-H). Reaction of 1,2,3,5-tetramethoxybenzene (1b) under the same conditions gave dienone (2) (51%) and quinone (3) (49%); both substrates gave small amounts (< 3%) of 4-nitro-5-X-1,2,3-trimethoxybenzene. Pure nitrodienone was converted slowly and quantitatively into quinone in CDCla with a trace of acetic acid.

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¹D. J. Blackstock, J. R. Cretney, A. Fischer, M. P. Hartshorn, K. E. Richards, J. Vaughan, and G. J. Wright, *Tetrahedron Letters*, 1970, 2793.