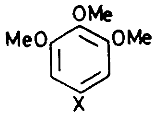
ipso-Nitration at an Aromatic Methoxy-group

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

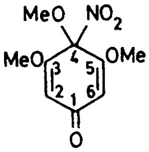
(*Department of Chemistry, University of Canterbury, Christchurch, New Zealand*)

Summary The major product from reaction of 5-acetoxy- or 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-2,5-dienone as common intermediate.

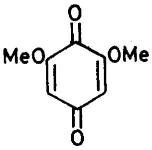
THE addition–elimination mechanism for aromatic acetoxylation has been established[1] for some alkylbenzenes, which are the only substrates to have yielded the key diene intermediates. We now report a dienone product, from the reaction of the substituted trimethoxybenzenes with nitric acid–acetic anhydride 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.



(1) a ; X = OAc
b ; X = OMe



(2)



(3)

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-3,4,5-trimethoxycyclohexa-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: $M^{+\cdot}$ $C_9H_{11}NO_6$; 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; $CDCl_3$) 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 $CDCl_3$ with a trace of acetic acid.

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