The Nitro Group as an Intramolecular Nucleophile

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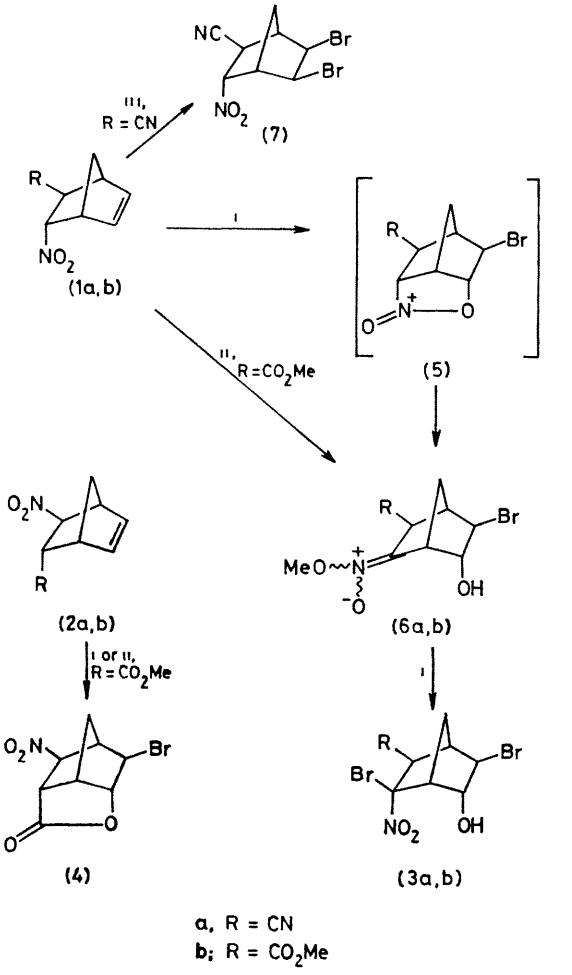
Summary The highly stereoselective, regiospecific bromination of two norbornenyl systems containing an *endo*-nitro group proceeds with nitro group participation, an *X*-ray crystal structure determination of product (**3a**) is reported

ALTHOUGH electrophilic attack at the oxygen atoms of nitronate anions is not uncommon,[1] nucleophilic behaviour is rarely displayed by the oxygen atoms of nitro groups themselves.[2] In principle, such behaviour should be facilitated if the electrophilic reaction partner can be sited intramolecularly such that capture by the nitro group is both sterically and stereoelectronically favourable. This sort of participation is indeed known, but reported examples usually involve nitroaromatic substrates like *o*-nitrostyrenes[3] and *o*-nitrobenzyl halides.[4] We now report transannular participation by an *endo*-nitro group, hitherto unprecedented, in the norbornenyl series.

The substrates under investigation are the *endo*-nitronorbornenes (**1a**) and (**1b**), formed, together with their isomers (**2**), in the Diels–Alder reaction between cyclopentadiene and (*E*)-3-nitropropenenitrile[5] or methyl (*E*)-3-nitropropenoate[5] respectively (ether, 0 °C, quantitative). These cycloadditions have been reported previously,[6] but under unnecessarily severe conditions (refluxing benzene, 5 h), in low yields (24% and 43% respectively), and without assignment of stereochemical outcome. We have found, using n.m.r. spectroscopy, that the ratio of *endo*-:*exo*-nitro products (**1**):(**2**) is 90:10 for R = CN, and 86:14 for R = CO_2Me. Isomer (**1a**) could be recrystallised from the (**1a**)/(**2a**) mixture using di-isopropyl ether, the (**1b**)/(**2b**) isomer mixture could not be separated, and was used as such in subsequent reactions.

When the adduct (**1a**) was treated with 2 equiv. of *N*-bromosuccinimide (NBS) in dry methanol at 20 °C, a single product (**3a**) was obtained (71%, recrystallised). Similarly, the (**1b**)/(**2b**) isomer mixture yielded the analogous compound (**3b**) (73%) together with the bromolactone (**4**) (6%). In view of the implications of these results, the structure of (**3a**), shown in the Figure, was unambigously determined by an *X*-ray diffraction study.



SCHEME *Reagents* I, NBS, MeOH, II, Br_2, $NaHCO_3$, MeOH, III, Br_2, $CHCl_3$

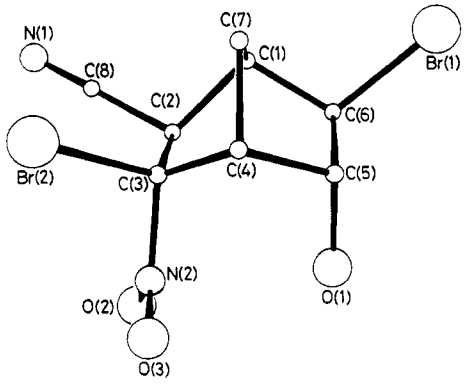


FIGURE. View of molecule (**3a**). Selected interatomic distances (Å) and bond angles (°) are: Br(1)–C(6), 2·03(3); Br(2)–C(3), 1·97(3); O(1)–C(5), 1·46(4); N(2)–C(3), 1·56(4); N(2)–O(2), 1·23(3); N(2)–O(3), 1·22(3); ∠ O(2)–N(2)–O(3), 122(3); ∠C(1)–C(7)–C(4), 93(3); O(1) . . . O(2), 2·99(4); O(1) . . . O(3), 3·08(4).

Crystal data: (**3a**), monoclinic, space group C_c–C_s^4 (no. 9), $a = 6{\cdot}691(1)$, $b = 16{\cdot}088(2)$, $c = 9{\cdot}910(2)$ Å, $\beta = 91{\cdot}67(2)°$, $U = 1066{\cdot}3$ Å^3, $D_m = 2{\cdot}09(2)$, $D_c = 2{\cdot}12$ g cm^{-3} for $Z[C_6H_8Br_2N_2O_3] = 4$. Intensity data were collected (for $2\theta < 50°$) on an automated Philips PW11000 four-circle diffractometer using Nb-filtered Mo-K_α radiation. Of the 481 unique reflections measured, 455 had $I > 2\sigma(I)$ and were used in the solution and refinement of the structure (using conventional Patterson, Fourier, and full-matrix least-squares methods) which has converged at $R = 0{\cdot}048$. Unit weights were used in the refinement with anisotropic temperature factors for the Br atoms and isotropic temperature factors for the remaining non-hydrogen atoms. Hydrogen atoms were not located.†

The transformations (**1**) to (**3**) are remarkable in achieving a high-yielding functionalisation of the norbornenyl double bond in a regiospecific and completely stereoselective manner. In particular, the position and *endo*-stereochemistry of the hydroxy group indicate its provenance as the original nitro group, which must participate in transannular fashion when ionic bromination occurs at the *exo*-face of the double bonds of (**1a**) or (**1b**) (peroxide-initiated free radical bromination with NBS fails). An intermediate (**5**) is thus suggested; in fact, analogous cyclic intermediates have been isolated, as tetrafluoroborate or hexafluoroantimonate salts, on treatment of *o*-nitrostyrenes with acid.[7] Subsequent methanolysis and deprotonation of (**5**) to the nitronate esters (**6**), followed by further bromination and demethylation, would then yield the observed products (**3**) (Scheme).

We have the following additional evidence for our postulated mechanism. When the isomer mixture (**1b**)/(**2b**) was treated with 1 equiv. of molecular bromine in dry methanol in the presence of sodium hydrogen carbonate at 20 °C, an unstable solid was obtained (48%) together with bromolactone (**4**) (12%). The spectroscopic data (i.r., n.m.r., m.s.) of the unstable compound are consistent with a nitronate ester (**6b**). Treatment of (**6b**) with NBS in methanol effected clean conversion into the product (**3b**) (97%, chromatographically pure). Unfortunately, we could not produce the nitronate ester from (**1a**) by this method, a complex mixture of products resulting instead, and the reaction of (**1a**) with bromine in chloroform yielded the *cis,exo*-dibromo product (**7**) (76%).

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† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication. The structure factor table is available as Supplementary Publication No. SUP 22986 (3 pp.) from the British Library, Lending Division. For details of how to obtain this material, see Notice to Authors No. 7, *J. Chem. Soc., Dalton* or *Perkin Trans.*, Index Issues.

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