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Aryl-*NNO*-azoxy-α-nitro- and -α,α-dinitro-alkanes

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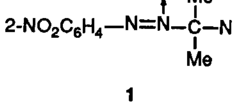
An approach to the synthesis of previously unknown aryl-*NNO*-azoxy-α-nitro- and -α,α-dinitro-alkanes has been developed, involving nitration of hydrazones and oxidation of the resulting diazenes.

Among the numerous and differently α-substituted nitro compounds, 2-(2-nitrophenylazoxy)-2-nitropropane **1**[1] is the only compound with an arylazoxy group as an α-substituent which has been described. It was obtained through trifluoroperacetic acid (TFPA) oxidation of the corresponding azo compound prepared from 2-nitrophenyldiazonium and 2-nitropropane salts. The location of the *N*-oxide oxygen atom in **1** was not determined, unfortunately. Our attempts to extend the above oxidation reaction to the analogous adducts with salts of nitro compounds of the $M^+ {}^-CXNO_2R$ kind (where R = alkyl, X = H or NO_2) failed. The oxidation did not occur with *m*-chloroperbenzoic acid (MCPBA), and the action of TFPA caused decomposition. The reasons for this may be that, in the case of R = H in acidic media, the adducts are known[2] to be hydrazones, thus making their transformation to diazene oxides difficult. When R = NO_2 oxidation by MCPBA is hindered by the insufficient basicity of the diazene moiety, which is accentuated by the instability of the substrate in TFPA.



$2\text{-}NO_2C_6H_4{-}N{=}\overset{O}{\overset{\uparrow}{N}}{-}\underset{Me}{\overset{Me}{C}}{-}NO_2$

1

Taking these circumstances into account, we have developed an approach to the synthesis of aryl-*NNO*-azoxy-α-nitroalkanes with the proton in the α-position both to the azoxy- and nitro-groups. Using this approach a series of aryl-*NNO*-azoxynitroalkanes, including α,α-dinitroalkanes and aryl-*NNO*-azoxytrinitromethane, were prepared.

The basic principle of the synthesis is shown in Scheme 1. The movable proton is protected with an acetoxymethyl group, which is preserved in the reaction conditions for nitration of hydrazones **2** by nitrogen oxides and for TFPA oxidation of diazenes **3**. The group is readily eliminated from the obtained diazene oxides **4** either by basic work-up followed by acidification to yield **5** or (at R = OCOMe) in a two-step method by removing the acetyl groups in acidic media to afford **6** followed by de-oxymethylation during basic nitration (leading to **7**).

In order to succeed in the application of this approach, it was necessary to use an aryl group with either 2-nitro- or 2,4-dinitro-phenyl substituents. The *o*-nitro-group, owing to its electron withdrawing and steric effects, produces regiospecific oxidation of the distal nitrogen atom leading to the atomic sequence ArN═N(O)—C—NO_2. The position of the *N*-oxide oxygen atom was determined by an X-ray analysis of **1**.† It is

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† *Crystal data* for **1**: monoclinic, space group *P*21/*n*, $a = 11.358(3)$, $b = 6.228(3)$; $c = 16.179(2)$ Å; $\beta = 97.9(5)°$, $U = 1133.5(6)$ Å^3, $Z = 4$, $D_c = 1.49$ g cm^{-3}; a total of 1983 reflections were observed, of which 1136 (57.3%) had intensities $I > 3\sigma$ (scanning to the angle $2\theta = 60°$). Structure solution, correcting of the positional and anisotropic thermal parameters and geometric calculations were made using the complex programs EXTL and XTL. Final *R*-factor = 0.052. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, *J. Chem. Soc., Chem. Commun.*, 1992, Issue No. 1.

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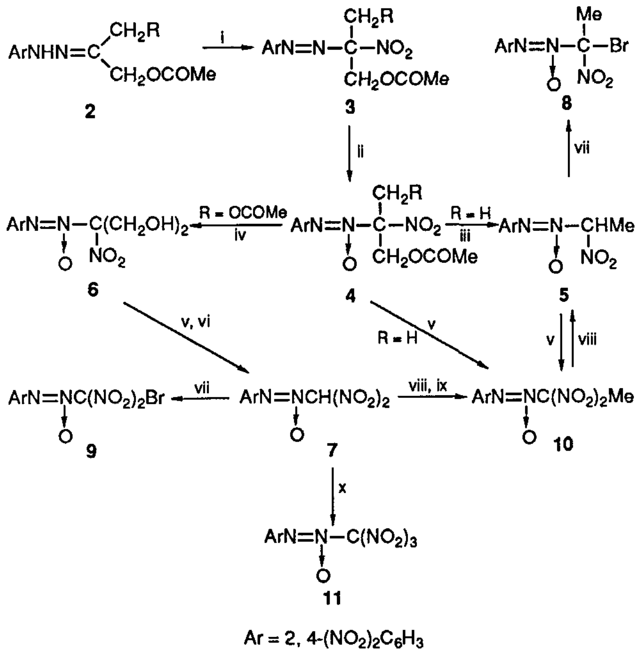

Scheme 1 *Reagents and conditions*: i, excess of N_2O_4, CH_2Cl_2, 0 °C (yield 85–86%); ii, $H_2O_2 + (CF_3CO)_2O$, CH_2Cl_2 [70% (R = H), 37% (R = OCOMe)]; iii, 1. KOH, MeOH, 2. diluted H_2SO_4 (86%); iv, excess of MeCOCl, MeOH (98%); v, 1. NaOH, MeOH, 2. $C(NO_2)_4$ [50% (from **5**), 38% (from **4**)]; vi, 1. NaOCOMe, 2. HCl gas (44%); vii, 1. KOH, Br_2 (75–85%); viii, Et_3N (48%); ix, MeI (30%); x, conc. HNO_3, conc. H_2SO_4, 63–70 °C (61%)

noteworthy that in **1** a *trans*-orientation of the substituent relative to the azoxy group is observed.

Another important feature of the molecular structure is the proximity of the aromatic nitro group nitrogen atom and the *N*-oxide oxygen atom: this intramolecular distance is 0.33 Å shorter than the sum of the van der Waals radii. This may be caused by electrostatic interaction of the above atoms having excess charge of opposite signs.

The structures of the other compounds obtained were confirmed by elemental analysis, IR, NMR (^{1}H, ^{13}C, ^{14}N, ^{5}N) and mass spectroscopic data, including samples selectively enriched with ^{15}N.

Arylazoxy-nitro- and -dinitro-alkanes **5** and **7** with an active α-proton, when prepared by the described method, are completely stable unlike analogous azo compounds (which isomerise into hydrazones) and display chemical properties typical of nitro compounds. The availability of the reactive proton makes **5** and **7** convenient synthones, providing ready access to a wide range of different derivatives. For example, they give salts with metals and nitrogen bases and undergo facile bromination to yield the corresponding bromonitrodiazene oxides **8** and **9**. The *mononitro derivative* **5** *readily undergoes nitration by tetranitromethane in basic media, leading to the* *gem*-dinitroethyl analogue **10** (the latter may also be obtained using these conditions from the protected precursor **4**).

We succeeded in nitrating dinitromethyldiazene oxide **7**, similarly to other dinitroalkanes, to give the trinitromethyl derivative **11**. It is interesting to note that the reaction of **7** with methyl iodide in the presence of a base gives both the C-alkylated product **10** and also forms **5** as a result of partial denitration of **10**. The possibility of this process occurring was proved by an independent experiment using an authentic sample of **10**.

All the α-nitroalkyldiazene oxides obtained are thermally stable compounds. Indeed, the oils **5** and **9** can be stored under ambient conditions; the solids **7**, **8**, **10** and even **11** melt without decomposition at 76, 82, 112 and 86 °C, respectively.

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