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Aryl-*ONN*-azoxy-α,α-dinitroalkanes

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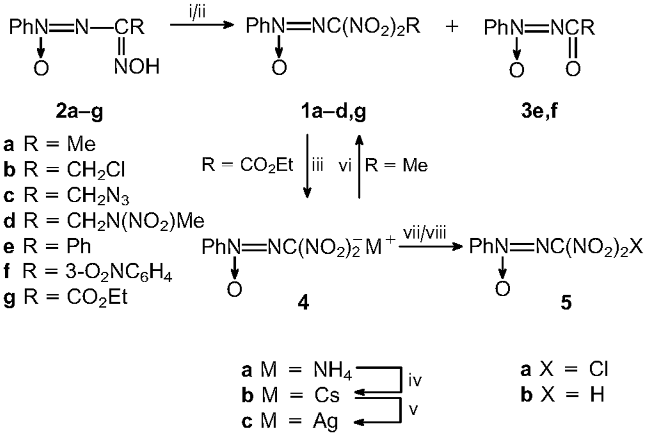
A method for the synthesis of previously unknown phenyl-*ONN*-azoxy-α,α-dinitroalkanes by nitration of *N*-phenyl-*N'*-(α-hydroxyiminoalkyl)diazene *N*-oxides has been developed.

We have already prepared the first examples of the proximal arylazoxydinitroalkanes (ADA) of general formula $ArN{=}N(O)C(NO_2)_2R$ and established that they are rather stable substances.[1] In this connection we decided to clarify the possibility of the existence, and to estimate the properties, of hitherto unknown distal ADA regioisomers $PhN(O){=}NC(NO_2)_2R$ **1**.

We have synthesised compounds **1** by nitration of the corresponding α-hydroxyiminoalkyldiazene oxides **2** (Scheme 1).[2] Mixtures of concentrated HNO_3 with Ac_2O or NH_4NO_3, nitrogen tetroxide, nitrogen pentoxide and even 70% HNO_3 can be used. The best results were obtained with an HNO_3–NH_4NO_3 mixture. Judging from the IR spectra of the product mixtures from nitration of **2** the deoximation of **2** takes place along with the formation of **1**, thus leading to carbonyl derivatives **3**.[†] The nitration products were isolated by TLC, in the course of which **3a–d** decomposed.

Compounds **1** thus obtained are low-melting crystalline or oily substances.[‡] The structures of **1** and other ADAs synthesised for the first time were confirmed on the basis of elemental analysis and IR, ^{13}C and ^{14}N NMR spectroscopic data (see Table 1). According to NMR spectroscopy the nitration product of **2b** is formed as a mixture of two probably geometrical isomers of **1b** (not isomers with different oxygen location in the *N*-oxide).

The distal ADAs described in the present work have a marked disadvantage in thermal stability in relation to their proximal analogues. Temperatures for the onset of decomposition of **1a–d** are within the range 70–100 °C; **1g** was not isolated due to its instability and **1e,f** completely decomposed in the course of TLC.



Scheme 1 *Reagents and conditions*: i, mixture of 10 mol HNO_3 and 10 mol NH_4NO_3, ~ 20 °C (yields of **1a–d**, 45–60%); ii, 2 mol of N_2O_4 in $ClCH_2CH_2Cl$, 60–70 °C (yields of **3**, ~ 50%); iii, NH_3 in CH_2Cl_2, 8–10 °C (45%); iv, CsOH in EtOH, 0 °C (50%); v, $AgNO_3$ in MeCN; vi, **4c** + excess MeI in MeCN, ~ 20 °C (5% of **1a**); vii, Cl_2 in H_2O (85% of **5a**); viii, 10% H_2SO_4, H_2O, 8–10 °C (~ 50% of **5b**).

Salts **4**[§] of the first member of the series of distal ADAs were obtained after treating crude **1g** with base. Contrary to the proximal analogues, the transformation of **4** to covalent compounds does not always proceed readily. While the acidification and halogenation lead without difficulties to **5**,[¶] which decompose at ~ 20 °C, the alkylation product **1a** forms in only a very low yield.

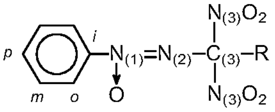
[†] **3e** was identified on the basis of the coincidence of its melting point (51.5–52.5 °C) with that given in the literature[3,4] (53 °C); IR (ν/cm^{-1}): 1700, 1490, 1440 and **3f** (m.p. 86–87 °C) on the basis of elemental analysis and ^{13}C, ^{14}N NMR (Table 1) and IR spectroscopic data; IR (ν/cm^{-1}): 1720, 1580, 1490, 1445, 1360.

[‡] Melting points/°C for **1a**: 36.5–37.5; for **1c**: 60–62; for **1d**: 62–64. IR (ν/cm^{-1}): **1a**: 1580, 1480, 1420, 1370, 1345; **1b** (oil): 1600, 1490, 1450, 1375; **1c**: 2120, 1610, 1490, 1440, 1360; **1d**: 1600, 1555, 1540, 1500, 1445, 1375, 1310.

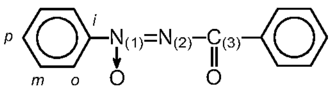
[§] **4a**, m.p. 84–85 °C (decomp.); IR (ν/cm^{-1}): 1680, 1610, 1475, 1420, 1345. **4b** (solvate with EtOH), m.p. 64 °C (decomp.); IR (ν/cm^{-1}): 1650, 1470, 1425, 1355.

[¶] IR (ν/cm^{-1}), **5a**: 1605, 1485, 1440, 1335; **5b**: 1600, 1485, 1435, 1335.

Table 1 ^{13}C and ^{14}N NMR spectral data for **1b–d**, **3f** and **4b** (solutions in [$^2H_6$]acetone, δ (ppm) from TMS for ^{13}C, from $MeNO_2$ for ^{14}N).



1, 4b



3f

Compound	R	Chemical shifts								
		p	*m*	*o*	*i*	$C_{(3)}$	$N_{(1)}$	$N_{(3)}$	R	
1b	CH_2Cl	136.3 134.9	131.0 130.5	123.7 123.4	147.1	121.2	−35.4 −43.9	−19.7	CH_2	44.3 42.3
1c	$CH_2N_I{=}\overset{+}{N}_{II}{-}\overset{-}{N}_{III}$	136.2	130.9	123.7	146.9	121.1	−35.5	−18.6	CH_2 N_I N_{II} N_{III}	52.9 −32.2 −136.4 −167.5
1d	$CH_2{-}N{<}^{Me}_{NO_2}$	136.3	131.0	123.8	147.0	119.6	−35.6	−18.4	CH_2 CH_3 NO_2	54.6 41.5 −28.8
3f	–	135.6	130.5 130.3/ 130.2	123.4	147.3	178.3	−46.1	–	C_p $C_{o,m}$	134.6 130.5 130.2/ 130.3
4b[a]	Cs	132.5	129.1	121.9	145.5	139.1	71.4	−34.8		–

[a] Solvent, D_2O.

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