Organic Chemistry

Aryl-*ONN*-azoxy-α,α-dinitroalkanes and some of their derivatives

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Previously unknown *N'*-dinitroalkyl-*NNO*-azoxybenzenes have been prepared (by nitration of *N'*-(α-hydroximino)alkyl-*NNO*-azoxybenzenes) and transformed to some derivatives.

Key words: distal azoxydinitroalkanes, nitration, deoxymation, halogenation.

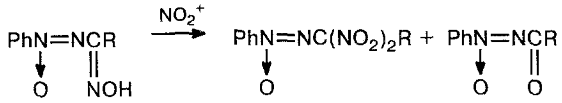
Earlier[1] we synthesized for the first time proximal azoxy-α,α-dinitroalkanes (ADAs) of the general formula $ArN{=}N(O)C(NO_2)_2R$ and showed that they exhibit an acceptable degree of thermal stability. This fact and a rather high partial content of active oxygen determine the good outlook for ADAs in creating energy-rich substances. In this connection we have studied the possibility of obtaining distal analogs of ADAs not previously described in the literature, namely, compounds of the general formula $PhN(O){=}NC(NO_2)_2R$.

The method of preparation of these compounds is based on the nitration reaction of the distal hydroximinoalkyldiazenoxides **1**, specially synthesized by us for this purpose.

The nitration of oximes to dinitrocompounds has a rather general character in the ketoxime series and frequently leads to positive results if one of the alkyl (aryl) radicals is replaced by a functionality (*cf.* Refs. 3, 4).

Simultaneous deoxymation nearly always takes place. This process sometimes predominates or becomes the sole reaction route.

We have established that treatment of *N'*-(α-hydroximino)alkyl-*NNO*-azoxybenzenes and their derivatives with nitrating agents actually leads to the formation of the target phenyl-*ONN*-azoxy-α,α-dinitroalkanes **2** as well as deoximation products **3**.



$$\underset{\substack{\downarrow\quad\ \|\\ O\quad NOH}}{PhN{=}NCR} \xrightarrow{NO_2^+} \underset{\substack{\downarrow\\ O}}{PhN{=}NC(NO_2)_2R} + \underset{\substack{\downarrow\quad \|\\ O\quad O}}{PhN{=}NCR}$$

1a–g **2a–d, g** **3e, f**

a: R = Me; **b**: R = CH_2Cl; **c**: R = CH_2N_3; **d**: R = $CH_2N(NO_2)Me$; **e**: R = Ph; **f**: R = $3\text{-}O_2NC_6H_4$; **g**: R = CO_2Et

Mixtures of concentrated HNO_3 with acetic anhydride or ammonium nitrate, nitrogen tetroxide or pentoxide, and even 70 % HNO_3 can be used as nitrating agents. The best results are obtained with the HNO_3—NH_4NO_3 mixture, the yields of **2** being within the range 45—60 %.

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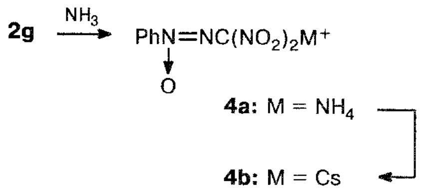
Compounds **2** are low—melting crystalline or oily substances. Their structures were confirmed by spectral methods and (for **2a,d**) by elemental analysis. In the case of **2b** the presence of two isomers (apparently geometric isomers about the N=N bond) was demonstrated by means of ^{13}C and ^{14}N NMR-spectroscopy. The fact of the side deoximation of **1** was confirmed by the presence of a band that is characteristic of the carbonyl group (ν = 1720 cm^{-1}) in the IR spectra of mixtures of the nitration products as well as by the isolation of **3e,f** in the individual state.

The distal ADAs **2** thus synthesized are inferior to proximal analogs in terms of thermal stability. Thus, **2c** starts to decompose already at ~70 °C, and intensive decomposition is observed at ~100 °C. Unlike **2a—d** compounds **2e,f** do not survive TLC conditions on silica gel, thus preventing them from being isolated as individual substances. At the same time we succeded in isolating **3e,f** from their mixtures with **2e,f** by the TLC method. Interestingly, in the case of **2a—d** and **3a—d** the opposite pattern was observed: **2a—d** were stable during chromatography while **3a—d** decomposed.

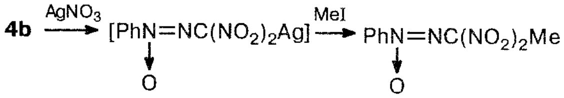
We supposed that thermal stability of the ADAs could be enhanced by passage from covalent derivatives to ionic ones. In this connection salts of phenyl-*ONN*-azoxydinitromethane **4** were prepared. The unstable **2g** was treated with ammonia and the ammonium salt **4a** thus obtained was converted to the cesium salt **4b** by treatment with CsOH in ethanol.



$$\mathbf{2g} \xrightarrow{NH_3} \mathrm{Ph}\underset{\underset{O}{\downarrow}}{N}{=}NC(NO_2)_2M^+$$

$$\mathbf{4a}\text{: } M = NH_4 \qquad \mathbf{4b}\text{: } M = Cs$$

The structures of the salts were confirmed by the NMR method (for **4a**), comparison of the IR spectra of **4a** and **4b**, elemental analysis of **4b**, and transformation of the salt **4b** *via* silver salt **4c** to the authentic product **2a**.



$$\mathbf{4b} \xrightarrow{AgNO_3} [\mathrm{Ph}\underset{\underset{O}{\downarrow}}{N}{=}NC(NO_2)_2Ag] \xrightarrow{MeI} \mathrm{Ph}\underset{\underset{O}{\downarrow}}{N}{=}NC(NO_2)_2Me$$

4c **2a**

As expected, the salts **4a,b** proved to be much more stable than starting ADA **2g**. However, they decompose within the range of 60—80 °C, too.

Acidification or chlorination of the salts **4a,b** caused formation of unstable oily substances, to which the structures of phenyl-*ONN*-azoxydinitromethane (**2h**) and

Table 1. Yields, melting points, and analytical and IR characteristics of the compounds obtained

Compound	Yield (%)	M.p./°C (solvent)	Found/Calculated (%) C	H	N	IR, ν/cm^{-1} (C(NO$_2$)$_2$, =N—O, C=O, N$_3$
2a	45	36.5—37.5 (hexane)	40.63 40.00	3.48 3.33	23.61 23.33	1580, 1480, 1420, 1370, 1345, 1320
2b	60	Oil	—	—	—	1600, 1490, 1450, 1375, 1370, 1310
2c	53	60—62 (hexane—ethyl acetate)	—	—	—	2120, 1610, 1490, 1440, 1360, 1280
2d	58	62—64 (hexane—chloroform)	—	—	34.82 34.88	1600, 1555, 1540, 1500, 1485, 1445
2h	48	Oil	—	—	—	1605, 1485, 1440, 1335
2i	85	Oil	—	—	—	1600, 1485, 1435, 1335
3e*	53	51.5—52.5 (hexane)				
3f	48	86—87 (hexane—ethyl acetate)	—	—	15.07 15.50	1720, 1620, 1580, 1540 1490, 1445
4a	45	84—85 (decomp., MeOH)	—	—	—	3360—3100, 1680, 1610, 1475, 1420, 1345, 1310
4b**	49	64 (decomp., MeOH)	21.91 22.34	1.95 1.86	14.50 14.89	3700—3200, 1650, 1470, 1425, 1390, 1355

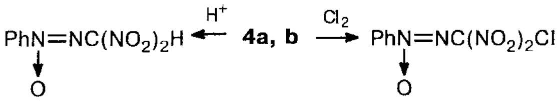
* Literature value *cf.* Ref. 5: 53 °C.

** Solvate is $C_7H_5CsN_4O_5 \cdot C_2H_5OH$.

Table 2. ^{1}H NMR spectroscopic data of **2** (δ, ppm relative to HMDS)

Compound	Solvent	Ph		CH_2R	Me
		o-H	*m,p*-H		
2a	CCl_4	8.27—8.02	7.64—7.35	—	2.39
2b	Acetone-d_6	8.37—8.03	7.75—7.40	5.00	—
2c	Acetone-d_6	8.33—8.05	7.88—7.33	4.76	—
2d	Acetone-d_6	8.38—8.08	7.88—7.26	5.50	3.38

phenyl-*ONN*-azoxydinitrochloromethane (**2i**) were assigned, respectively.



$$\underset{O}{\overset{\downarrow}{\mathrm{PhN}}}{=}NC(NO_2)_2H \xleftarrow{H^+} \textbf{4a, b} \xrightarrow{Cl_2} \underset{O}{\overset{\downarrow}{\mathrm{PhN}}}{=}NC(NO_2)_2Cl$$

2h **2i**

In conclusion, a method of synthesis of hitherto unknown aryl-*ONN*-azoxy-α,α-dinitroalkanes and their derivatives was developed. The distal ADAs were shown to be inferior to the proximal analogs in terms of thermal stability.

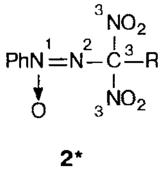
Experimental

^{1}H NMR spectra were recorded on Tesla BS-467 (60 MHz), Bruker WM-250 (250 MHz), and Bruker AM-300 (300 MHz) instruments in $CDCl_3$, $(CD_3)_2CO$, and $(CD_3)_2SO$ with HMDS as an internal standard, and ^{13}C (75.5 MHz) and ^{14}N (21.7 MHz) NMR spectra were recorded on a Bruker AM-300 spectrometer. Chemical shifts in ^{14}N NMR spectra are given relative to $MeNO_2$ (δ = 0.0 ppm) as an external standard without correction for diamagnetic susceptibility. IR spectra were obtained on UR-20 and Specord IR spectrophotometers for crystal compounds in KBr pellets and for liquids without a solvent. UV spectra were measured with a Specord UV VIS instrument. The silica gel Silpearl with a luminophore was used for TLC. Melting points were measured on a Koffler table. Yields, analytical data, and parameters of IR spectra are given in Table 1, and those of NMR spectra are given in Tables 2 and 3.

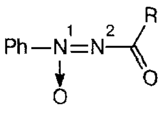
Substituted 1-(phenyl-*ONN*-azoxy)-1,1-dinitroethanes (2). To 100 % HNO_3 (10 mol per 1 mol of the oxime **1**) an eqimol amount of finely dispersed NH_4NO_3 was slowly added with protection from atmospheric moisture. The mixture was stirred at ~20 °C until a colorless homogeneous solution was formed (30—40 min), and then **1** was added. After completion of the reaction the mixture was poured onto ice and extracted with chloroform or methylene chloride, the extract was washed with water and dried over $MgSO_4$, the solvent was removed, and **2** was isolated from the residue by TLC.

Aroyl-*NNO*-azoxybenzenes (3). A solution of 2 mol of N_2O_4 in anhydrous dichloroethane was added to a solution of **1e** (**1f**) in the same solvent, heated to 60—70 °C, and stirred

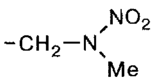
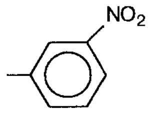
Table 3. ^{13}C, ^{14}N NMR spectroscopic data of compounds **2** and **3f** (in acetone-d_6)



2*



3f

Compound	R	δ							
		p	*m*	*o*	*i*	C(3)	N(1)	N(3)	R
2b	CH_2Cl	136.3 134.9	130.4 130.9	123.7 123.3	147.1	121.2	−35.4 −43.5	−19.7	CH_2 42.3 44.3
2c	$CH_2N_a{=}N_b{=}N_c$	136.2	130.9	123.7	146.9	121.1	−35.5	−18.6	CH_2 52.9 N_a 322 N_b 136.4 N_c 167.5
2d		136.3	131.0	123.8	147.0	119.6	−35.6	−18.4	CH_2 54.6 CH_3 41.5 NO_2 −28.8
3f		135.6	130.5 130.3 130.2	123.4	147.3	—	−46.1	—	C=O 178.3 C*p* 134.6 C*o,m* 130.5 130.3/130.2
4b**		132.5	129.1	121.9	145.5	139.1	−71.4	−34.8	—

* The signal of ^{13}C(3) is highly broadened due to ^{13}C-^{14}N spin-spin coupling *via* one bond; detected by ^{13}C—{^{1}H, ^{14}N} triple resonance with simultaneous decoupling of protons and ^{14}N.

** Solvent is D_2O.

until the starting **1** was completely consumed, the mixture was cooled and washed with water, and **3** was isolated by TLC on silica gel.

Ammonium salt of phenyl-*ONN*-azoxydinitromethane (4a). Compound **1g** was nitrated with an HNO_3+NH_4NO_3 mixture as described above. The extract was dried over $MgSO_4$ for 15—20 min and concentrated at ~20 °C *in vacuo* on a rotatory evaporator, the residue was dissolved in anhydrous methylene chloride, and dry NH_3 was bubbled through the solution at 8—10 °C until the starting light yellow color changed to purple. The mixture was stirred with cooling for 40 min and at ~20 °C for 20 min, most of the solvent was evaporated at ~20 °C, and the **4**a formed was separated by filtration and washed on a filter with anhydrous methylene chloride until the mother liquor became colorless.

Cesium salt of phenyl-*ONN*-azoxydinitromethane (4b). A solution of 1.5-fold excess of LiOH in the mimimum amount of anhidrous ethanol was added dropwise to a solution of the salt **4a** in anhydrous ethanol at 0 °C, and the precipitated **4b** was separated by filtration and purified by recrystallization from methanol with large losses of **4b** caused by its decomposition.

Preparation and alkylation of the silver salt of phenyl-*ONN*-azoxydinitromehane (4c). A solution of an equimolar amount of $AgNO_3$ in anhydrous MeCN was added to a solution of **4b** in the same solvent, the precipitated $CsNO_3$ was separated by filtration, to the solution of the salt **4c** an excess of MeI was added, the mixture was stirred in the dark at ~20 °C for 1 h, the precipitated AgI was filtered off, the filtrate was evaporated, and **1**a was isolated by TLC of the residue on silica gel.

Action of an acid on the salt 4b. 10 % H_2SO_4 was added dropwise to a solution of the salt **4b** (0.18 g) in the minimum amount of water at 8—10 °C until the pH reached 2—3, the resulting slightly yellowish solution was extracted with ether, and the extract obtained was dried over $MgSO_4$ and concentrated *in vacuo* on a rotatory evaporator to yield 0.08 g of **2h** as an yellow oil.

Chlorination of the salt 4b. Cl_2 was bubbled through a solution of the salt **4**b (0.1 g) in water until the color changed from orange-red to slighly yellow, the mixture was extracted with ether,and the extract was dried over $MgSO_4$ and concentrated *in vacuo* on a rotatory evaporator at ~20 °C to yield 0.07 g of the product **2i** as an orange oil.

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