

Synthesis of 4-diazo-3,5-dinitropyrazole and characteristic features of its behaviour towards nucleophiles

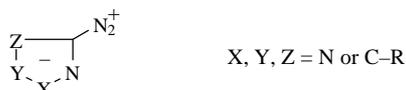
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Diazopyrazole containing two nitro groups in the ring – 4-diazo-3,5-dinitropyrazole – has been synthesised for the first time by diazotisation of the corresponding aminodinitropyrazole. 4-Diazo-3,5-dinitropyrazole reacts with salts of methylene-active compounds, $\text{CH}_2(\text{CN})\text{NO}_2$ and $\text{CH}_2(\text{COCH}_3)_2$, to give azo coupling products, whereas its interaction with nucleophiles such as Br^- , N_3^- or $\text{H}_2\text{O}(\text{H}^+)$ involves replacement of one of the nitro groups yielding 4-diazo-3-R-5-nitropyrazoles.

Diazoazoles, derivatives of NH-azoles, exist as zwitterions in which the heteroaromatic ring serves as the counter-ion of the diazonium group.



This structure determines the typical chemical properties of diazoazoles.¹ A well known reaction of diazoazoles is their interaction with nucleophiles, which usually involves the diazonium group and gives either azo coupling products or products of the substitution of the nucleophile for the N_2^+ group. However, an important aspect of the reactivity of diazoazoles, namely, the possibility of nucleophilic substitution of other groups with the N_2^+ group remaining unaffected, has not been studied, due to the absence of appropriate compounds.

To be competitive with the N_2^+ group, which exhibits extremely strong $-\text{I}$ and $-\text{M}$ effects ($\sigma_m = 1.76$, $\sigma_p = 1.91^2$), another leaving group should be a very strong nucleofuge. In our opinion, a nitro group, which is among the best leaving groups in aromatic nucleophilic substitution,³ could be suitable for this purpose. This choice is supported by some analogies found in the literature: individual examples of nucleophilic substitution of the *ortho*-nitro group in phenyl- and naphthyl-diazonium salts have been reported.^{4,5} In addition, a reported attempt to carry out diazotisation of 3,5-diamino-4-nitropyrazole in water led to 3,5-bis(diazo)pyrazolone, *i.e.*, together with diazotisation of the amino group, the substitution of a hydroxy for the nitro group occurred.

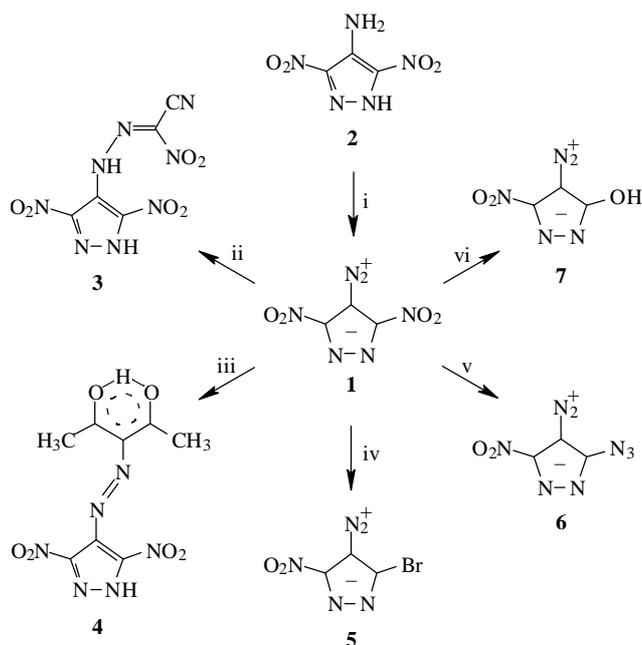
In order to obtain an appropriate object needed for the investigation of the above reactions and in a continuation of our studies dealing with the synthesis and investigation of the properties of nitropyrazoles,^{7,8} we have prepared 4-diazo-3,5-dinitropyrazole **1** by diazotisation of 4-amino-3,5-dinitropyrazole **2**[†] (Scheme 1). The basicity of the aminodinitropyrazole **2** is fairly low ($\text{p}K_{\text{BH}^+} = -5.43$, protonation at the amino group); however, its diazotisation requires no special procedures. This compound is diazotised under mild conditions (0–3 °C) upon treatment with NaNO_2 in 20% H_2SO_4 . The diazopyrazole **1** thus formed is a stable yellow compound. The structure of **1** as a zwitterionic diazo compound has been determined based on IR, ^{13}C NMR and ^{14}N NMR spectroscopy (see Table 1) and confirmed by elemental analysis. The diazopyrazole **1** is the first diazodinitropyrazole to be synthesised, and in fact the first diazopyrazole containing two strong electron-withdrawing groups apart from a diazo group.

We have studied reactions of the diazopyrazole **1** with some

nucleophiles: Br^- , N_3^- , $\text{H}_2\text{O}+\text{H}^+$, $\text{CH}^-(\text{COCH}_3)_2$ and $\text{CH}^-(\text{CN})\text{NO}_2$ (Scheme 1). We found that **1** reacts readily with nucleophiles in water; however, the reaction pathway depends on the nature of the nucleophile.

The interaction with salts of the above methylene-active compounds follows a pathway typical of diazoazoles, namely, involving the N_2^+ group and affording azo coupling products **3** and **4**, as indicated by the IR and ^1H and ^{13}C NMR spectral data. The double set of signals in the ^{13}C NMR spectrum of hydrazone **3** implies that this compound forms as a mixture of *syn*- and *anti*-isomers. In the case where **1** reacts with the acetylacetonate anion, the azo coupling product **4** possesses an azo-structure, because its ^{13}C NMR spectrum exhibits signals corresponding to ‘carbonyl’ carbon atoms, the chemical shifts of which are typical of the enol form of a β -diketone fragment, as well as a signal due to the central carbon atom with an indirect spin coupling constant with the proton of the hydroxyl group of the enol, $J_{^{13}\text{C}-\text{H}} = 11.4 \text{ Hz}$.⁹

However, when **1** is treated with nucleophiles that cannot form azo coupling products, for example, with bromide or azide anions, one of the nitro groups rather than the diazonium group is substituted, and these reactions afford 4-diazo-3-bromo-5-nitropyrazole **5** and 4-diazo-3-azido-5-nitropyrazole **6**, respectively. The IR and ^{14}N NMR spectroscopic data as well



Scheme 1 Reagents and conditions: i, NaNO_2 in 20% H_2SO_4 , 0–5 °C, 1h; ii, $1. \text{NH}_4^+\text{C}(\text{NO}_2)_2\text{CN}$ in H_2O , 0–5 °C, 1h; 2. 20% H_2SO_4 ; iii, 1. $\text{Na}^+\text{CH}(\text{COCH}_3)_2$ in H_2O , 0–5 °C, 1h; 2. 20% H_2SO_4 ; iv, KBr in 47% HBr , 20–25 °C, 20 h; v, 1. NaN_3 in H_2O , 0–5 °C, 2h; 2. 20% H_2SO_4 ; vi, 20% H_2SO_4 , 60–70 °C, 2h.

[†] Aminodinitropyrazole **2** (mp 155 °C) was prepared by alkaline hydrolysis of 3,5-dinitro-4-(methoxycarbonyl)aminopyrazole, described in our study published in *Izv. Akad. Nauk, Ser. Khim.*, 1993, 1616 (*Russ. Chem. Bull.*, 1993, 42, 1552). The synthesis and properties of compound **2** will be described in detail later.

Table 1 Characteristics of the synthesised diazonitropyrazoles 1–7.

Compound	Yield (%)	$T_{\text{dec}}/^{\circ}\text{C}$ (solvent for crystallisation)	IR spectrum ^a ν/cm^{-1}	NMR spectra ($[\text{}^2\text{H}_6\text{]acetone}$) ^b δ (ppm)	
				^{13}C (δ_{TMS})	^{14}N ($\delta_{\text{CH}_3\text{NO}_2}$)
1 ^c	66	151 (H ₂ O)	1320, 1580 (NO ₂) 2240 (N ⁺ ≡N)	80.00 (C–N ₂ ⁺) 155.95 (C–NO ₂)	–29.04 (NO ₂) –157.45 (N ⁺ ≡N)
3	100	135 (H ₂ O)	1330, 1570 (NO ₂) 2250 (C≡N) 3300 (NH)	100.04, 106.53 (CN) 110.36 (C–NH=N=) 116.57, 118.13 (C–CN) 142.62 (C–NO ₂)	
4 ^d	76	194 (dichloroethane)	1340, 1500 (NO ₂) 1680 (CO) 3150 (OH)	16.80 (q, Me, 127.8) 22.13 (q, Me, 129.2) 109.54 (d, C–CO, 11.4) 128.03 (s, C–N=N) 131.58 (s, C–NO ₂) 187.42, 189.45 (s, CO)	
5	84	165	1330, 1550 (NO ₂) 2210 (N ⁺ ≡N)	83.28 (C–N ₂ ⁺) 134.17 (C–Br) 157.82 (C–NO ₂)	–29.50 (NO ₂) –152.00 (N ⁺ ≡N)
6	100	110 (dichloroethane)	1330, 1580 (NO ₂) 2150 (N ₃) 2240 (N ⁺ ≡N)	69.59 (C–N ₂ ⁺) 116.57 (C–N ₃) 143.92 (C–NO ₂)	–28.80 (NO ₂) –147.49 (N ⁺ ≡N)
7 ^e	80	175 (dichloroethane)	1330, 1520 (NO ₂) 2200 (N ⁺ ≡N) 3200 (OH)	54.39 (C–N ₂ ⁺) 135.43 (C–NO ₂) 154.08 (C–OH)	–27.93 (NO ₂) –137.10 (N ⁺ ≡N)

^a IR spectra were recorded on a Specord M-80 instrument in KBr pellets. ^b NMR spectra were recorded on a Bruker AM-300 instrument (300 MHz). ^c UV spectrum (Specord UV VIS): λ_{max} (H₂O) 303 nm. ^d ¹H NMR (δ_{TMS} , in $[\text{}^2\text{H}_6\text{]acetone}$): 2.24 (s, Me), 2.54 (s, Me), 14.34 (s, OH). ^e ¹H NMR (δ_{TMS} , in $[\text{}^2\text{H}_6\text{]acetone}$): 11.75 (br. s., OH); ¹⁷O NMR ($\delta_{\text{H}_2\text{O}}$, CD₃CN): 583.04 (NO₂), 286.64 (OH).

as data from ¹³C–¹⁴N heteronuclear double resonance, made it possible to establish reliably the structures of the compounds **5** and **6** as products resulting from substitution of a nucleophile for the nitro group.

Heating of diazonium salts with a dilute acid is known⁵ to be a standard method for the replacement of an aromatic diazonium groups by a hydroxy group. We found that interaction of the diazopyrazole **1** with 20% H₂SO₄ leads to the substitution of a hydroxy for one of the nitro groups rather than for the diazonium fragment and yields 4-diazo-3-hydroxy-5-nitropyrazole **7**.[‡]

The structure of **7** was determined similarly to those of **5** and **6** and, in addition, by resorting to ¹⁷O NMR spectroscopy. The ¹⁷O NMR spectrum of **7** exhibits a signal at ~286 ppm due to the OH group. The reaction of the diazopyrazole **1** with 20% H₂SO₄ to give **7** proceeds slowly even at room temperature; however, without an acid, compound **1** does not react with water even at elevated temperatures, and can be recrystallised from water.

Apparently, the observed acid catalysis of the hydrolysis of the nitro group does not involve preliminary protonation of the ring nitrogen atom with 20% H₂SO₄ ($H^0 = -1.1^{10}$), since the introduction of the diazo group in an azole ring decreases the basicity of the ring by ~10 pK units;¹ for the diazopyrazole **1**, this should lead to $\text{p}K_{\text{BH}^+} \approx -6.5$ to -7 . (For 3,5-dinitropyrazole, $\text{p}K_{\text{a}} = 3.14^{11}$).

Thus, we have obtained a highly electrophilic diazoazole – 4-diazo-3,5-dinitropyrazole – and accomplished nucleophilic substitution of an electron-withdrawing group other than diazonium, namely, of the nitro group.

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[‡] **Caution!** Diazonitropyrazoles **1**, **5**, **6** and **7** are sensitive to mechanical impact.

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Received: Moscow, 19th June 1996

Cambridge, 11th November 1996; Com. 6/04349F