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^{1}H, ^{13}C and ^{15}N NMR Spectra of the Reaction Product of Benzenediazonium Fluoroborates with 1-Phenyl-3-methyl-4-(α-acet-ethylidene)-pyrazol-5-one

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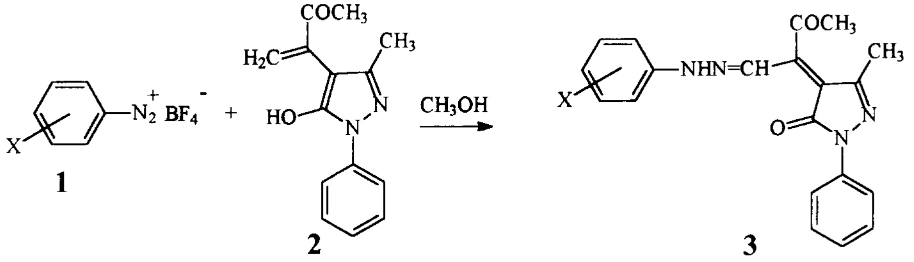
ABSTRACT

Contrary to previously published data (Mustroph and Bach, Z. Chem, *1985), we have found that the reaction product of 4-X-benzenediazonium fluoroborates ($X=H$, NO_2) with 1-phenyl-3-methyl-4-(α-acet-ethylidene)-pyrazol-5-one corresponds to 5′-hydroxy-5,5′-dimethyl-2-phenyl-1′-(4-X-phenyl)-1′,5′-dihydro-2*H*-[4,4′]bipyrazolylidene-3-ones (**4a,b**) and not to compounds **3**. The structural elucidation is based on analysis of ^{1}H, ^{13}C and ^{15}N NMR spectra of non- and ^{15}N-selectively labelled samples. © 1997 Elsevier Science Ltd*

Keywords: 5′-Hydroxy-5,5′-dimethyl-2-phenyl-1′-phenyl-1,5′-dihydro-2H-[4,4′]bipyrazolylidene-3-ones, ^{1}H NMR, ^{13}C NMR, ^{15}N NMR.

INTRODUCTION

In 1985, Mustroph and Bach [1] reported the preparation and absorption spectra of the reaction product of benzenediazonium fluoroborates (**1**) with 1-phenyl-3-methyl-4-(α-acet-ethylidene)-pyrazol-5-one (**2**). It was expected that the structure of these products corresponds to compounds **3** (Scheme 1). These compounds would be interesting models in which azo–hydrazone tautomerism can exist. In hydrazone forms, expected by the authors of the paper [1], there are two possibilities of the existence of either seven-membered or eight-membered rings due to hydrogen bonding. The aim of this paper was to measure and analyse ^{1}H, ^{13}C and ^{15}N NMR spectra of non- and the ^{15}N selectively labelled reaction products of benzenediazonium fluoroborate (**1a**) and 4-nitrobenzediazonium fluoroborate (**1b**) with 1-phenyl-3-methyl-4-(α-acet-ethylidene)-pyrazol-5-one (**2**).

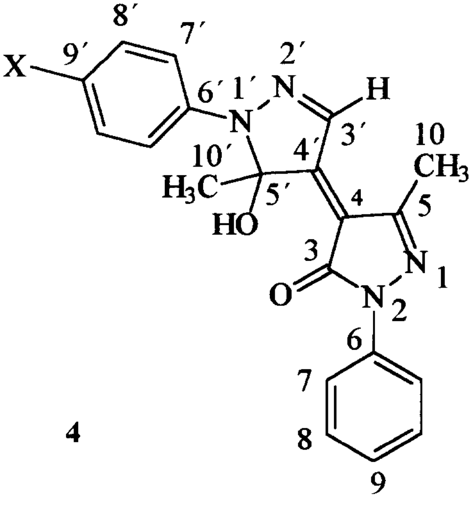


Scheme 1

RESULTS AND DISCUSSION

^{1}H, ^{13}C and ^{15}N NMR spectra of the reaction product of benzenediazonium fluoroborate (**1a**) or 4-nitrobenzediazonium fluoroborate (**1b**) with 1-phenyl-3-methyl-4-(α-acet-ethylidene)-pyrazol-5-one (**2**) were measured and analysed. Two-dimensional NMR spectra [2] were used with the aim of assigning proton and carbon chemical shifts unambiguously. H,H-COSY (homonuclear chemical shift correlation spectroscopy), NOESY (two-dimensional nuclear Overhauser effect spectroscopy) and H,C-COSY [3] were applied. The results are collected in Tables 1 and 2.

Contrary to the previously published data [1], we have found that the reaction product of benzenediazonium fluoroborate corresponds to 5′-hydroxy-5,5′-dimethyl-2,1′-diphenyl-1′,5′-dihydro-2*H*-[4,4′]bipyrazolylidene-3-one (**4a**, X = H) for the following reasons:



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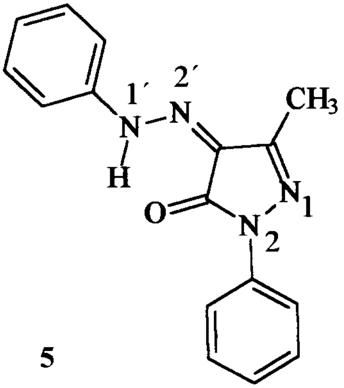
The proton NMR spectrum consists of signals of two phenyl rings, two methyl groups, =CH– and an acidic proton resonating at 8.31 ppm only. In the ^{13}C NMR spectrum, there is no signal of the carbonyl group from $COCH_3$, the $\delta(^{13}C)$ of which could be expected at ca. 200 ppm. Nitrogen-15 chemical shifts are relatively very close to those in compound **5** [4] in deuteriochloroform ($\delta(^{15}N_1) = -75.3$, $\delta(^{15}N_2) = -191.5$, $\delta(^{15}N_{1'}) = -205.6$, $J(^{15}N_{1'},H) = 96.3$ Hz [5], $\delta(^{15}N_{2'}) = -18.9$) but the coupling constant, $J(^{15}N_{1'},H) = 5.1$ Hz, is apparent only in the reaction products. These experimental data are not consistent with the structure **3** (Scheme 1).



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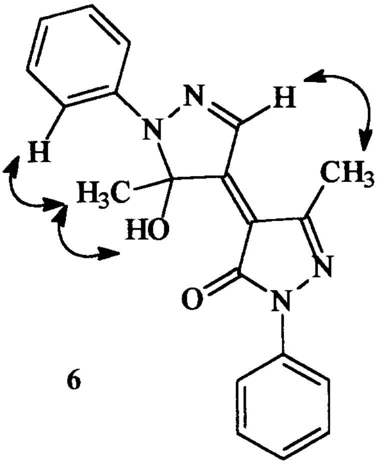
The NOESY [6] spectrum (Fig. 1) provides the key pieces of information. The most important through-space proximity of protons are shown in formula **6**.



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The structure **4** allows us to explain all above-mentioned ‘discrepancies’. As is apparent from the structure, there is no $COCH_3$ group in the molecule.

TABLE 1

^{1}H, ^{13}C and ^{15}N Chemical Shifts and $J(^{15}N,X)$ Coupling Constants (Hz ± 0.3 Hz), and NOESY Correlations for Compound **4a** in Deuteriochloroform

	$\delta(^{1}H)$	$\delta(^{15}N)/\delta(^{13}C)$	$J(^{15}N(1'),^{13}C)$	$J(^{15}N(1'),H)$	*NOESY*
N-1	—	−72.1			
N-2	—	−189.7			
C-3	—	165.71			
C-4	—	115.22			
C-5	—	148.32			
C-6	—	137.86			
C-7	7.86	119.46			H(7)/H(8)
C-8	7.41	128.86			H(8)/H(7) H(8)/H(9)
C-9	7.21	125.56			H(9)/H(8)
C-10	2.42	16.77			H(10)/H(3′)
N-1′	—	−180.2[a]			
N-2′	—	−1.5[a]			
C-3′	7.56	130.98	1.4	12.4; 6.6[b]	H(3′)/H(10)
C-4′	—	162.49			
C-5′	—	98.37			
C-6′	—	139.73	5.3		
C-7′	7.71	117.89	2.7		H(7′)/H(8′) H(7′)/H(10′)
C-8′	7.38	129.19			H(8′)/H(7′) H(8′)/H(9′)
C-9′	7.17	125.02			H(9′)/H(8′)
C-10′	1.91	24.58		2.2	H(10′)/OH H(7′)/H(10′)
OH	8.31	—		5.1	OH/H(10′)

[a] $^{1}J(^{15}N(1'),^{15}N(2')) = 12.8$ Hz.
[b] $^{3}J(^{15}N(2'),^{1}H)$.

$J(^{15}N_{1'},H)$ is small because the acidic proton is not directly bonded to nitrogen $N_{1'}$. $\delta(^{1}H)$ of the hydroxy group is 8.31 ppm (δ(NH/OH) is typically in the region of 13–17 ppm in the hydrazone forms of azo dyes [5]) because the hydroxy group is bonded to an sp^{3} carbon and, due to reasons of geometry, the hydrogen bonding (if any) is very weak.

Analogous ^{1}H and ^{13}C NMR measurements were used in the analysis of the reaction product of 4-nitrobenzenediazonium fluoroborate. ^{1}H and ^{13}C NMR data observed (Table 2) are in agreement with the proposed structure **4b** (X = NO_2).

The empirical formulae of compounds **3** and **4** are the same and, therefore, the reaction products cannot be differentiated using elemental analysis data or the *m/e* value in the mass spectrum. A possible reaction pathway consists of formation of compound **3** followed by nucleophilic attack of nitrogen on the carbonyl group and proton transfer.

TABLE 2

^1H and ^{13}C Chemical Shifts in Compound **4b** in Deuteriochloroform

	$\delta(^1H)$	$\delta(^{13}C)$
C-3	—	165.21
C-4	—	118.31
C-5	—	148.12
C-6	—	137.37
C-7	7.88	119.39
C-8	7.43	128.96
C-9	7.24	125.96
C-10	2.45	16.81
C-3′	7.71	133.38
C-4′	—	160.63
C-5′	—	97.21
C-6′	—	144.27
C-7′	7.79	116.21
C-8′	8.24	125.31
C-9′	—	143.25
C-10′	1.98	23.96
OH	8.13	—

EXPERIMENTAL

The compounds 5′-hydroxy-5,5′-dimethyl-2,1′-diphenyl-1′,5′-dihydro-2*H*-(4,4′)bipyrazolylidene-3-one (**4a**) and 5′-hydroxy-5,5′-dimethyl-2-phenyl-1′-(4-nitrophenyl)-1′,5′-dihydro-2*H*-[4,4′]bipyrazolylidene-3-one (**4b**) were prepared as reported previously.[1]

The $^{15}N_{1'}$ (20% ^{15}N) and $^{15}N_{2'}$ (95% ^{15}N) doubly labelled isotopomer of **4a** was prepared analogously using aniline-^{15}N (20% ^{15}N) and $Na^{15}NO_2$ (95% ^{15}N), respectively.

The ^1H NMR (360.13 MHz), ^{13}C NMR (90.566 MHz) and ^{15}N NMR (36.501 MHz) spectra of compounds **4** dissolved in deuteriochloroform were recorded at 300 K on a Bruker AMX 360 spectrometer equipped with 5 mm broadband probe and X32 computer using the UXNMR software (Version 940501.3). ^1H and ^{13}C chemical shifts were referred to internal tetramethylsilane (δ = 0.00). One-dimensional ^{15}N NMR spectra were measured in 5 mm NMR tubes with 64 K data points and a spectral width of 11 100 Hz using the non-refocused INEPT (insensitive nuclei enhanced by polarisation transfer)[8] technique optimised for $J(^{15}N.H)$ = 10 and 5 Hz, respectively. Nitrogen-15 chemical shifts were referred to external nitromethane (δ = 0.0) placed in a coaxial capillary.

Positive values of chemical shifts denote downfield shifts with respect to standards.

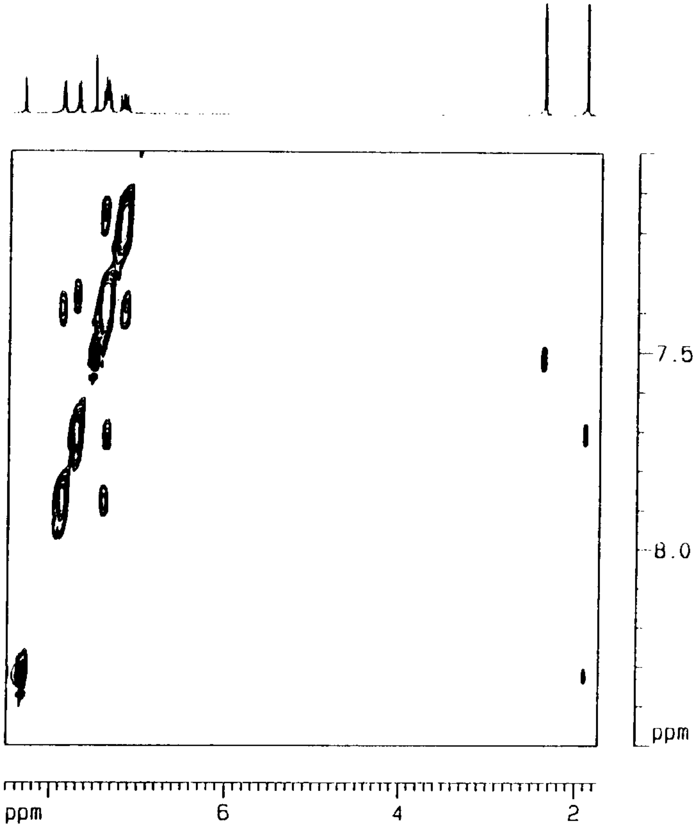

Fig. 1. NOESY spectrum of compound **4a** in deuteriochloroform measured using a 1 s mixing time.

Experimental conditions of two-dimensional H,H-COSY, NOESY, H,C-COSY and H,C-COSYLR were similar to data reported previously[7]. Mixing times in NOESY spectra were 0.5 and 1 s.

ACKNOWLEDGEMENTS

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