Chemistry of Heterocyclic Compounds, Vol. 31, No. 9, 1995

MULTINUCLEAR MAGNETIC RESONANCE STUDY OF SOME MESOIONIC OXATRIAZOLES CONTAINING NITROGENOUS EXOCYCLIC GROUPS

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^1H, ^{13}C, ^{14}N, and ^{15}N NMR measurements are reported for four mesoionic 1-oxa-2,3,4-triazoles containing exocyclic nitrogenous groups. The NMR signal assignments are discussed and compared with those previously published for some corresponding oxatriazoles. The results obtained support the proposed cyclic mesoionic structures for the compounds studied. The questions of possible charge delocalization and valence tautomerism are addressed. Compound with N^-H as a exocyclic group (Fig. 1) is found to be relatively unstable, this is attributed to proton migration in the corresponding non-cyclic form of this molecule.

KEY WORDS: ^1H, ^{13}C, ^{14}N, and ^{15}N NMR; chemical shifts; line widths; mesoionic oxatriazoles; charge localization; valence tautomerism

INTRODUCTION

Previously we have employed ^1H, ^{13}C, ^{14}N, ^{15}N, and ^{17}O NMR measurements in structural investigations on mesoionic oxatriazoles and thiatriazoles [1, 2]. In these studies we have established the presence of cyclic structures and reported some simple additivity rules for the ^{15}N chemical shifts. As an extension of this work we are now reporting the results of our investigation on some related mesoionic oxatriazoles containing nitrogenous exocyclic group. Our aims in undertaking this study are first, to demonstrate the presence of the mesoionic cyclic structures given in Fig. 1; second to determine the extent of possible charge delocalization in the ring and, finally, to investigate the potential of the compounds studied to undergo valence tautomerism. This later point is illustrated in Fig. 2.

A further aspect of note is that the molecules studied are closely related to compounds which have known hypotensive properties [3, 4].

RESULTS AND DISCUSSION

In Table 1 we report the result of a ^{14}N and ^{15}N NMR study on the compounds given in Fig. 1.

The nitrogen chemical shift assignments given are derived from procedures established in our earlier work [1, 2]. The ^{14}N measurements show only one signal, due to the presence of rapid quadrupolar relaxation. The rate of quadrupole controlled nuclear relaxation is very dependent upon the magnitude of the electric field gradient at the nucleus in question. This field gradient is normally reduced for positively charged atoms in a molecule. Thus, the single ^{14}N NMR signal observed is readily attributable to the nitrogen atom in position 3 for the molecules studied. Consequently, the ^{15}N assignment for this atom is

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0009-3122/95/3109-1103$12.50

TABLE 1. The ^{14}N and ^{15}N NMR Data for Some Mesoionic 1-Oxa-2,3,4-triazoles with Exocyclic Nitrogenous Groups

Compound (exo group)	^{15}N NMR chemical shifts, ppm (^{14}N NMR linewidth, Hz)[a]			
	N2	N3	N4	exo-N
1 (NH^-)	-17[b] (900)	-71[b] (40)	-145[b] (640)	-242[b] (540)
2 (NH_2Cl^-)	-4,4	-69,7 (640)	-139,3	-296,5 br
3 (N^-Ph)	-18,2	-72,4 (450)	-143,3	-210,0
4 (N^-COPh)	-8,6	-71,0 (430)	-133,0	-210,8
5 (O^-)[c]	-8,8 (905)	-71,6 (50)	-154,8 (865)	—
6 (S^-)[c]	12,9 (1200)	-64,5 (70)	-107,5 (1200)	—

[a] ^{15}N NMR chemical shifts in ppm, ^{14}N NMR linewidth in Hz. The measurements were taken on DMSO-d_6 solution (compounds **2-4**) and on acetone-d_6 (**1**, **5**, and **6**). Reference: CH_3NO_2, δ = 0 ppm.

[b] The data were collected by ^{14}N NMR technique.

[c] Compounds **5** and **6** previously studied, and given only for comparison purposes. The measurements for **5** and **6** were taken on acetone-d_6 solutions.

TABLE 2. ^1H and ^{13}C NMR Data for Some Mesoionic 1-Oxa-2,3,4-triazoles with Nitrogenous Exocyclic Groups

Compound (exo group)	^{13}C NMR chemical shifts, ppm (^1H chemical shifts, ppm)[a]					
	C5	1'	2'	3'	4'	exo-group
1 (NH^-)	167,2[b]	134,2 —	121,3 (8,04)	130,2 (7,70)	133,4 (7,78)	— (7,1)[b]
2 (NH_2Cl^-)	172,0	133,0 —	122,7 (8,17)	131,3 (7,78)	135,9 (7,88)	—
3 (N^-Ph)	162,4[b]	134,0	121,6 (8,11)	130,3 (7,73)	133, 8 (7,80)	C1" 145,1 C2" 122,9 (7,27)[c] C3" 128,9 (7,33) C4" 122,5 (7,03)[c]
4 (N^-COPh)	171,2	133,8	122,0 (8,19)	130,4 (7,78)	134,3 (7,85)	CO 172,5 C1" 136,3 C2" 129,1 (8,15) C3" 128,2 (7,49) C4" 132,1 (7,57)
5 (O^-)[d]	166,2	139,9	122,0 (7,49)	131,5 (7,76)	134,5 (7,82)	—
6 (S^-)[d]	193,4	131,2	122,5 (8,18)	131,2 (7,79)	135,1 (7,86)	—

[a] All measurements in DMSO-d_6 solution, except **5** and **6** (acetone-d_6 solution). Reference: solvent peak (δ_H = 2.49 ppm; δ_C = 39.5 ppm in respect to TMS).

[b] Broad peak.

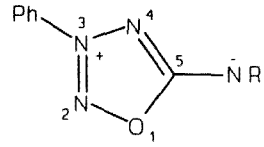
[c] Assignment can be opposite.

[d] Compounds previously studied, and given for comparison purposes.

supported by the ^{14}N data. An additional point to make is that we prepared a sample of compound **3** with an enriched ^{15}N content in position 2. Hence, the increased ^{15}N signal intensity for this atom provided an unambiguous assignment for N2 in this compound and, by comparison, for N2 in the other molecules investigated.

For comparison purposes our previously published [1, 2] NMR data for compounds **5** and **6**, shown in Fig. 3, are included in Tables 1 and 2.

Table 2 contains the results of our ^1H and ^{13}C NMR measurements. In agreement with our previous findings [1, 2], the signal for C5 is normally at the highest frequency in the ^{13}C NMR spectrum of the compounds **1-4**. An exception is provided by compound **4** which contains a carbonyl group. In this case the C5 and carbonyl signals are distinguished between



1) R = H
2) R = H * HCl
3) R = Ph
4) R = COPh

Fig. 1. Mesoionic oxatriazoles with nitrogen exocyclic groups.

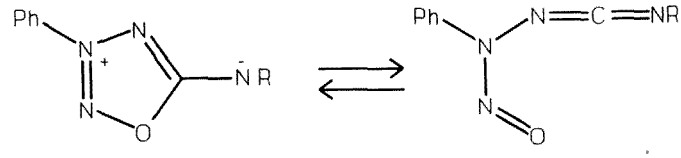
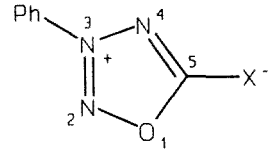


Fig. 2. Potential valence tautomerism of mesoionic oxatriazoles studied.



5) X = O
6) X = S

Fig. 3. Mesoionic oxatriazoles previously studied.

by means of ^{13}C-^{1}H couplings. For C5 we do not observe such couplings, whereas the carbonyl carbon signal shows a splitting of about 1 Hz due to $^{3}J(^{13}C$-$^{1}H)$ interactions with a proton on the neighboring phenyl group. The phenyl ^{13}C assignments, and those for the ^{1}H signals reported in Table 2, are based upon the observed multiplicities of these signals as reported in our earlier work on related compounds [1].

The case of compound **1** is an interesting one. In the solid state over a desicant it is stable for several days. However, in DMSO solution some decomposition is noted after about 30 minutes. This is sufficient time to enable us to obtain ^{1}H and ^{13}C NMR data for this compound, as shown in Table 2, but not sufficient for ^{15}N NMR measurements. Due to the extra sensitivity of ^{14}N NMR at natural abundance, we have obtained a ^{14}N NMR spectrum of compound **1** in a saturated acetone-d_6 solution in about 15 minutes.

From the collected ^{1}H, ^{13}C, ^{14}N, and ^{15}N NMR data given in Tables 1 and 2, we are able to deduce that compounds **1-4** have mesoionic cyclic structures. Comparison with the corresponding results for compounds **5** and **6** serve to confirm this statement. The nitrogen chemical shifts, in particular, for the non-cyclic valence isomers of compounds **1-4** are expected to differ significantly from those observed in the present study [5]. Nitrogen chemical shift differences of more than 100 ppm are expected between the values for a given nitrogen atom in the ring of compounds **1-4** and the corresponding nitrogen atom in the relevant non-cyclic structure. A further comment to support the structure given in Fig. 1, is that we note that the ^{14}N NMR

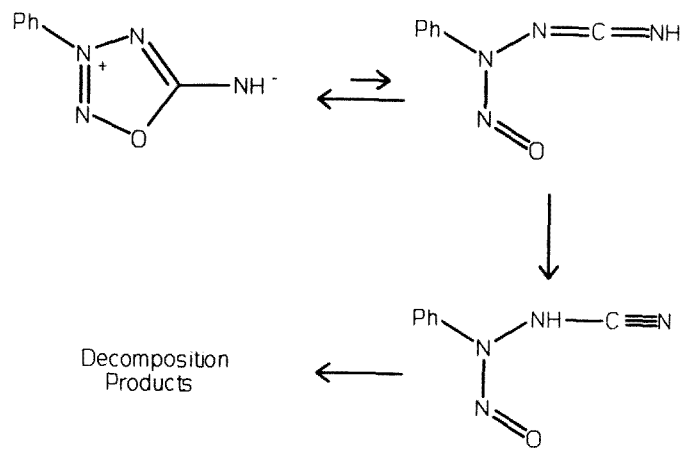


Fig. 4. Proposed pathway for decomposition of Compound 1

signal for N3 is relatively sharp for compounds **1-4**, indicating the localization of the positive charge on this atom. The corresponding negative charge, in the neutral mesoionic species is to be found on the exocyclic groups. Support for this interpretation is provided by comparison of the ^{15}N NMR data for compound **2**, with these for compounds **1**, **3**, and **4**. Compound **2** is a hydrochloride salt. The values of the nitrogen chemical shifts for the ring atoms of this molecule are closely similar to those of the other compounds studied, whereas the exocyclic nitrogen atom of compound **2** is shielded by about 70 ppm in comparison to the corresponding nitrogen atoms of compounds **1**, **3**, and **4**. This clearly shows the formation of the hydrochloride salt by protonation of the exocyclic nitrogen atom. In addition, the ^{15}N signal of the exocyclic atom of compound **2** is considerably broadened, showing the presence of proton exchange at this position.

Our proposed pathway for the decomposition which we observed of compound **1** is given in Fig. 4. This involves proton migration in the non-cyclic form from the imino group; thus is possible for compound **1** but not for the other molecules studied here. A similar observation has been made for the sydnonimine corresponding to compound **1** [6].

CONCLUSIONS

We conclude that nitrogen NMR and the ^{13}C NMR signal of C5 provide decisive information on the structures of compounds **1-4**. The occurence of possible isomerization or transformation would be clearly apparent from a study of these NMR data. The compounds studied are shown to have mesoionic cyclic structures with a positively charged N3 atom and a negative charge on the exocyclic group which is the preferred site of protonation.

EXPERIMENTAL

The compounds studied **1**, **2**, **4** [7], and **3** [8] were prepared by previously published procedure. All NMR measurement were taken on a Bruker AM 500 instrument. For the ^{15}N NMR measurements a pulse width of 45°, a relaxation delay of 4 sec, an acquisition time of ~2 sec and about 10000 scans were employed. For the ^{14}N NMR studies a pulse width of 90°, a relaxation delay of 0 sec, an acquisition time of 0.25 sec and about 3000 scans were used. The ^{1}H and ^{13}C spectra were obtained by standard instrumental procedures. Solutions of 0.5-1.0 M concentration in DMSO-d_6 were used for the NMR studies.

ACKNOWLEDGEMENT

This work was partially supported by the Polish State Committee for Scientific Research (KBN) Grant No 259/TO9/95/09, we also gratefully acknowledge support from The British Council and KBN under the auspieces of their joint research collaboration programme, project number WAR 992/051.

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