¹H and ¹³C NMR study on some substituted azolidine derivatives*

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Abstract—The ¹H and ¹³C NMR spectra carried out on $RN \cdot CH_2 \cdot CH_2 \cdot X \cdot C=O$ (where for R = H, X = NH, NMe, NEt, CH_2 , S, O; for R = Me, X = NMe, CH_2 ; for R = Et, X = NEt) are reported. The comparison of these results with those obtained for the thionic and selonic isologues shows that sulphur and selenium have a greater deshielding effect on the ring than oxygen. The resonance of the carbons not involved in the π system have been correlated with the σ charges calculated by the DEL RE method.

INTRODUCTION

We have widely investigated the chemistry of some penta-atomic heterocyclic molecules having the general formula the tautomeric equilibrium thione-thiol. $\underline{4}$ has been included in a study on cyclic and open ureas, thioureas and some of their related compounds by KALINOWSKI and KESSLER [18], who found a linear correlation between the carbonyl and the thiocarbonyl ¹³C reson-

where R = H, X = NH, NMe, NEt, CH_2 , O, S, Se; R = Me, X = NMe, S, Se; R = Et, X = NEt; and Y = O, S, Se;

with several techniques [1-16]. Since it is well known that the chemical behaviour of the thionic (Y = S) and selonic (Y = Se) compounds is quite different from the ketonic, we have mainly focused our interest on the former derivatives.

As part of the research, we have recently reported [16] on a 1 H and 13 C NMR study on the thionic and selonic derivatives.

In the present paper, we report an analogous study on the ketonic (Y = O) derivatives, having chosen the following compounds for this investigation:

$$\begin{array}{ccccc}
R & X \\
H & NH & 1 \\
H & NMe & 2 \\
H & NEt & 3 \\
H & NEt & 3 \\
H & NEt & 3 \\
H & NEt & 5 \\
H & CH_2 & 6 \\
Me & CH_2 & 7 \\
H & S & 8 \\
H & O & 9 \\
\end{array}$$

where all the rings are labelled as reported above, in order to avoid confusion in the discussion. The ¹³C NMR spectra of <u>1</u>–<u>3</u> have already been reported in d_6 -DMSO by FAURE *et al.* [17] together with some pentaatomic and esa-atomic thionic rings in order to study

ances. The aim of our study is to ascertain the influence of the *endo* X substitutent on the ¹H and ¹³C resonances of the penta-atomic rings and to compare them with those previously reported for the thionic and selonic isologues [16, 17].

EXPERIMENTAL

Imidazolidin-2-one, pyrrolidin-2-one and N-methyl pyrrolidin-2-one have been purchased from Fluka and purified by recrystallization or distillation. N-Methyl and N-ethyl imidazolidin-2-one were prepared by oxidation of the corresponding thionic compounds $(2.6 \times 10^{-2} \text{ mol})$ dissolved in water (150 ml) with potassium permanganate (5.3×10^{-2} mol in 1.5 l) added over 30 min at 60°C. After 1 h, the manganese dioxide was filtered off and the solution concentrated to 50 ml. After cooling, the solution was filtered to remove some potassium sulphate. The filtrate was extracted with benzene (50 ml) and from this N-methyl imidazolidin-2-one: m.p. 110°C, (lit. 113-114°C [20]) and N-ethyl imidazolidin-2-one; m.p. 41-43°C (lit. 41-43°C[21]) were obtained. N,N'dimethyl and N, N'-diethyl imidazolidin-2-one were obtained by reacting N, N'-dimethyl or N, N'-diethyl ethylendiamine (0.12 mol) in benzene (90 ml) with phosgene (0.12 mol) and anhydrous potassium carbonate (0.18 mol) in benzene (450 ml). The reaction mixture was maintained for 2 h on an ice-bath, then overnight at room temperature. After filtration to remove the solid, the solution was concentrated by distillation and the residue distilled at reduced pressure. N, N'-dimethyl imidazolidin-2-one was fractioned with b.p. 94-95°C at 10 torr (lit 94-95°C at 1 torr [20]) while N,N'diethyl imidazolidin-2-one was fractioned with b.p. 98-102°C at 10 torr (lit 122°C at 22 torr [22]). Thiazolidin-2-one and oxazolidin-2-one were synthesized and purified according to [23, 24]

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The NMR spectra have been recorded with a Varian FT-

80-A spectrometer operating at a nominal frequency of 80 and 20 MHz for ¹H and ¹³C respectively at 32° C in CDCl₃ solutions. The chemical shifts were digitally computed using TMS as internal reference. For multiplets, the mean value has been reported.

The σ charge calculation has been carried out with a program written for the DEL REmethod using the parameters reported in [19].

RESULTS AND DISCUSSION

The ¹³C chemical shifts of $\underline{1-9}$ are reported in Fig. 1. The resonances of C(2), ranging within 157–180 ppm, show that this carbon atom is the most deshielded of all. The comparison of these values with those obtained for the corresponding thionic and selonic derivatives, whose values range within 177–202 ppm, indicates a greater shielding effect for oxygen than for sulphur and selenium in the isologue molecules.

FAURE et al. [17] have interpreted the different shieldings of C(2) of the imidazolidine ring for the ketonic and thionic compounds in terms of the tautomeric equilibrium:



They evaluate a low but detectable contribution of the thiol form in the sulphur compounds, and a completely inexistent one of the enolic form in the oxygen derivatives. In our opinion this difference can also be explained on the basis of the contribution of the zwitterionic forms (B) and (C) to the resonance equilibrium:



In fact, this contribution increases on passing from oxygen to sulphur and selenium, as observed in other investigations [14]. An increase of the positive charge on the N-C-X system with a deshielding effect corresponds to the above increase.

Now, if the C(2) resonances for 1–9 are considered, it is possible to distinguish two sets of values: the former, at about 160 ppm, for the imidazolidines 1-5 and the oxazolidine 9, the latter at ca. 177 ppm for the pyrrolidines $\overline{6}$, 7 and the thiazolidine 8. This different behaviour could be explained in terms of the distribution of the fractional positive charge on the atoms involved in the π -charge distribution; in fact, in 1–5 and 9 the positive charge is distributed on the three atoms NCX, whereas in 6-8 it is on the NC atoms. This argumentation is fairly weak for 9, since here there is expected to be a low contribution of (C) to the resonance and hence 9 should be more similar to 6-8 than to 1-5. However, this apparent discrepancy can be explained by taking into account the electronegativity of oxygen, which increases both the electron-release of nitrogen in (B) and the π -bond



Fig. 1. ¹³C Chemical shifts in CDCl₃.



Fig. 2. σ Charges calculated by the DELRE method. The values in parentheses are referred to the hydrogens.

order on C = Y, with the global effect of an increase in shielding on C(2).

This point of view is supported by the fact that the v(C=O) vibration falls at 1725 cm⁻¹ for 9 and below 1690 cm⁻¹ for all the others, indicating that, in 9, C = O has a higher double-bond character.

In order to assign the C(4) and C(5) resonances to the thionic compounds [16], the chemical shifts were tentatively correlated with the charge densities calculated both by CNDO/2 and by the semiempirical DEL R_E calculations [19]. Although the latter calculation considers only the σ skeleton, the correlation between the σ charges and the frequencies of the carbons not involved in the π system was fairly good. This assignment contrasts with that reported by FAURE et al. [17] on the basis of the alkyl group effect in the disubstituted imidazolidines. The σ charges calculated for the present compounds with the DEL RE method are reported in Fig. 2. Also in this case the correlation seems to be good, as demonstrated by Fig. 3, where the carbon chemical shifts (δ_c ppm) of the ketonic derivatives together with those of the thionic ones are reported vs. the σ charges on the carbons (q_c) . The correlation also considers the carbons of the alkyl groups of side chains.

The ¹H chemical shifts of the hydrogens bonded to the carbons are reported in Fig. 4. The frequencies of the NH hydrogens are not considered here because they are very sensitive to concentration and it was not possible to realize identical concentrations for all the



Fig. 3. Linear correlation between the chemical shifts of the carbons having only σ bonds and their charge densities calculated by the DEL RE method for ketonic (\Box) and thionic (O) derivatives. The correlation coefficient is 0.903.

compounds, since 1 and 9 have very low solubilities in CDCl₃. Although the calculation of the charges on the hydrogens in 1-9 gives the same values obtained in the corresponding thionic compounds, the ¹H chemical shifts in 1-9 are on the whole of *ca*. 0.2 ppm lower than those in the isologue sulphur compounds, thus confirming a global deshielding effect due to the substitution of oxygen with sulphur (or selenium).



Fig. 4. ¹H Chemical shifts in CDCl₃. * A range of frequencies has been reported because the spin system is complicated.

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