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6-PIVALOYL-1,2,3,3a,6-PENTAAZAPENTALENE. STERIC EFFECTS ON THE 2-AZIDOIMIDAZOLE/IMIDAZO[1,2-d]TETRAZOLE EQUILIBRIUM

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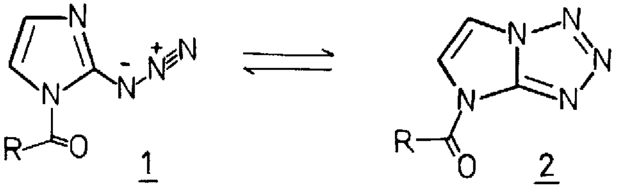
Recently N-acetyl-2-azidoimidazole was reported as the first simple azidoazole in wich the existence of an azido/tetrazole tautomerism can be detected.[1,2] In trying to look for an explanation of this unusual fact we have prepared and studíed by NMR several N-substituted-2-azidoimidazoles, having found that there are two determining factors to shift equilibrium to tetrazole form: the electron-withdrawing ability of substituent,[2,3] and the size of the said group. Our present paper refers to this last point.

The Table shows the values in DMSO-d_6 and acetone-d_6 of ΔH and ΔS for the equilibrium 1 ⇌ 2 (ref. 4).

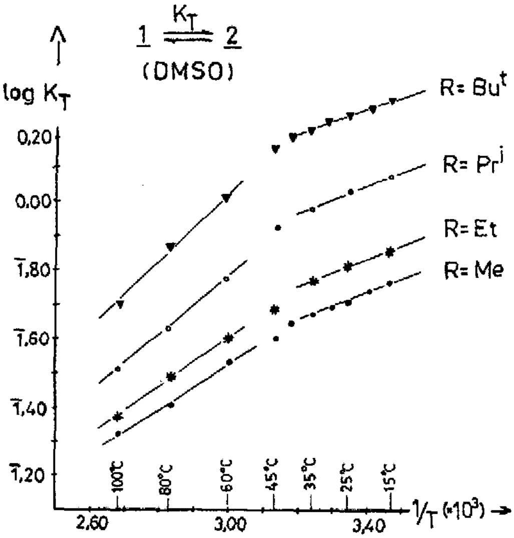


The tetrazole form 2 becomes gradually more favoured, both in DMSO and acetone, on changing from R=Me to R=Bu^t. This last compound has a special interest because in solid state[5] it is found entirely in tetrazole form (imidazo[1,2-d]tetrazole or 1,2,3,3a,6-pentaazapentalene system), as it is evidenced by its IR spectrum in Nujol where no azide band appears. This compound is the first simple azido-azole isolated in bicyclic form. Another interesting fact is the non-equivalence of the methyl groups in 1, R=Bu^t (in DMSO, δ=1,32ppm (2Me), and δ=1,19ppm (1Me)).

As can be inferred from the values of ΔH and ΔS calculated within the temperature ranges cited,[4] the higher or lower percentage of bicyclic compound is determined by the term $T\cdot\Delta S$. In fact, ΔH keeps approximately constant within each series, whereas ΔS becomes less and less negative. This may be interpreted to the effect that the bulky group obliges the azide group to adopt the proper arrangement for the cyclization, thus the entropy loss from 1 to 2 is smaller, or that the presence of azide group restricts the internal rotation of COR, Table. Thermodynamic data from NMR spectra[4]

	DMSO-d_6		acetone-d_6	
	ΔH (kcal/mole)	ΔS (e.u.)	ΔH (kcal/mole)	ΔS (e.u.)
R=Me	-2,0±0,2	-8,0±0,6	-1,3±0,3	-8,1±1,1
R=Et	-2,0±0,2	-7,5±0,6	-1,2±0,3	-7,4±1,0
$R=Pr^i$	-1,9±0,4	-6,2±1,3	-1,1±0,3	-6,4±1,0
$R=Bu^t$	-1,8±0,3	-4,8±1,0	-1,2±0,2	-5,0±0,7

and this the more the bulkier R is; when azide cyclizes to tetrazole this hindering decreases considerably, whereby the entropy loss due to the cyclization is partly offset by the entropy gain due to the rotation of COR. The fact that in the case $R=Bu^t$ the three methyls of 2 are equivalent and those of 1 are not, confirms this last assumption.[6]



When the measures of K_T are obtained in a wider temperature range (up to 100ºC, in DMSO), the representation of log K_T versus 1/T *takes the form of the showed figure. It* can be seen from this figure that there is a change in slope, particularly marked for $R=Bu^t$ and $R=Pr^i$, when going from temperatures close to room temperature to above ~40ºC. The values of K_T obtained in the *range from* 60ºC to 100ºC are not very reliable, because a partial decomposition of the product is observed, but if this is ignored, the values calculated for ΔH (R=Me, -2,9±0,5 kcal/mole; R=Et, -3,1±0,5; $R=Pr^i$, -3,6±0,5; $R=Bu^t$, -4,0 ±0,5), and for ΔS (about 11-12 e.u. in all cases), seem to indicate that at high temperatures the equilibrium position is preferentially determined by the enthalpic term.

REFERENCES AND FOOTNOTES

1.- E. Alcalde & R. Claramunt, Tetrahedron Letters, 1975, 1523.
2.- R. Granados, M. Rull, & J. Vilarrasa, J. Heterocyclic Chem., 13, 281 (1976).
3.- M. Rull & J. Vilarrasa, J. Heterocyclic Chem., submitted for publication.
4.- Perkin-Elmer R-12B NMR-spectrometer. Values calculated from the variation of K_T *with* temperature (range: 15-45ºC in DMSO, 0-40ºC in acetone).
5.- Sample obtained by recrystallization in acetone of mixture $1 \rightleftharpoons 2$, $R=Bu^t$.
6.- The conformational study of these compounds will be reported at a later date.