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STUDY AND CHARACTERIZATION OF TAUTOMERIC TRIAZOLIUM YLIDS

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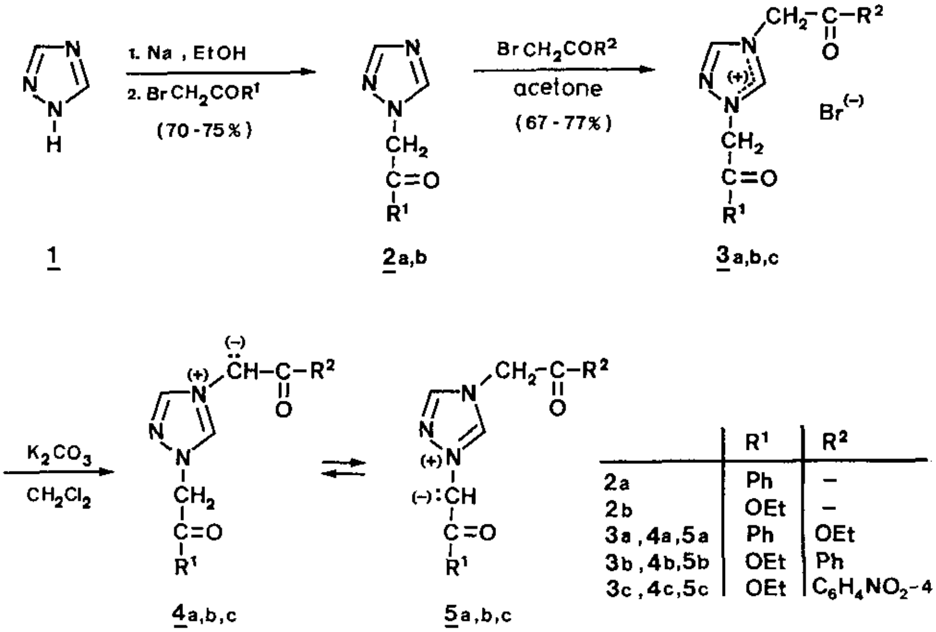
Abstract - *The presence of two tautomeric forms in equilibrium for some triazolium ylids has been revealed by nmr spectroscopy and confirmed by trapping with picryl chloride.*

As a part of our studies dealing with the structure and reactivity of cycloimmonium ylids[1] we were particularly interested in the synthesis and chemical properties of triazolium ylids.[2] The unsymmetrical distribution of the three nitrogen atoms in a five-membered heterocyclic framework such as 1,2,4-triazole (1) appeared to be particularly suitable to reveal the different tautomeric ylids. We have thus linked successively two methylene groups bearing various functions (keto and ester) on the 1- and 4-N atoms of the triazole ring giving rise to the different salts (3a,b,c), as shown in Scheme 1.

Due to the presence of two possible deprotonation sites in the salts (3a,b,c) their treatment with potassium carbonate or triethylamine[3] gives rise to a mixture of the ylids (4a,b,c) and (5a,b,c) (Scheme 1).



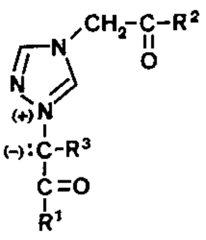
	R^1	R^2
2a	Ph	–
2b	OEt	–
3a ,4a,5a	Ph	OEt
3b ,4b,5b	OEt	Ph
3c ,4c,5c	OEt	$C_6H_4NO_2$-4

Scheme 1

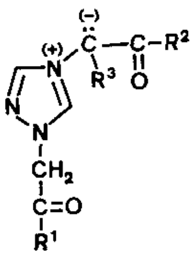
Table 1. ^{1}H Nmr Analysis (400 MHz, 23°C) of Ylids 4 + 5.

	Product distribution		Chemical shift (ppm)			
Ylid	DMSO-d_6	Acetone-d_6	CH_2	H_{ylidic}	H_3	H_5
4a	45	-	5.92	6.95	8.81	9.45
5a	55	-	5.38	7.16	8.88	10.38
4b	39	55	5.50	6.95	8.52	9.40
5b	61	45	5.10	7.15	8.85	10.40
4c	34	-	5.56	7.05	8.82	9.42
5c	66	-	5.17	7.36	8.79	10.42

^1H Nmr analysis clearly reveals the presence of two tautomeric forms and permits unambiguously to determine the composition of the reaction mixture (Table 1). The assignment of the different signals to the structure (4) and (5) was made on the basis of the chemical shift of the remaining methylenic protons. The use of partially deuterated 2-bromoacetophenone ($Br\text{-}CD_2\text{-}CO\text{-}C_6H_5$) in the synthesis of the salts clearly establishes that the protons of the methylene connected to the keto group are more deshielded than those of the methylene bound to the ester group. The difference between the chemical shift of 3-H and 5-H protons which is more important in the ylidic form (5) can be ascribed to a greater disymmetry of this form. Except one analysis performed in acetone-d_6, the determination of the composition of the mixture is only significant with DMSO-d_6 as solvent. Indeed with others solvents the tautomeric equilibrium is noticeably disturbed by the dimerization of the ylids.[4] However the presence of such an equilibrium can be confirmed using classical chemical reactions and specially the substitution of the hydrogen located on the ylidic carbon atom by picryl chloride, a well known reaction in ylid chemistry.[3,5] Thus any mixture of ylids 4 + 5 gives rise exclusively to one disubstituted ylid (6a), (7b) or (7c) respectively in which the picryl moiety is solely connected to the ylidic carbon atom bearing the keto group. Ylids (6) and (7) were characterized by ^1H and ^{13}C nmr spectroscopy.[6] In particular the chemical shift of the C-atom of the ester function (COOEt) is not affected (δ ca 165 ppm) whereas the chemical shift of the ketonic C-atom is shielded due to the proximity of the ylidic C -atom (δ ca 175 ppm, Table 2).



6a



7b,c

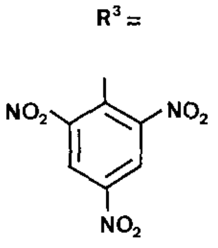


Table 2. Comparison of the chemical shifts of the carbon atoms in ester and ketone groups for salts (3) and ylids (6) and (7).

Compound	$\delta_{(\underline{C}=O)}$ (ppm) Ester	Ketone
3a	166.05	190.27
6a	165.66	178.56
3b	165.80	190.34
7b	165.90	176.03
3c	165.71	189.65
7c	165.20	174.94

To our knowledge the work reported here represents the first revealed tautomeric equilibrium in the cycloimmonium ylids series.

REFERENCES

1. G. Surpateanu, J. P. Catteau, P. Karafiloglou, and A. Lablache-Combier, Tetrahedron, 1976, 32, 2647 ; G. Surpateanu and A. Lablache-Combier, Heterocycles, 1984, 22, 2079.
2. G. Surpateanu, A. Lablache-Combier, P. Grandclaudon, and B. Mouchel, Heterocycles, 1987, 26, 863.
3. F. Kröhnke, Ber., 1935, 68, 1177 ; ibid, 1937, 70, 543 ; A. W. Johnson, "Ylid Chemistry," Academic Press Inc., New-York, 1966, pp. 251-281 ; I. Zugravescu and M. Petrovanu, "N-Ylid Chemistry," Mc Graw-Hill, New-York, 1976.
4. H. Albrecht, J. Froehlich, V. Hobermoltz, and F. Kröhnke, Tetrahedron Lett., 1967, 3649.
5. M. Petrovanu, G. Surpateanu, M. Bourceanu, and V. Barboiu, Tetrahedron, 1985, 41, 3673 and references cited therein.
6. Ylids (6) and (7) exhibited spectroscopic data (ir, nmr and ms) in accord with the assigned structure and gave satisfactory microanalyses.

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