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REACTIVITY OF CYCLOIMMONIUM YLIDES

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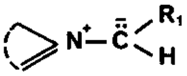
1. INTRODUCTION

Ylides are zwitterionic compounds in which an anion is covalently bonded to a positive charged heteroatom. There are many classes of ylides, but in this paper we refer only to the cycloimmonium ylides of the types (1) and (2).



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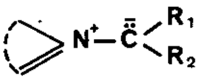

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The positive nitrogen atom belongs to an azaheterocycle. The R_1 and R_2 radical bonded to the ylide carbon atom are strong electron with-drawing groups : CN, $CONH_2$, COR, COOR, etc....

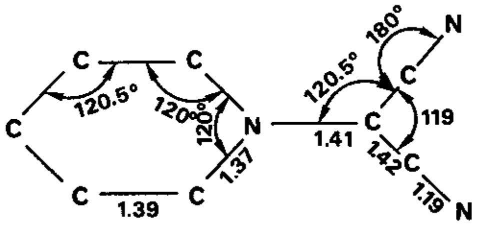
The cycloimmonium ylides can themselves be classified in carbanion monosubstituted 1 and carbanion disubstituted 2 cycloimmonium ylides, by the nature of the carbanion[1].

2. STRUCTURE OF CYCLOIMMONIUM YLIDES

In the litterature are limited date on the molecular structure of ylide systems.

2.1. The X-ray diffraction spectra

The data obtained from X-ray diffraction spectra of pyridinium dicyanomethylide crystal[2] are as follow :



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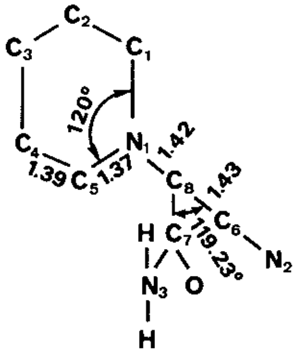

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The pyridinium ring is coplanar with the ylide carbon atom. The two cyano groups are both in a same plane which make an angle of 3° with the ring one. All the distances measured in the molecule are known with an accuracy of ± 0.01 Å. The ylide C-N bond length (1.41 Å) is smaller than that expected (1.42 Å). This is almost the same as the bond length of the single C-C bond (sp-sp^2)

in acrylonitrile (1.426 Å) but much smaller than the single C-C ($sp-sp^2$) bond in propionitrile (1.458 Å).

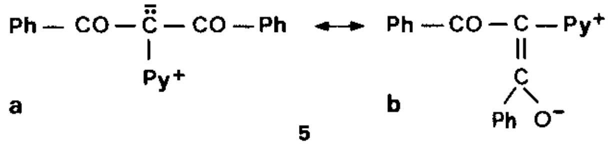
It can be concluded from these data that the ylide C atom is almost trigonally hybridised and that there is a weak interaction between the pyridine ring and the carbanion. Similar data[3] by X-ray diffraction spectra, on the geometry of ylide 4 have been obtained.

The ylide carbon atom is deviated with -0.0804 Å in respect to the plane described by the $C_6H_7N_1$ atoms. We find in the ylide 4 for the common structural elements, the geometry of ylide system 3. The ylide carbon atom has a trigonal configuration.

2.2. The IR spectra of cycloimmonium ylides

The existence of some cycloimmonium ylides as isolable stable compounds is due to the delocalization of positive and negative charges on the heterocycle and carbanion respectively[4].

IR spectra of some cycloimmonium ylide in Nujol or chloroformic solution are complex[5,6]. In the spectra of ylide 5 (Py = pyridine) an absorption band to 1490 cm^{-1} ($\nu_{C=C}$) is found.



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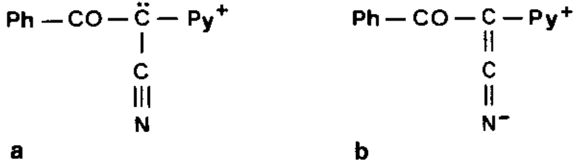
Ylide 6 presents an absorption band to 2166cm^{-1} (ν_{CN}).



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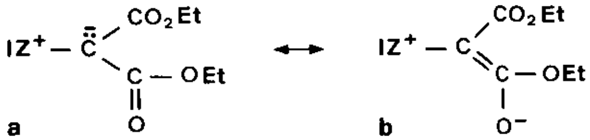
These two absorption bands may be explained respectively by the contributions of resonance structures 5b and 6b.

Similar deplacements for the estheric or carbonilic $\nu_{C=O}$ are observed[7]. In the ylide 7 the $\nu_{C=O}$ appears at 1600 cm^{-1} (iz = isoquinoline).



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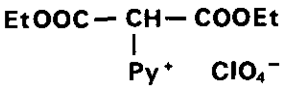
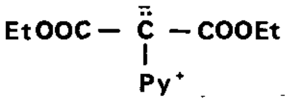
2.3. H-NMR spectra of cycloimmonium ylides

The NMR spectra of cycloimmonium ylides are complex. In the perchlorate 8 the chemical shift of the δ pyridinic ring protons is at δ = 9.21 ppm (DMSO d_6).



$$\underset{\displaystyle Py^{+}\quad ClO_4^{-}}{EtOOC-CH-COOEt}$$

8



$$\underset{\displaystyle Py^{+}}{EtOOC-\overset{-}{\ddot{C}}-COOEt}$$

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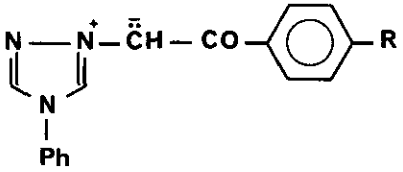

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The chemical shift of the protons of ylide 9[1] is δ = 8.63 ppm ($CDCl_3$). The width of H-NMR spectra of hydrogens bonded to the ylide carbon atom in cycloimmonium monosubstituted ylides of the type 10 is large[8]. That suggests the existence of diastereoisomers at the $\overset{+}{N}-\overset{-}{C}$ bond in asymmetrical ylides systems.

2.4. UV-vis spectra of cycloimmonium ylides

All known cycloimmonium ylides are coloured compounds. They present intensive absorption bands in visible range. These absorption bands are assigned to an intramolecular charge transfer[9,10].

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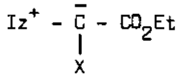
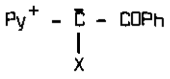
The variation of visible absorption band positions is related to the solvent Z parameter (empirical polarisability). This is the dominant argument in favour of formation of intramolecular charge transfer complex[11, 12, 13]. There is a correlation between group electro-negativities χ and *the energies of the absorption maximum bands in visible*[14, 15, 16].

A linear relationship between the Pauling scale atomic electro-negativity of H, Cl, Br (χ) and the difference energie ΔE [ΔE being the difference between the maximum absorption energy of isoquinolinium ylides having X = Br, Cl and those of the isoquinolinium ylide with X = H], have been established.

Using the relation in Table 1 the group electro-negativity of the substituent X were determined. This procedure was extended to the other ylide systems (Table 1). All studied ylides have as common structural elements the heterocyclie and a group R and differ only by the nature of substituent X.

The group electro-negativity values obtained by this procedure are in good agreement with another values deduced by different theoretical or spectral procedures[17].

Table 1. Group electro-negativities

Ylide system	Substituent	Electro-negativity
	X	χ
 $Iz^+ - \bar{C}(X) - CO_2Et$	H	2,20
	CSNHPh	2.52
	$SO_2C_6H_4CH_3$	2.74
	CONHPh	2.82
	SO_2Ph	2.86
$\chi = 0.07\ Et + 2.3$	$CO_2C_2H_5$	2.93
	$COCH_3$	3.07
	$COC_3H_7(n)$	3.08
	COPh	3.10
	CN	3.14
 $Py^+ - \bar{C}(X) - COPh$	$COCH_3$	3.07
	COPh	3.10
	CN	3.16

3. MOLECULAR ORBITAL CALCULATIONS ON THE CYCLOIMMONIUM YLIDES

The exact knowledge of the spatail structures of cycloimmonium ylides 3 and 4 allows us to perform molecular orbital (MO) calculations by the CNDO[2,18] and EHMO[19] procedure methods. Generaly, whatever the ylide structure, the geometries of these systems are maintained constant at the ylide carbon atom. Geometry of the azaheterocycles and of the ylidic carbon atom substituents were approximated by the data described in literature[1].

3.1. MO calculations for the carbanion monosubstituted cycloimmonium ylides

In the Table 2 are given the geometries of a series of monosubstituted cycloimmonium ylides, used in CNDO/2 calculations[20].

Table 2. The geometries of some monosubstituted carbanion cycloimmonium ylides

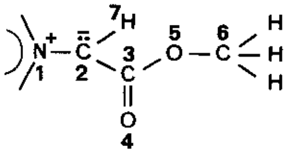
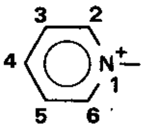
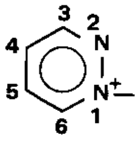
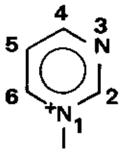
Group	Lengths	in Å	Angles in degrees		Ref.
	$r_{N_1C_2}$	1.41	$N_1C_2H_7$	120°	21
	$r_{C_2C_3}$	1.50	$N_1C_2C_3$	120°	
	$r_{C_3O_4}$	1.22			
	$r_{C_3O_5}$	1.43			
	$r_{O_5C_6}$	1.34			
	r_{CH}	1.08			
	r_{NC}	1.353	$C_2N_1C_6$	112°	22
	r_{CC}	1.39	$N_1C_2C_6$	120°	
	r_{CH}	1.08	$C_2C_3C_4$	119°	
			$C_3C_4C_5$	120°	
	r_{NN}	1.525	$N_1N_2C_3$	117.2°	
	r_{NC}	1.33	$N_2C_3C_4$	120°	
	r_{CC}	1.34	$C_3C_4C_5$	122.4°	
	r_{CH}	1.08			
	$r_{N_1C_2}$	1.32	$N_1C_2N_3$	128°	23
	$r_{C_2N_3}$	1.32	$C_2N_3C_4$	114°	
	$r_{N_3C_4}$	1.32	$N_3C_4C_5$	125.5°	
	$r_{C_4C_5}$	1.36	$C_4C_5C_6$	113°	

Table 2 : continued

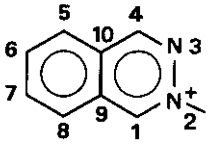
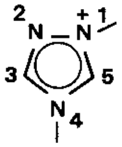
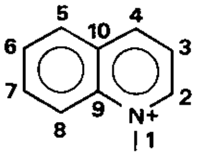
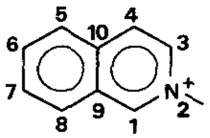
Group	Lenghts	in Å	Angles in degrees		Ref.
	$r_{C_5C_6}$ $r_{N_1C_6}$ r_{CH}	1.36 1.32 1.08	$C_5C_6N_1$ $C_6N_1C_2$	125.5° 114°	
	$r_{C_1N_2}$ $r_{N_2N_3}$ $r_{N_3C_4}$ $r_{C_4C_{10}}$ $r_{C_{10}C_5}$ $r_{C_5C_6}$ $r_{C_6C_7}$ $r_{C_8C_9}$ $r_{C_9C_{10}}$ $r_{C_1C_9}$ r_{CH}	1.37 1.34 1.36 1.42 1.42 1.36 1.345 1.42 1.39 1.40 1.08	$C_1N_2N_3$ $N_2N_3C_4$ $C_4C_{10}C_9$ $C_{10}C_5C_6$ $C_5C_6C_7$ $C_6C_7C_8$ $C_7C_8C_9$ $C_8C_9C_{10}$ $C_{10}C_9C_1$ $C_9C_1N_2$	121.6° 120.9° 119° 119.5° 121.5° 121.5° 119.5° 119° 119° 120°	
	$r_{N_1N_2}$ $r_{N_2C_3}$ $r_{C_3N_4}$ r_{CH}	1.40 1.30 1.36 1.08	$N_1N_2C_3$ $N_2C_3N_4$ $C_3N_4C_5$	128.5° 106.5° 70°	24
	$r_{N_1C_2}$ $r_{C_2C_3}$ $r_{C_3C_4}$ $r_{C_4C_{10}}$ $r_{C_{10}C_5}$ $r_{C_5C_6}$ $r_{C_6C_7}$ $r_{C_7C_8}$ $r_{C_8C_9}$ $r_{C_9C_{10}}$ r_{CH}	1.33 1.38 1.40 1.42 1.42 1.35 1.34 1.35 1.42 1.39 1.08	$C_9N_1C_2$ $N_1C_2C_3$ $C_2C_3C_4$ $C_4C_{10}C_9$ $C_{10}C_5C_6$ $C_5C_6C_7$ $C_7C_8C_9$ $C_8C_9C_{10}$	119° 121° 120° 115° 119.3° 121.5° 119.3° 124°	

Table 2 : continued

Group	Lengths	in Å	Angles in degrees		Ref.
	$r_{C_1N_2}$	1.37	$C_1N_2C_3$	121.6°	
	$r_{N_2C_3}$	1.34	$N_2C_3C_4$	120.9°	
	$r_{C_3C_4}$	1.36	$C_4C_{10}C_4$	119°	
	$r_{C_4C_{10}}$	1.42	$C_{10}C_5C_6$	119.5°	
	$r_{C_{10}C_5}$	1.42	$C_5C_6C_7$	121.5°	
	$r_{C_5C_6}$	1.36	$C_6C_7C_8$	121.5°	
	$r_{C_6C_7}$	1.345	$C_7C_8C_9$	119.5°	
	$r_{C_7C_8}$	1.36	$C_8C_9C_{10}$	119°	
	$r_{C_8C_9}$	1.42	$C_{10}C_9C_1$	119°	
	$r_{C_9C_{10}}$	1.39	$C_9C_1N_2$	120°	

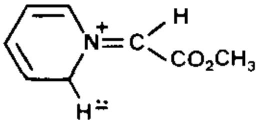
In all these ylides the hydrogen and carbomethoxy group bonded to the ylide carbon atom is the constant structural element. This ylidic carbon atom is successively bonded to pyridine, isoquinoline, quinoline, pyridazine, pyrimidine, phthalazine and 4-phenyl-1,2,4-triazole.

Using CNDO/2 procedure method the total atomic charges, the frontier molecular orbital energies HOMO *(the higest occupied molecular orbital)* and LUMO (the lowest unoccupied molecular orbital), and the atomic orbital coefficients of some atoms, which are potential reaction centers, have been calculated.

A survey of the Table 3 data leads to the *following conclusions : the ylide carbon atoms are* significantly charged negative. Their atomic total charges have negative values in the range 0.2602-0.3801. The ylide nitrogen atoms are charged positively. Their values are in the range 0.1623-0.2876.

The total atomic charges of cyclic carbon atoms adjacent to the ylide nitrogen atom have unsignificant positive or negative values. The total atomic charges of the cyclic nitrogen atoms adjacent to the nitrogen ylide atom in pyridazinium, phthalazinium and 4-phenyl-1,2,4-triazolium ylides 4,6 and 7 (Table 3) have small negative values.

We may thus conclude that the resonance interaction between carbanion and azaheterocycle (for example structures 12 and 13) are unsignificant. All these data allow us to consider that the positive and negative charges are respectively strongly delocalized on the heterocycle and the carbanion. The values of the atomic orbital coefficients of ylide carbon atom in frontier molecular orbitals HOMO and LUMO are important 0.6738-0.7379. This suggests a great reactivity at the ylide carbon atom.



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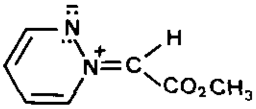

13

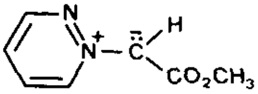

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Table 3. The frontier orbital energies, the total atomic charges and the p_z orbital coefficients

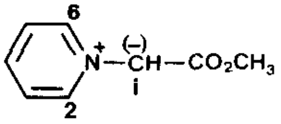
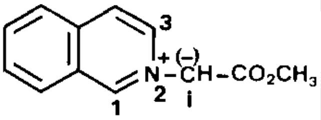
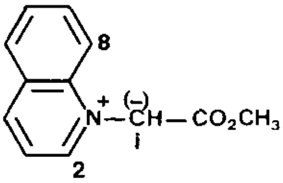
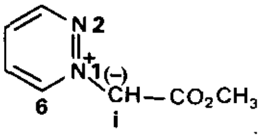
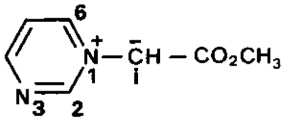
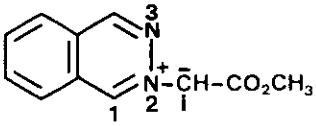
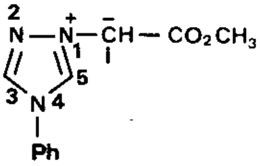
N°	Molecule	Frontier orbital and atomic charge	Orbital energy (eV)	Atomic orbital coefficients			
1				N_1	C_2	C_6	C_i
		HOMO	-8.79171	-0.0616	-0.3086	0.3111	0.7271
		LUMO	2.04585	-0.5711	0.2800	0.3375	0.2545
		Q		0.2195	0.0143	0.0147	0.2875
2				N_2	C_1	C_3	C_i
		HOMO	-9.08205	0.0955	0.3959	0.1725	-0.6985
		LUMO	0.5883	-0.4502	0.4651	-0.0717	0.2338
		Q		0.1940	-0.0113	0.0002	-0.2824
3				N_1	C_2	C_8	C_i
		HOMO	-0.8166	0.1104	0.3413	0.0689	-0.7007
		LUMO	0.7716	0.4810	-0.2921	-0.2983	-0.2519
		Q		0.2032	0.0019	-0.0042	-0.2719
4				N_1	N_2	C_6	C_i
		HOMO	-9.5723	0.0259	0.3390	-0.3177	-0.7123
		LUMO	1.1897	0.5558	-0.4620	-0.0929	-0.2906
		Q		0.2876	-0.1343	-0.0066	-0.2602

Table 3 : continued

N°	Molecule	Frontier orbital and atomic charge	Orbital energy (eV)	Atomic orbital coefficients				
5				N_1	N_3	C_2	C_6	C_i
		HOMO	-9.4564	0.0828	-0.0594	0.2806	0.2844	-0.7379
		LUMO	1.3796	0.5433	-0.3179	-0.1812	-0.4646	-0.2389
		Q		0.1623	-0.1060	0.0914	0.0736	-0.2999
6				N_2	N_3	C_1	C_i	
		HOMO	-9.1237	-0.0619	-0.1819	-0.4232	0.6738	
		LUMO	0.5514	0.3948	0.1423	-0.4435	-0.2275	
		Q		0.2452	-0.1061	-0.0459	-0.2611	
7				N_2	N_1	N_4	C_5	C_i
		HOMO	-8.4496	0.2442	-0.1112	-0.1650	-0.3835	0.7356
		LUMO	2.0158	-0.1943	-0.2762	-0.2338	0.3916	0.1326
		Q		-0.0647	0.2432	-0.1246	0.0179	-0.3081

3.2. MO calculations for the disubstituted carbanion cycloimmonium ylides

The MO calculations, CNDO/2 procedure method on the disubstituted cycloimmonium ylides have been performed (Table 4)[26]. The studied ylides have the same carbanion (two carbomethoxy groups bonded to the ylide carbon atom), bonded to the pyridine, isoquinoline, pyridazine, pyrimidine, phthalazine and 4-phenyl-1,2,4-triazole.

The geometries of the ylide systems in which the ylide carbon bonded hydrogen have been substituted by a symmetrical disposed carbomethoxy group have been approximated. In each case the ylide carbon atom keep the trigonal configuration. From data presented in Table 4 one observes that the ylide carbon atom have negative total atomic charges in the range of 0.2214-0.2783. The ylide nitrogen atoms are positively charged, their total atomic charges being in the range of 0.1406-0.2648. The values of total atomic charges of the adjacent carbon and nitrogen atoms in heterocycle are unsignifiant. That, permit us to conclude that even for the disubstituted carbanion cycloimmonium ylides, the resonance interaction is not a dominant stabilization factor.

Table 4. The frontier orbital energies, the total atomic charges and p_z orbital coefficients

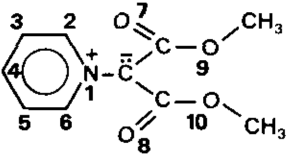
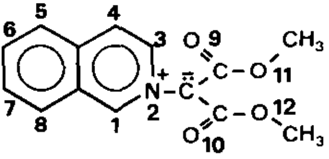
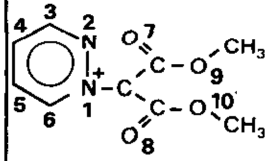
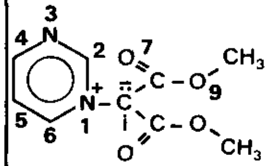
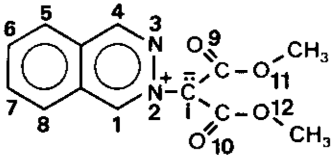
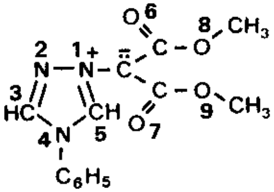
N°	Molecule	Frontier orbital and atomic charge	Orbital energy	Atomic orbital coefficients							
				N_1	C_2	C_6	C_i	O_7	O_8	O_9	O_{10}
1		HOMO	-10.36980	+0.1071	+0.2434	+0.2435	-0.6411	+0.4306	+0.4306	+0.0168	+0.01689
		LUMO	0.29018	+0.5739	-0.4063	-0.4062	-0.2048	+0.1381	+0.1381	+0.0405	+0.0405
		Q		+0.1406	+0.0190	+0.0191	-0.2672	-0.3548	-0.3548	-0.2486	-0.2486
2				N_2	C_1	C_3	C_i	O_9	O_{10}	O_{11}	O_{12}
		HOMO	- 9.70682	-0.1360	-0.3506	-0.1334	+0.6555	-0.3722	-0.3649	-0.0514	-0.0557
		LUMO	- 0.23409	-0.4868	+0.5048	+0.0226	+0.1909	-0.1259	-0.1350	-0.0369	-0.0316
		Q		+0.1462	+0.0217	+0.0249	-0.2783	-0.3796	-0.3750	-0.2304	-0.2324
3				N_1	N_2	C_6	C_i	O_7	O_8	O_9	O_{10}
		HOMO	-10.19021	-0.0476	-0.2895	-0.2661	+0.6671	-0.3811	-0.3949	-0.0469	-0.0342
		LUMO	0.45075	-0.5650	+0.4808	+0.1708	+0.2287	-0.1596	-0.1553	-0.0444	-0.0392
		Q		+0.2487	-0.0844	+0.0112	-0.2624	-0.3701	-0.3533	-0.2282	-0.2320
4				N_1	C_2	C_6	C_i	O_7	O_8	O_9	O_{10}
		HOMO	- 9.82031	-0.0995	-0.2533	-0.2453	-0.6961	-0.3842	-0.3802	-0.0617	-0.0561
		LUMO	1.12724	-0.5228	+0.1861	+0.4758	+0.1642	-0.1277	-0.1298	-0.0373	-0.0345
		Q		+0.1881	+0.1154	+0.0873	-0.2639	-0.3990	-0.3956	-0.2307	-0.2325

Table 4 : continued

N°	Molecule	Frontier orbital and atomic	Orbital energy (eV)	Atomic orbital coefficients							
				N_2	N_3	C_1	C_i	O_9	O_{10}	O_{11}	O_{12}
5		HOMO LUMO Q	- 9.47529 0.29132	-0.0909 +0.3820 +0.2648	-0.1632 +0.1318 -0.0765	-0.3701 -0.4660 -0.0272	+0.6546 -0.1621 -0.2214	-0.3744 +0.1017 -0.3899	-0.3482 +0.1170 -0.3918	-0.0429 +0.0295 -0.2353	-0.0647 +0.0275 -0.2284
				N_1	N_2	C_5	C_i	O_6	O_7	O_8	O_9
6		HOMO LUMO Q	- 9.15840 1.47544	-0.1283 -0.3279 +0.2300	-0.1407 -0.1814 -0.0838	-0.3259 +0.4639 +0.0562	+0.6854 +0.1059 -0.2624	-0.3721 -0.0873 -0.4129	-0.3979 -0.0744 -0.3899	-0.0657 -0.0222 -0.2319	-0.0433 -0.0229 -0.2412

The absolute values of atomic orbital coefficients of ylide carbon atom in HOMO orbitals are in the range of 0.6411-0.6961.

It can be concluded from the total atomic charges and atomic orbital coefficients that the ylide carbon atoms of disubstituted carbanion cycloimmonium ylides are nucleophilic reagent.

A comparative analysis of total atomic charges and atomic orbital coefficients of ylide carbon atoms in HOMO orbitals for each pair mono and disubstituted cycloimmonium ylides (for example : ylide 1 (Table 3)-ylide 1 (Table 4) shows clearly that the nucleophilic character of monosubstituted cycloimmonium ylides is larger then the one of disubstituted cycloimmonium ylides.

We shall now discuss of two types of reactions of previously described cycloimmonium ylides :

1) the cycloimmonium ylides as nucleophilic reagents and

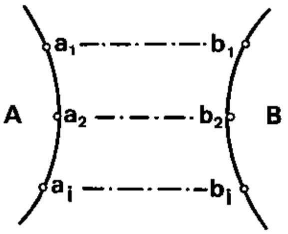
2) the cycloimmonium ylides as dipole in cycloadditions.

4. CYCLOIMMONIUM YLIDES AS NUCLEOPHILIC REAGENTS

Before discussing this question, we present some general aspects on the calculation of interaction energy ΔE in generalized perturbation theory[27,28,29].

For an interaction between two closed shell molecular systems A and B by their atoms a and b, respectively (Figure 4.1), the energy ΔE is calculated as follow :

Figure 4.1. The interaction between two molecular systems A and B



Equation 4.1.

$$\Delta E = -\sum_{ij}(q_i+q_j)\beta_{ij}S_{ij} + \sum_{a_i<b_i}\frac{Q_{ai}Q_{bj}}{\varepsilon R_{a_ib_j}}\alpha - \left[\sum_{\mu}^{OCC.2a}\sum_{\nu}^{UNOCC.b} - \sum_{\mu}^{UNOCC.a}\sum_{\nu}^{OCC.2b}\right]\frac{2}{b_\nu - a_\mu}$$

$$\sum_{ij}\left[A_{\mu i}B_{\nu j}\beta_{a_ib_j}\right]^2$$

where : q_i and q_j are the electron populations in the atomic interacting orbitals i and j of a and b atoms.

β_{ij} and S_{IJ} are the resonance and overlap integrals respectively

Q_{ai} and Q_{bj} are total atomic charges on the interacting atoms a and b.

ε is the local dielectric constant.

$R_{ai\ bj}$ are the distance between interacting atoms a and b.

$A_{\mu i}$ and $B_{\nu j}$ are the atomic orbital coefficients belonging to the interacting orbitals of the atoms a and b, in molecular orbitals μ and ν of A and B, respectively.

a_μ and b_ν are the energies of the molecular orbitals μ and ν respectively.

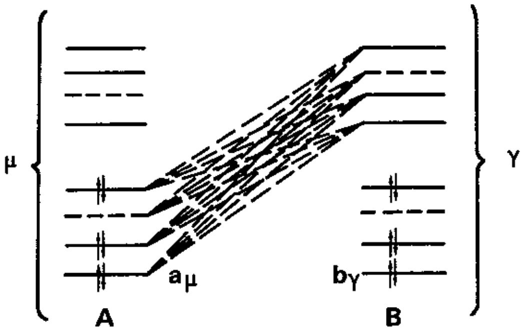
α is a constant ($\alpha = 14.4$) which permits the calculation of the second term of equation 4.1 in electron-volts (eV), when the total atomic charges and interatomic distances in the atomic units (UR) and Angströms (Å) respectively, are given.

$\sum_{i,j}$ means that summation by the pair of atomic orbital i and j has been realized.

Σ shows that the product of total atomic charges between pairs of atoms a and b is made.

The summations in parenthesis of the third term of equation 4.1 indicate the kind of summation of atomic orbital coefficients $A_{\mu i}$ and $B_{\nu j}$ (Figure 4.2.).

Figure 4.2. The interaction between μ and ν molecular orbitals (the term $^{\text{occ.2a}}$ $^{\text{unocc.b}}$)



The first term of equation 4.1 is closed-shell repulsion term. The second one is a Coulombic repulsion or attraction term realized between molecular systems A and B by their interacting atoms a and b.

The third term of equation 4.1 in its general form :

$$T_3 = -\left[\sum_{\mu}^{\text{OCC.a}} \sum_{\nu}^{\text{UNOCC.b}} - \sum_{\mu}^{\text{UNOCC.a}} \sum_{\nu}^{\text{OCC.b}}\right] \frac{\delta}{b - a_\mu} \sum_{ij} \left[A_{\mu i} B_{\nu j} \beta_{ij}\right]^2$$

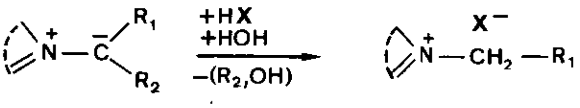
is called either delocalization or charge transfer stabilization. This last term is the second order perturbation term and it is only if $b_\nu \neq a_\mu$. When $b_\nu \approx a_\mu$, the interaction is better described in charge transfer terms and the perturbation is then a first order one of the form $2A_{\mu i}B_{\nu j}$ δ is a parameter which has different values in function of the type of interacting orbitals.

For a donor A-acceptor B reaction, the equation 4.1 becomes of the form :

$$\Delta E = T_1 + T_2 + \sum_{\mu}^{\mathrm{OCC.2a}} \sum_{\nu}^{\mathrm{UNOOC.b}} \frac{2}{b_\nu - a_\mu} \sum_{ij} \left[A_{\mu i} B_{\nu j} \beta_{a_i b_j}\right]^2$$

4.1. Protonation of the cycloimmonium ylides

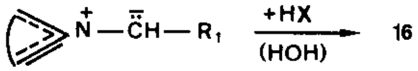
The carbanion disubstituted cycloimmonium ylides of type 15 in the presence of strong acids (H_2SO_4, $HClO_4$), in aqueous solution loses a substituent giving the cycloimmonium salt[16,30,31,32].



15 16

$R_1 = R_2 = -COC_6H_5$
$R_1 = R_2 = -COOR$
$R_1 = CN,\ R_2 = -COC_6H_5$
$R_1 = CN,\ R_2 = COOR$
$X = HSO_4^-,\ ClO_4^-$

This reaction occurs for all the azaaromatic ylides previously studied. The monosubstituted carbanion cycloimmonium ylides 17 in the same experimental conditions give the respective cycloimmonum salts 16 without loss of the substituent.



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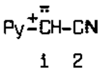
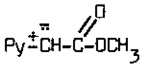
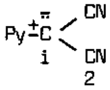
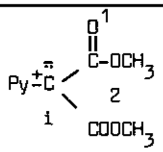
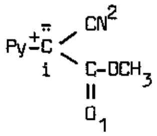
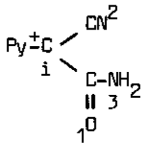
Taking into account the above experimental results, a theoretical study on the protonation of a series of mono and disubstituted pyridinium ylides has been done (Table 5)[33].

The geometries of all studied pyridinium ylides are given in the Table 5.

Table 5. The geometries of some pyridinium ylides

N°	Ylide	Lengths in Å and angles in degrees
1	 $\mathrm{Py}\overset{\pm}{-}\underset{i}{\overset{=}{\mathrm{C}}}\mathrm{H}-\underset{2}{\mathrm{CN}}$	Pyridinium rings as in ylide 3 the group HCCN : r_{CC} r_{CN} r_{C_i+C} r_{CH} 1.42 1.13 1.41 0.96 HCN HCN CCN 120° 120° 180°
2	 $\mathrm{Py}\overset{\pm}{-}\overset{=}{\mathrm{C}}\mathrm{H}-\overset{O}{\overset{/\!/}{\mathrm{C}}}-\mathrm{OCH_3}$	The group $Py\overset{\pm}{-}CH$ as in ylide 3 The group $-COOCH_3-$ as in Table 2
3		Ref. 2
4		As in Table 4
5		Ref. 32
6		Ref. 32

Using the EHMO noniterate procedure method the total atomic charges, the atomic orbital coefficients and the molecular orbital energies habe been calculated.

We give in the first part of Table 6, the total atomic charges and in the second one the square of the atomic orbital coefficients in the frontier molecular orbital. From the atomic charges in a static point one could infer that the N^2, N^3, O^1 and O^2 atoms are more reactive than the ylide carbon atoms C^i. From the atomic orbital coefficients we conclude that the same atoms are less reactive than the ylide carbon atoms. The square values C^2_{HOMO} of C^i atoms are the larger.

Table 6. The total charges and the coefficients C^2_{HOMO} for atoms in ylides involved in the protonation

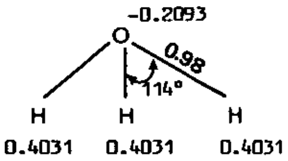
Ylide	ATOMS					
	N^2	N^2	N^3	C^i	O^1	O^2
1	0.1386	-1.1068	-	-0.2187	-	-
2	0.1256	-	-	-0.2311	-1.1802	-0.7331
3	0.1329	-0.10641	-	-0.0131	-	-
4	0.1093	-	-	-0.0276	-1.1451	-0.7178
5	0.1205	-1.0571	-	-0.0276	-1.1532	-0.7194
6	0.1199	-1.0633	-0.5604	-0.0499	-1.1730	-
1	-	0.1852		0.5165		
2	-			0.4886	0.0877	0.0571
3	-	0.1475	-	0.4242	-	-
4	-	-	-	0.4271	0.0671	0.0374
5	-	0.0467	-	0.4193	0.0668	0.0369
6	-	0.0518	0.1419	0.4173	0.0462	-

Normally, the protonation of ylides is a donor (ylide)-acceptor (hydronium cation) reaction.

In order to obtain more rigorous data on the protonation of pyridinium ylides, we applied the equation 4.3 by the calculation of energies ΔE.

The geometric of hydronium ion is those in Figure 4.3.

Figure 4.3. The geometry of hydronium cation and the total atomic charges



In the same Figure the total atomic charges of all atoms in hydronium ion are given. We supposed that a hydrogen atom of the hydronium ion interacts by its 1s orbital with $2p_z$ orbitals of different atoms in ylide carbanion. The interactin in which ΔE has minimum value (the largest absolute value) is energicaly favorized.

A survey of Equation 4.1 shows that :

Equation 4.4.

$$\Delta E = f\,(R_{a_i b_j})$$

The interaction energies ΔE, versus $Ra_i b_j$ in the range 3.3-1.5 have been calculated for all ylides presented in Table 6. The β and S integrals as functions of distances $Ra_i b_j$, are presented in papers[34-36]. The obtained numerical data are given in the Tables 7 to 12.

Table 7. ΔE values for the interaction between ylide 1 and hydronium ion (ΔE in eV)

Distances R_{AB} (Å)	The interacting atoms	
	C^1-H	N^2-H
1.5	-9.181	-9.185
1.6	-7.313	-7.646
1.7	-5.761	-6.423
1.8	-4.505	-5.464
1.9	-3.507	-4.720
2	-2.728	-4.145
2.1	-2.129	-3.700
2.2	-1.675	-3.355
2.3	-1.334	-3.084
2.4	-1.079	-2.868
2.5	-0.891	-2.694
2.6	-0.752	-2.550
2.7	-0.650	-2.429
2.8	-0.574	-2.324
2.9	-0.518	-2.233
3	-0.475	-2.146
3.1	-0.443	-2.077
3.2	-0.417	-2.009
3.3	-0.397	-1.947

Table 8. ΔE values for the interaction between ylide 2 and hydronium ion (ΔE in eV)

Distances R_{AB} (Å)	The interacting atoms		
	C^i-H	O^1-H	O^2-H
1.5	-8.692	-7.997	-6.518
1.6	-6.937	-6.708	-5.265
1.7	-5.479	-5.718	-4.317
1.8	-4.298	-4.962	-3.607
1.9	-3.360	-4.386	-3.079
2	-2.627	-3.944	-2.686
2.1	-2.063	-3.602	-2.393
2.2	-1.635	-3.333	-2.171
2.3	-1.313	-3.117	-2.001
2.4	-1.072	-2.941	-1.867
2.5	-0.894	-2.792	-1.759
2.6	-0.762	-2.665	-1.670
2.7	-0.664	-2.554	-1.595
2.8	-0.599	-2.455	-1.530
2.9	-0.536	-2.366	-1.472
3	-0.495	-2.284	-1.420
3.1	-0.463	-2.209	-1.372
3.2	-0.438	-2.139	-1.329
3.3	-0.417	-2.074	-1.288

Table 9. ΔE values for the interaction between ylide 3 and hydronium ion (ΔE in eV)

Distances R_{AB} (Å)	The interacting atoms	
	N^2-H	C^1-H
1.5	-8.902	-6.839
1.6	-7.419	-5.339
1.7	-6.239	-4.097
1.8	-5.313	-3.093
1.9	-4.591	-2.300
2	-4.032	-1.686
2.1	-3.598	-1.218
2.2	-3.260]	-0.867
2.3	-2.995	-0.608
2.4	-2.783	-0.418
2.5	-2.611	-0.282
2.6	-2.468	-0.185
2.7	-2.439	-0.117
2.8	-2.246	-0.070
2.9	-2.155	-0.037
3	-2.071	-0.016
3.1	-2.002	-0.001
3.2	-1.936	-0.007
3.3	-1.875	-0.013

Table 10. Δ E values for the interaction between ylide 4 and hydronium ion (ΔE in eV)

Distances R_{AB} (Å)	The interacting atoms		
	O^1-H	C^--H	O^2-H
1.5	-7.722	-6.722	-6.368
1.6	-6.482	-6.301	-5.145
1.7	-5.529	-4.122	-4.219
1.8	-4.801	-3.169	-3.526
1.9	-4.246	-2.415	-3.011
2	-3.820	-1.828	-2.627
2.1	-3.490	-1.379	-2.341
2.2	-3.230	-1.041	-2.124
2.3	-3.022	-0.789	-1.958
2.4	-2.851	-0.603	-1.827
2.5	-2.708	-0.468	-1.722
2.6	-2.585	-0.370	-1.635
2.7	-2.478	-0.299	-1.561
2.8	-2.382	-0.248	-1.497
2.9	-2.295	-0.212	-1.441
3	-2.216	-0.186	-1.390
3.1	-2.143	-0.167	-1.344
3.2	-2.076	-0.153	-1.301
3.3	-2012	-0.143	-1.261

Table 11. ΔE values for the interaction between ylide 5 and hydronium ion (ΔE in eV)

Distances R_{AB} (Å)	The interacting atoms			
	N^2-H	O^1-H	C^--H	O^2-H
1.5	-8.589	-7.885	-6.965	-6.636
1.6	-7.121	-6.528	-5.272	-5.168
1.7	-6.000	-5.568	-4.070	-4.236
1.8	-5.122	-4.835	-3.098	-3.540
1.9	-4.438	-4.276	-2.330	-3.021
2	-3.909	-3.847	-1.734	-2.636
2.1	-3.500	-3.515	-1.734	-2.348
2.2	-3.180	-3.253	-0.937	-2.130
2.3	-2.929	-3.044	-0.684	-1.963
2.4	-2.729	-2.872	-0.498	-1.832
2.5	-2.566	-2.727	-0.363	-1.726
2.6	-2.431	-2.604	-0.267	-1.639
2.7	-2.361	-2.495	-0.198	-1.565
2.8	-2.218	-2.399	-0.150	-1.501
2.9	-2.131	-2.312	-0.116	-1.444
3	-2.050	-2.232	-0.092	-1.393
3.1	-1.983	-2.159	-0.076	-1.347
3.2	-1.919	-2.090	-0.065	-1.304
3.3	-1.859	-2.027	-0.057	-1.264

Table 12. ΔE values for the interaction between ylide 6 and hydronium ion (ΔE in eV)

Distances R_{AB} (Å)	The interacting atoms			
	N^2-H	O^1-H	C^i-H	N^3-H
1.5	-8.589	-7.885	-6.965	-6.636
1.6	-7.170	-6.622	-5.475	-5.335
1.7	-6.041	-5.651	-4.240	-4.316
1.8	-5.155	-4.910	-3.242	-3.528
1.9	-4.467	-4.344	-2.452	-2.926
2	-3.934	-3.909	-1.839	-2.471
2.1	-3.521	-3.573	-1.370	-2.128
2.2	-3.199	-3.308	-1.017	-1.870
2.3	-2.946	-3.095	-0.755	-1.676
2.4	-2.745	-2.921	-0.563	-1.527
2.5	-2.581	-2.774	-0.423	-1.412
2.6	-2.445	-2.648	-0.322	-1.321
2.7	-2.330	-2.538	-0.250	-1.248
2.8	-2.230	-2.440	-0.198	-1.187
2.9	-2.143	-2.351	-0.168	-1.136
3	-2.061	-2.270	-0.137	-1.088
3.1	-1.994	-2.196	-0.119	-1.053
3.2	-1.930	-2.126	-0.106	-1.017
3.3	-1.870	-2.061	-0.096	-0.985

For a good understanding of these values the graphic representations in three cases are shown in the Figures 4.4, 4.5 and 4.6.

From the data in Tables 7-15 and Figures 4.4, 4.5 and 4.6, at the transition states, $Ra_ib_j \approx 1.5$ Å, we deduce that there are two different types of protonation : in the monosubstituted carbanion cycloimmonium ylides protonation occurs at ylide carbon atom ; in the disubstituted cycloimmonium ylide it occurs at the oxygen or nitrogen atom of the substituents bonded of ylide carbon atom.

The above theoretical results explain the losses of a substituent in disubstituted cycloimmonium ylides in aqueous acid solutions.

Figure 4.4. The variation of ΔE versus Ra_ib_j in reaction between cyanoamydopyridinium methylide and hydronium cation.

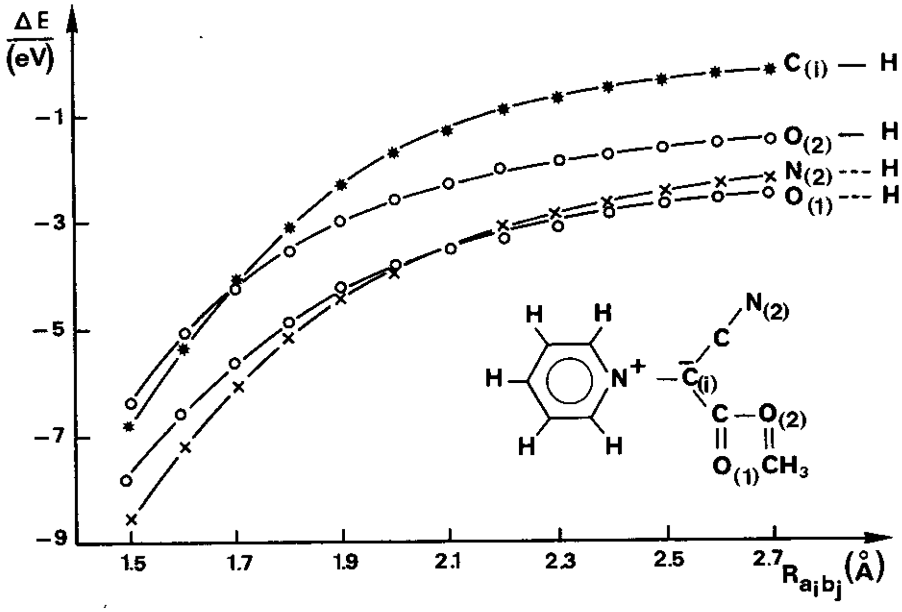


Figure 4.5. The variation of ΔE versus Ra_ib_j in reaction between ylide 4 (table 10) and hydronium cation.

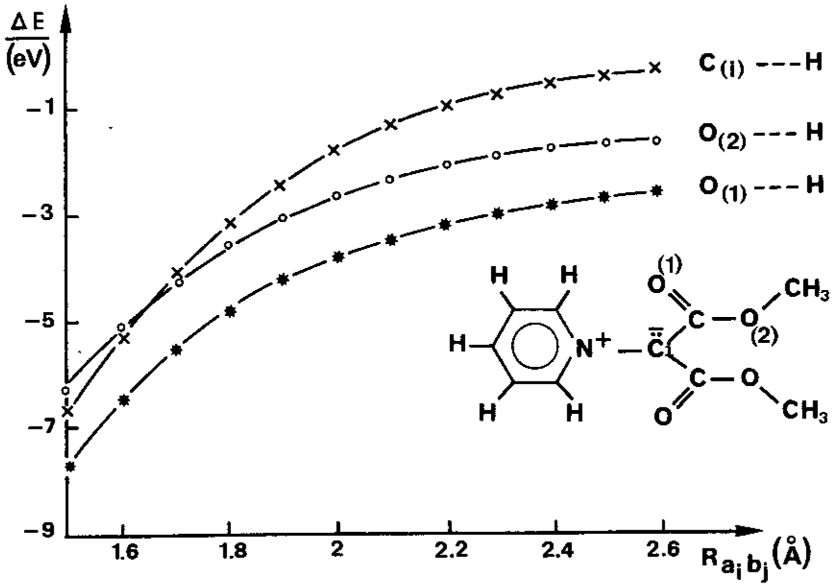
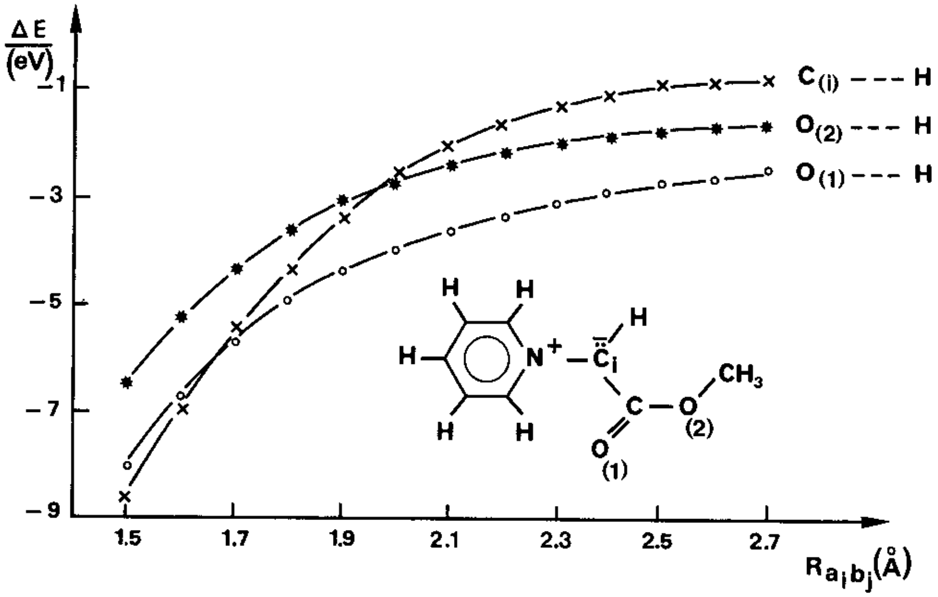
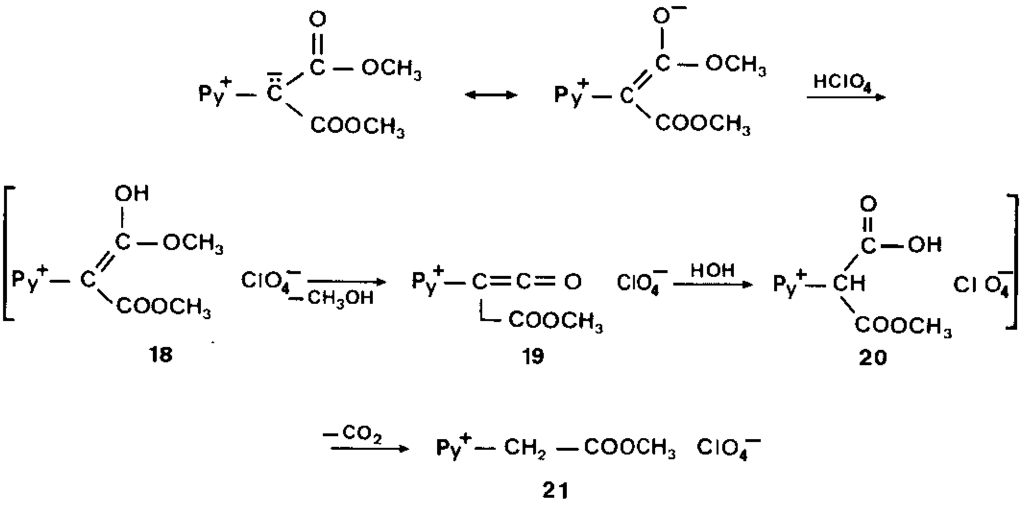
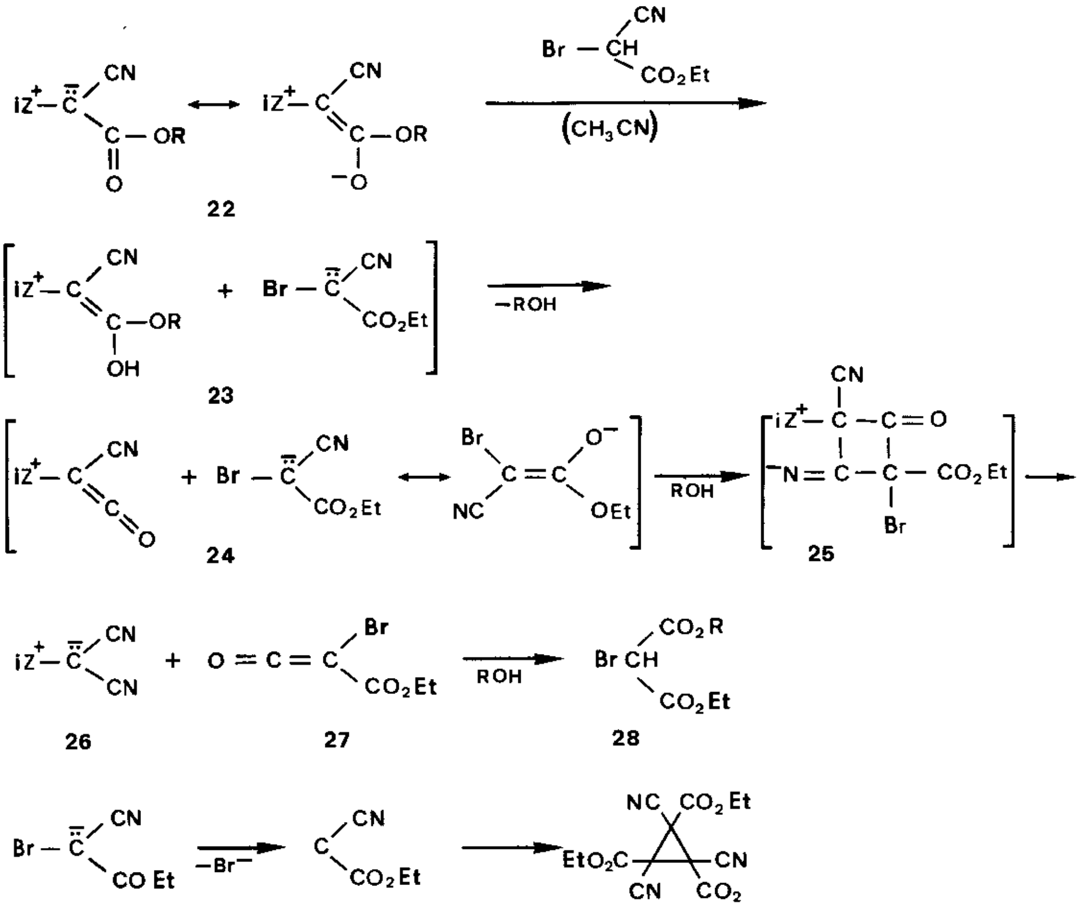


Figure 4.6. The variation of ΔE versus Ra_ib_j in reaction between ylide 3 (Table 9) and hydronium cation.

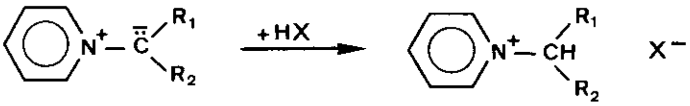




In precedent Scheme an intermediate ketene formation 19 is involved. A supplementary argument for these types of reactions is the next substituent exchange reaction.


22 23 24 25 26 27 28 29 30

Taking into consideration protonation of cycloimmonium ylides some analytical methods for quantitative determination of acids in nonaqueous organic medium have been realized[37,38].

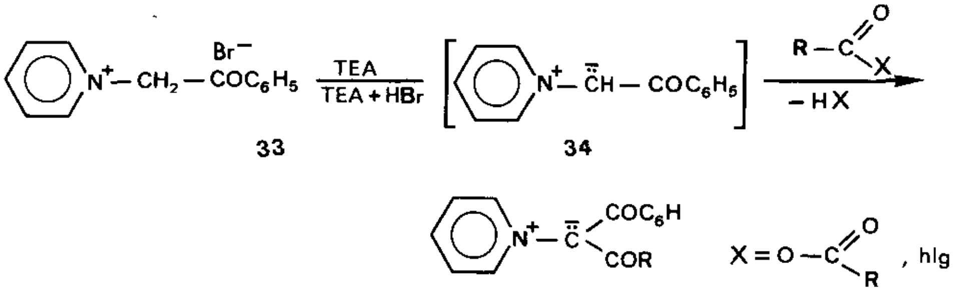

31
coloured

32
colourless

The intensively coloured cycloimmonium ylides react with acids giving colourless cycloimmonium salts 32. These reactions being reversible the ylides can be used as acid-basic indicators[39].

4.2. Acylation of the monosubstituted carbanion cycloimmonium ylides

The pronounced nucleophilic character of monosubstituted cycloimmonium ylides is evidenced by the reactions between these compounds and acyl chlorides or anhydrides[40,44].

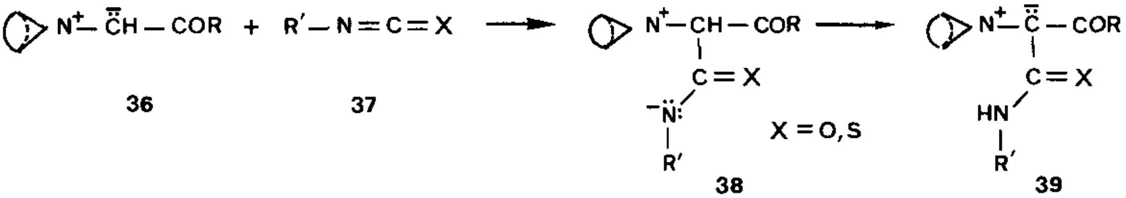


33 **34** **35**

The cycloimmonium salt 33 reacts with triethylamine (TEA) and gives "in situ" the monosubstituted cycloimmonium ylide 34, which reacts with acyl chlorides and anhydrides and gives the disubstituted cycloimmonium ylides of the type 35.

4.3. Action of isocyanates and isothiocyanates on the monosubstituted carbanion cycloimmonium ylides

Some monosubstituted pyridine[45], isoquinoline[46] and 4-phenyl 1,2,4-triazole[47], cycloimmonium ylides react with isocyanates and isothiocyanates giving the cycloimmonium disubstituted ylides, respectively.



36 **37** **38** **39**

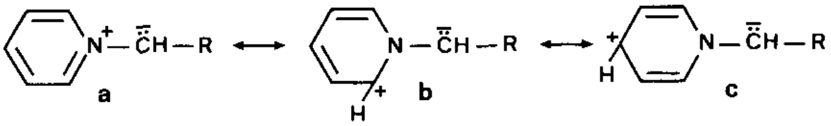
R = OEt, OMe, $-C_6H_5$ $-C_6H_4-X$(p) etc.

R = $-C_2H_5$, C_6H_5, $-C_6H_4CH_3$ (p), $-C_6H_4CH_3$(o), $-C_6H_4Br$ (p) etc.

The unstable intermediate compounds 38 leads to the stable ylides 39 by an isomerisation.

5. CYCLOIMMONIUM YLIDES AS 1,3-DIPOLE IN CYCLOADDITIONS

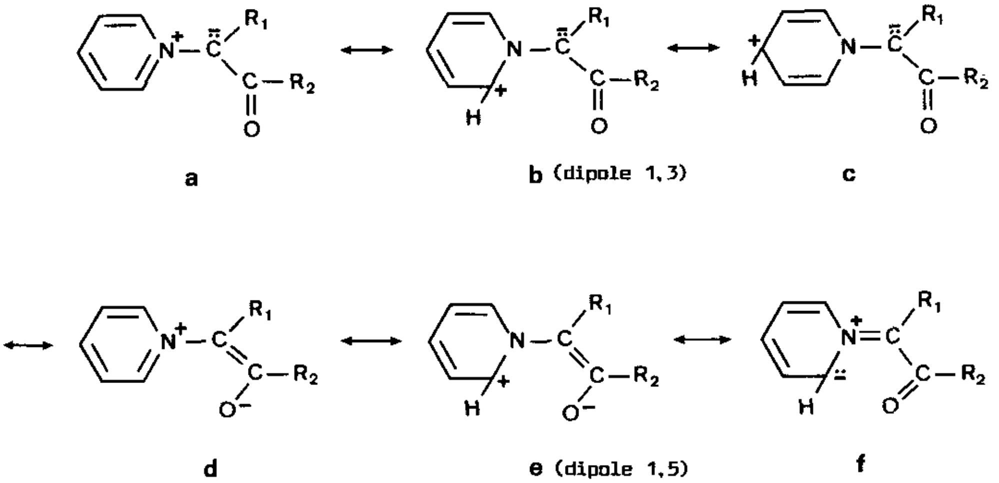
In the case of monosubstituted cycloimmonium ylides in which there are not a large delocalization of the negative charge, the following resonance structure are assumed.



40
(dipole 1,3)

The monosubstituted cycloimmonium ylides reacts by their resonance structures 40b as 1,3-diple in 3+2 cycloadditions.

For the disubstituted cycloimmonium ylides it is possible to represent a larger number of resonance structures. Among them, 41b and 41c explain the behaviour of these systems as dipoles 1,3 and 1,5 respectively.



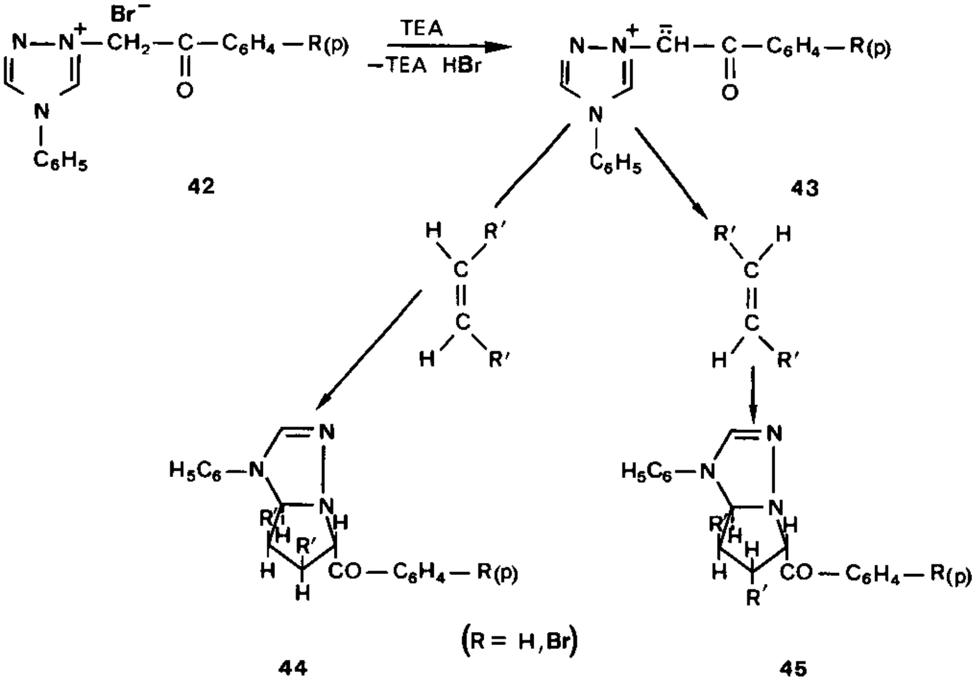
41

There are in the litterature many examples of cycloadditions where the ylides reacts as dipole 1,3.

References[25,1] and [48] deals with monograph on this subject. We shall now refer only to the theoretical and experimental data on the cycloadditions published after years 1976-1977. We present successively the stereochemistry, regiochemistry and corochemistry of cycloadditions 3+2 with cycloimmonium ylides as dipole-1,3.

5.1. Stereochemistry of [3+2]cycloadditions

Monosubstituted cycloimmonium ylides react with dimethyl fumarate and maleate giving cycloadducts. Thus, 4-phenyl-1,2,3,4-triazolium phenacyclides 43 generated "in situ" from their cycloimmonium salts 42 reacts with fumaric and maleic esthers leading to compounds 44 and 45 respectively[49].

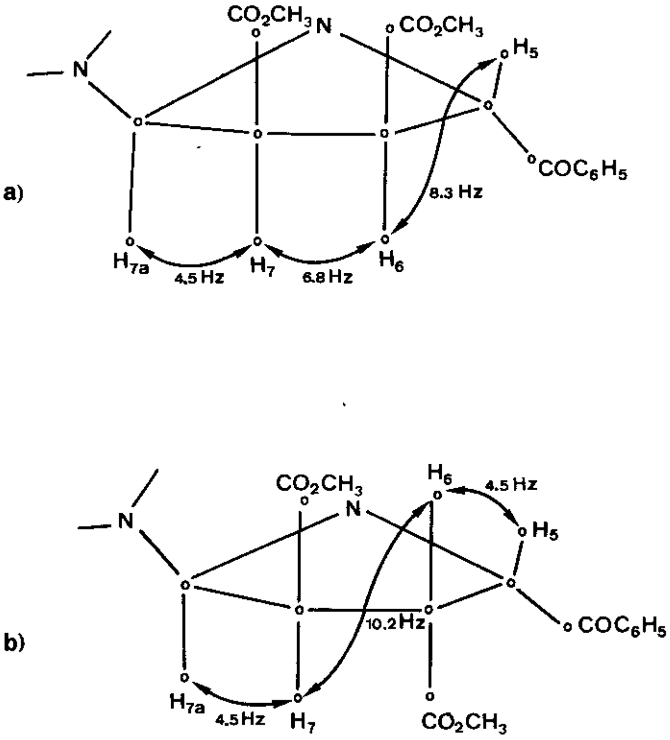


These reactions occur stereospecifically.

In Figure 5.1., some NMR spectral date of the pyrrole cycle of the compounds 44 (R=H) and 45 (R=4) are given.

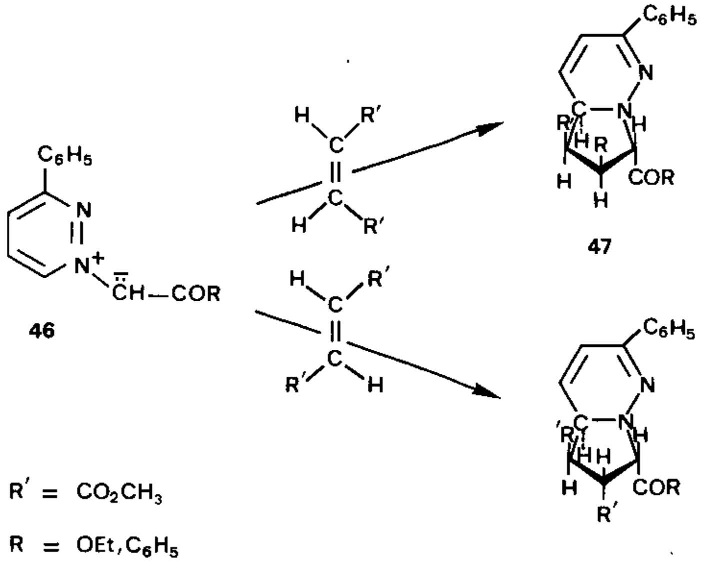
Figure 5.1. The spatial distributions of the protons in pyrrole cycle and the coupling constants

a) 44 (R=H, R'=CO_2CH_3) ; b) 45 (R=H, R'=CO_2CH_3)



These compounds have a characteristic ketonic band at 1685 cm^{-1}. The remaining of a ketonic group proves the 1,3-dipole character of these monosubstituted carbanion cycloimmonium ylides in such cycloadditions.

Analogous results in the reactions between pyridazinium ylides and maleic and fumaric esters have been published[50,51,52].



46

47

48

$R' = CO_2CH_3$

$R = OEt, C_6H_5$

5.2. Regiochemistry of [3+2] cycloaddition

The regiochemistry (regioselectivity and regiospecificity) of cycloadditions has to be determined. The regiochemistry is controlled by the steric, electronical and orbital factors.

We shall present briefly several aspects of the application of the frontier molecular orbital theory to the study of the regiochemistry. The regiochemistry of a cycloaddition could be predictted by the following sequences :

1) Estimate the energies of the HOMO and LUMO orbitals of both components.

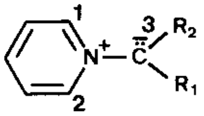
2) Identify which HOMO-LUMO pair is closer is energy.

3) Using this HOMO-LUMO pair, estimate the relative size of the coefficients of the atomic orbitals on the atoms at which bonding is to take place.

4) Match up the larger coefficient on one component with the larger on the other[53-50]. All these facts are the result of the "principle of narrow the inter-frontier level separation", applied to the study of the chemical interactions[54]. The energy of the HOMO orbitals of the donor increases and the energy of the LUMO orbitals of the acceptor decreases versus the reaction co-ordinates.

First, a theoretical study, in frontier orbital theory terms, on the regiochemistry of cycloadditions, betwen a series of pyridinium ylides and dipolarophiles with double and triple bonds, has been realized.

Table 13. The total atomic charges

Nº	Compound	Total atomic charges		
		Q_{C_1}	Q_{C_2}	Q_{C_3}
1	R_1 = H ; R_2 = CN	-0.0008	-0.0002	-0.2238
2	R_1 = R_2 = CN	+0.0118	+0.0118	-0.3823
3	R_1 = H ; R_2 = CO_2CH_3	-0.0042	+0.0246	-0.2710
4	R_1 = R_2 = CO_2CH_3	+0.0190	+0.0478	-0.3672
5	R_1 = H ; R_2 = COC_6H_5	-0.0015	+0.0181	-0.2246
6	R_1 = H ; R_2 = $COCH_3$	+0.0147	-0.0143	-0.2875
	CH_2 = CH - R	Q_{C_1}	Q_{C_2}	
7	R = CN	-0.0306	+0.0622	
8	R = CO_2CH_3	+0.0163	-0.0724	
	HC ≡ C - R	Q_{C_1}	Q_{C_2}	
9	R = CN	-0.0341	-0.0527	
10	R = CO_2CH_3	-0.0331	-0.0603	

Using the CNDO/2 procedure methods, the total atomic charges (Table 13), the frontier molecular orbital energies and the atomic orbital coefficients of the potential reaction centers (Table 14), have been calculated.

In the reactions between pyridinium ylides and Z substituted alkenes (methyl acrylate, acrylonitrile) or alkynes (methyl propiolate, cyanoacetylene), many cycloadducts may be obtained[57,58].

Table 14. The frontier orbital energies and the p_z atomic orbital coefficients

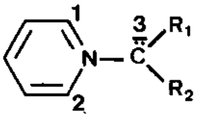
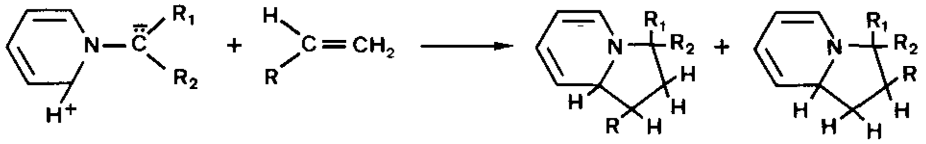
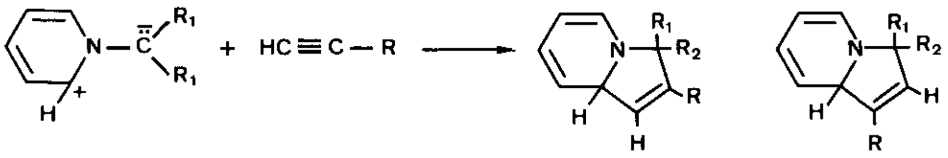
N°	Compounds	Orbital	Orbital energy (eV)	Atomic orbital coefficients		
				C_{c_1}	C_{c_2}	C_{c_3}
1	R_1 = H ; R_2 = CN	HOMO LUMO	-8.52186 1.72130	0.3264 0.3015	0.3248 0.3013	-0.7120 0.3475
2	R_1 = R_2 = CN	HOMO LUMO	-10.37667 -1.66241	0.2600 0.4200	0.2600 0.4200	-0.6274 0.2986
3	R_1 = H ; R_2 = CO_2CH_3	HOMO LUMO	-8.80478 1.89203	0.3086 0.2777	0.3116 0.3216	-0.7252 0.2685
4	R_1 = R_2 = CO_2CH_3	HOMO LUMO	-10.36980 0.29018	0.2434 -0.4063	0.2435 0.4062	-0.6411 -0.2048
5	R_1 = H ; R_2 = COC_6H_5	HOMO LUMO	-8.94658 1.13297	-0.2979 -0.3133	-0.2963 -0.3628	0.6618 -0.1917
6	R_1 = H ; R_2 = $COCH_3$	HOMO LUMO	-8.79171 2.0.4585	-0.3111 0.3575	-0.3086 0.2800	0.7271 0.2542
	RCNO				C_c	C_o
7	R = H	HOMO LUMO	-12.8950 4.1330		-0.5600 0.6770	0.802 0.298
8	R = CH_2	HOMO LUMO	-11.9540 4.0520		-0.5240 0.6040	0.764 0.284
	$\overset{1}{CH_2} = \overset{2}{CH} - R$				C_{c_1}	C_{c_2}
9	R = CN	HOMO LUMO N HOMO N LUMO	-14.11488 3.50279 -14.33695 4.03385		0 -0.6531 -0.6046 0	0 -0.5241 -0.4934 0

Table 14. Continued

N°	Compounds	Orbital	Orbital energy (eV)	Atomic orbital coefficients	
10	R = CO_2CH_3	HOMO	-13.55033	0	0
		LUMO	2.77134	-0.6194	0.4286
		N HOMO	-13.81001	0.3708	0.2859
		N LUMO	6.87399	0	0
1 2 CH = C - R				C_{c_1}	C_{c_2}
11	R = CN	HOMO	-15.25562	-0.5645	-0.4361
		LUMO	4.21719	0.5732	-0.4186
12	R = CO_2CH_3	HOMO	-14.40777	0	0
		N HOMO	-14.57747	0.2858	0.2092
		LUMO	3.15969	-0.5010	0.2896



49 **50** **51**



R = CO_2CH_3, CN

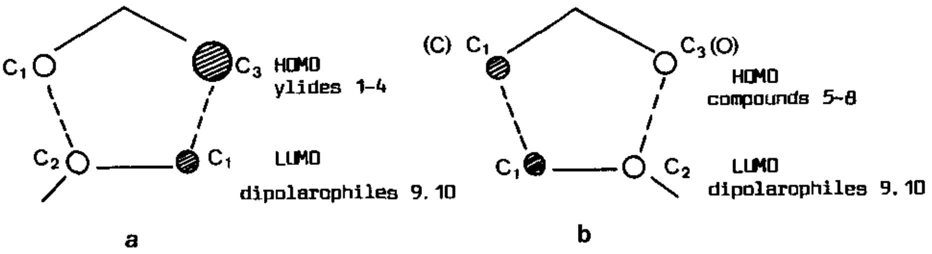
52 **53**

By the data presented in Table 14 two general representations of frontier orbital interactions could be constructed :

1) A representation as in Figure 5.2a, in which the cycloadditions are HOMO controlled in respect to the ylides 1-4 and

2) a representation as in Figure 5.2b, in which the cycloadditions are HOMO controlled in respect to the dipole 5-8. In cases, shown in Figure 5.2a there is a good agreement between the classically accepted polarization in ylides and in the Z substituted dipolarophiles. There is a disagreement in other cases, such as the one of Figure 5.2b ; this correlation does not work.

Figure 5.2. The interfrontier orbital interactions (compounds in Table 14).

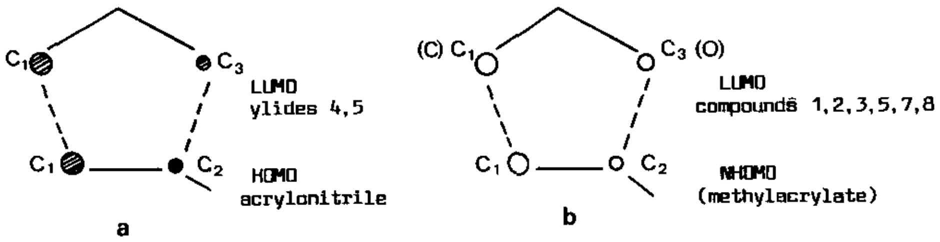


In all our representations we used the circles 0 for the positive, ● for the negative, values of the atomic orbital coefficients. We think that the cycloadditions take place between the p_z orbitals of dipoles and the p_z orbitals of the C_1 and C_2 atoms in dipolarophiles.

The previous diagrams are energetically favoured because small differences between frontier orbital energies are involved.

Next, we present some representations possible from theoretical view point, but energetically unfavoured.

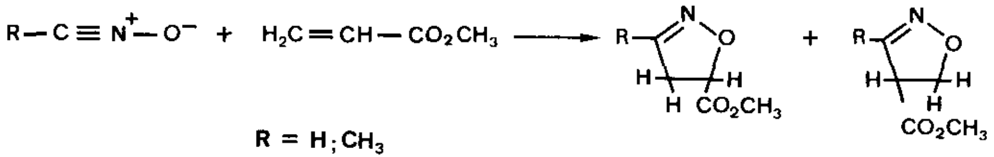
Figure 5.3. The interfrontier orbital interactions (compounds in Table 14).



Since the atomic orbital coefficients of C_1 and C_2 atoms in dipolarophiles 9 and 10 one are equal to zero, we use their values in NHMO (next HOMO) orbitals.

In Table 14 the frontier molecular orbital energies and the atomic orbital coefficients of C and O atoms in nitrile oxides have been presented too.

The nitrile oxide 54 (R = H) reacts with acrylonitrile giving stereospecificaly, only, the cycloadduct 55 (R = H)[59,60]. In the same experimental conditions the nitrile oxide 54 (R = CH_3) reacts with acrylonitrile regioselectivity, giving the cycloadducts 55 (R = CH_3) 94.9% and 56 (R = CH_3) 4.1%.

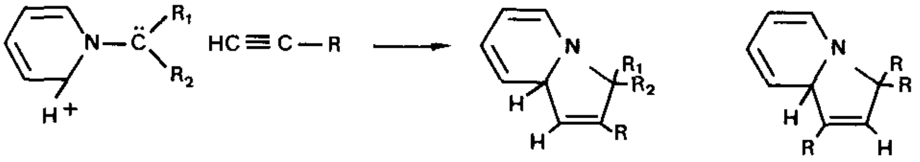


R = H;CH_3

54 55 56

A re-examination of above theoretical and experimental results shows that there is a good agreement between them. The main reaction products 51 and 55 involved cycloaddition opposite to the general accepted polarizations in these dipoles and dipolarophiles. We can appreciate that in such cycloadditions the orbital factors have the dominant role. By their small total atomic charges of potential reaction centers in dipolarophiles, presented in Table 13, the electrostatic interactions could be not significant. For the cycloaddition between the pyridinium ylides of Table 14 and triple bond dipolarophiles (cyanoacetylene, methyl propiolate), many interfrontier orbital representations may be constructed theoriticaly[58].

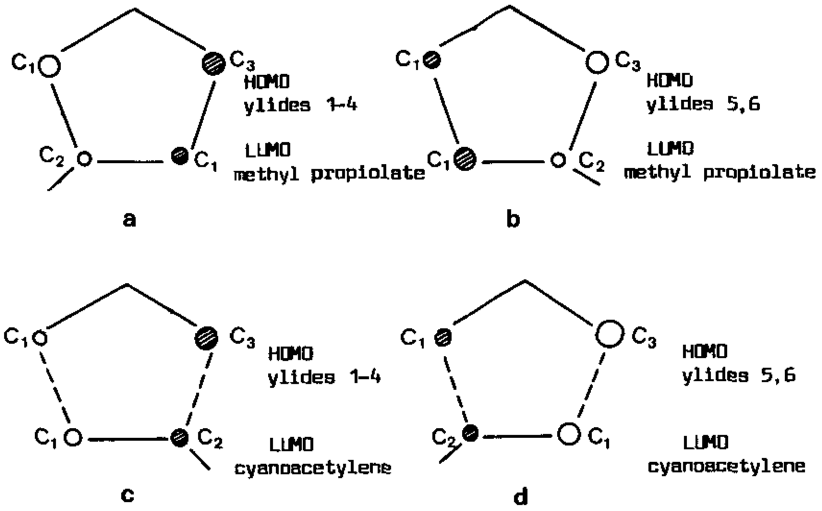
Scheme 24



57 58

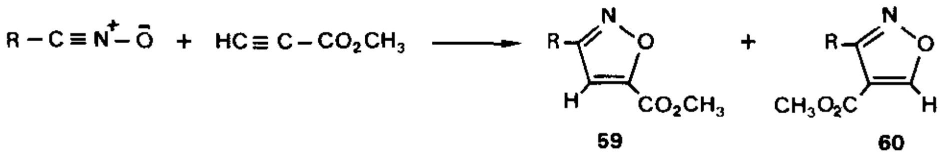
Next, we present some representative diagrams.

Figure 5.4. The interfrontier orbital interactions (compounds in Table 14).



According to the representation in Figure 5.4a, the ylides 1-4 react with methyl propiolate giving the cycloadducts of the type 58. According to the diagram in Figure 5.4, the ylides 5 and *6 forms with the same dipolarophile compounds of type 57. The cycloadditions between ylides* listed in Table 14 and cyanoacetylene, differently occurs.

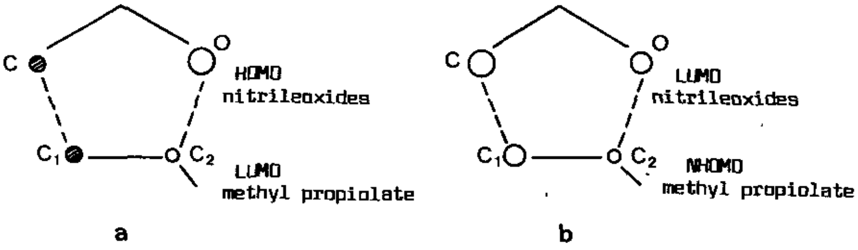
From the numerical data in Table 14, others interfrontier orbital representations, less energetically favoured, may be constructed theoretically. The nitriloxides react with methyl propiolate[59] giving regioisomers 59 and 60.



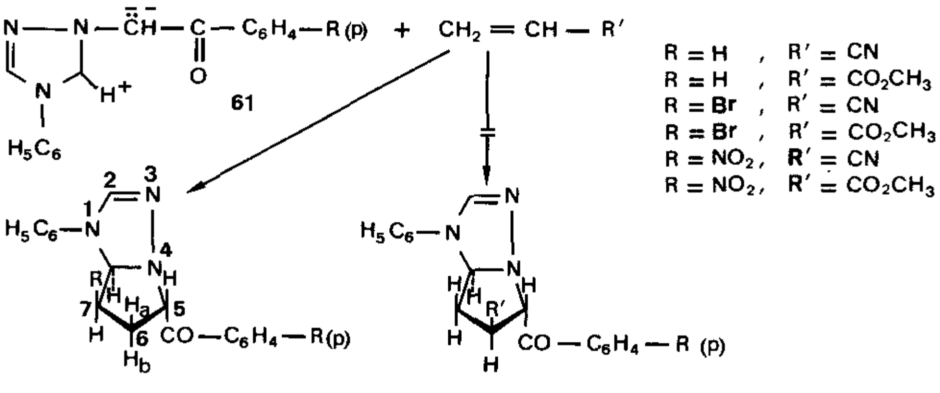
The first type compounds are the main reaction products. Even in these cases we find a good agreement between theoretical interfrontier representation and experimental data.

The principal formation of the adducts of the type 59 is orbitally and energetically favoured but it is in disagreement with general accepted polarizations in nitriloxides and methyl propiolate. *The data in Figure 5.5b show that all atomic* orbital coefficients of reaction centers are positive. It permit us to suppose that the formation of cycloadducts 60, less favoured, is not excluded. We consider that these cycloadditions regioselectively occur.

Figure 5.5. The interfrontier orbital interactions (compounds in Table 14).



Some examples of a cycloadditions, in the class of 1,2,4-triazolium ylides, involving concerted regiospecific mechanism are given[61].



62

63

The NMR spectra and $Pr(fod)_3$ induced chemical shifts permited us to elucidate the proton spatial distributions in pyrrolic ring in compounds 62. We used general indications presented in papers[62,64].

These cycloadditions take place in way opposite to the classically accepted electronic displacement in these dipoles and dipolarophiles.

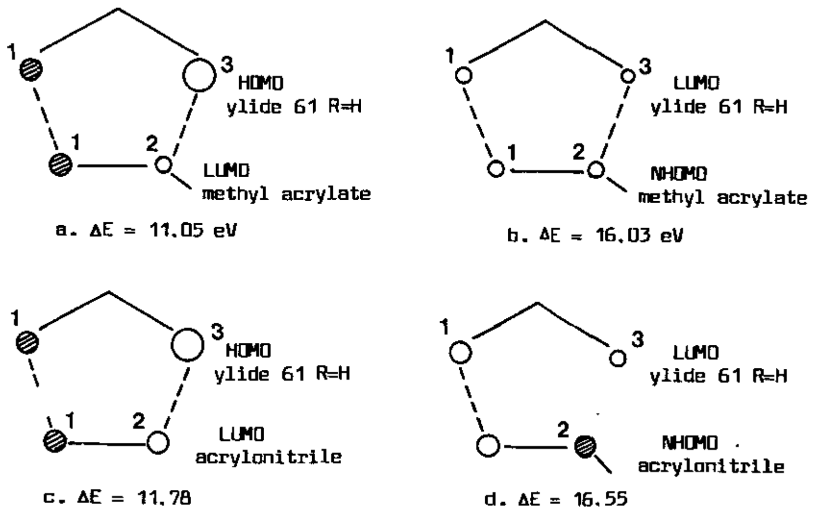
By CNDO/2 procedure method the frontier molecular orbital energies, the atomic orbital coefficients of C_1 and C_3 atoms in ylide 61 (R = H) have been calculated. The results in the Table 15 are presented.

Table 15. The frontier orbital energies and the p_z atomic orbital coefficients of the C_1, C_3 carbon atoms in 4-phenyl-1,2,4-triazoliumphenacylide.

Orbital	Energy (eV)	C_1	C_3
HOMO	-8.28	-0.3583	0.7019
LUMO	2.22	0.4411	0.1008

Using these numerical date and those in Table 14, the following interfrontier orbital representations could be constructed :

Figure 5.6. The interfrontier orbital interactions (compounds in Tables 14 and 15).

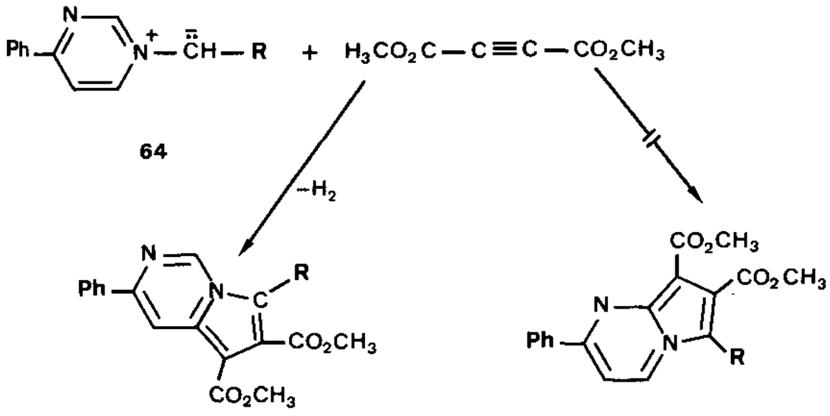


a. ΔE = 11.05 eV b. ΔE = 16.03 eV

c. ΔE = 11.78 d. ΔE = 16.55

A survey on the diagrams presented in Figure 5.6a,b,c,d, points out that the cycloadditions between ylide 61 (R = H) and methyl acrylate or acrylonitrile are HOMO controlled in respect to ylide. This reaction which is opposite to classical electronic deplacements, take place too.

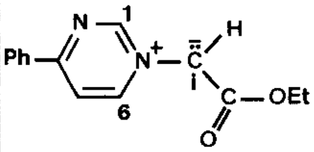
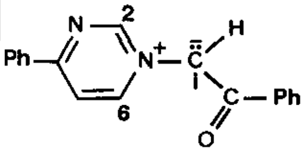
Next, we present and example of cycloadditions which involves an orientation in respect to 1,3-dipole in pyrimidinium ylides 64. It is the reaction between ylides 64 and dimethylacetylenedicarboxylate (DMAD)$^{66-68}$.



65 66

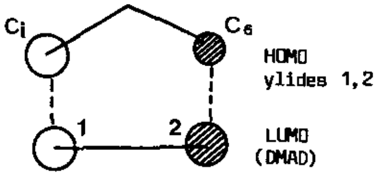
In these reactions two types of cycloadducts, 65 and 66 may be obtained after aromatization. Experimentally, only the cycloadducts 65 have been obtained. Their structures have been established from their NMR-H spectra.

Table 16. The frontier orbital energies, the total atomic charges and the p_z atomic orbital coefficients.

N°	Compound	Orbital	Energy (eV)	Coefficients		
				C_i	C_2	C_6
1		HOMO LUMO Q	-7.08142 +1.38556	+0.7124 +0.1967 -0.2793	-0.2588 +0.2161 +0.1526	-0.2465 +0.3502 +0.0594
2		HOMO LUMO Q	-8.64433 +0.51494	+0.7103 +0.1660 -0.2642	+0.2518 +0.1936 +0.1531	-0.2611 +0.3279 +0.0647
				C_1	C_2	
3	$H_3C-O_2C-\overset{1}{C}\equiv\overset{2}{C}-CO_2-CH_3$	HOMO LUMO Q	-13.71421 +1.92875	-0.2742 +0.4178 +0.0401	-0.2742 -0.4178 +0.0401	

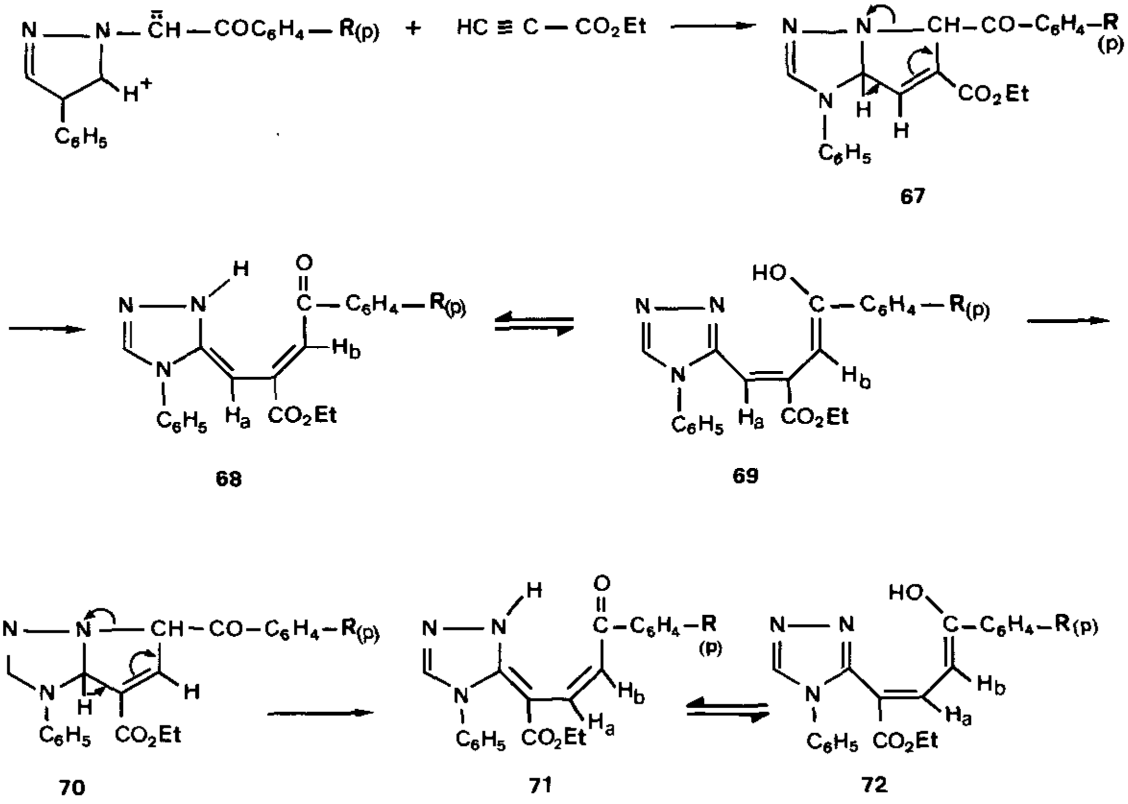
Using numerical data in Table 16 the following interfrontier orbital interactions may be constructed. It represents the energically favoured reaction pathway in these cycloadditions.

Figure 5.7. The interfrontier orbital interactions (compounds in Tables 16).



The regiochemistry of cycloadditions between 1,2,4-triazolium ylides and ethylpropiolate is more complex[69,70]. The intermediate cycloadducts 67 are unstable. By an opening of pyrrole ring a tautomeric mixture were obtained. Their composition depends on the nature of triazolium ylides. In the above scheme the two reaction possibilities are given.

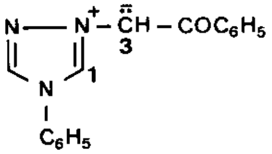
Scheme 28.



R = H, Br, NO_2, OCH_3

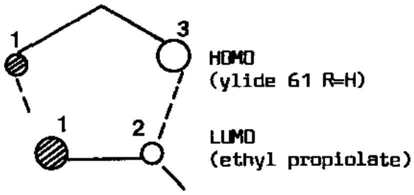
The intermediate formation of the cycloadducts 67 has been verified using 2,5-dideuterated triazolium ylides and induced chemical shifts by Pr $(fod)_3$. The frontier orbital energies and the atomic orbital coefficients of the compounds 1 and 2 in Table 17, by the CNDO/2 procedure method have been calculated.

Table 17. The frontier orbital energies and the p_z atomic orbital coefficients.

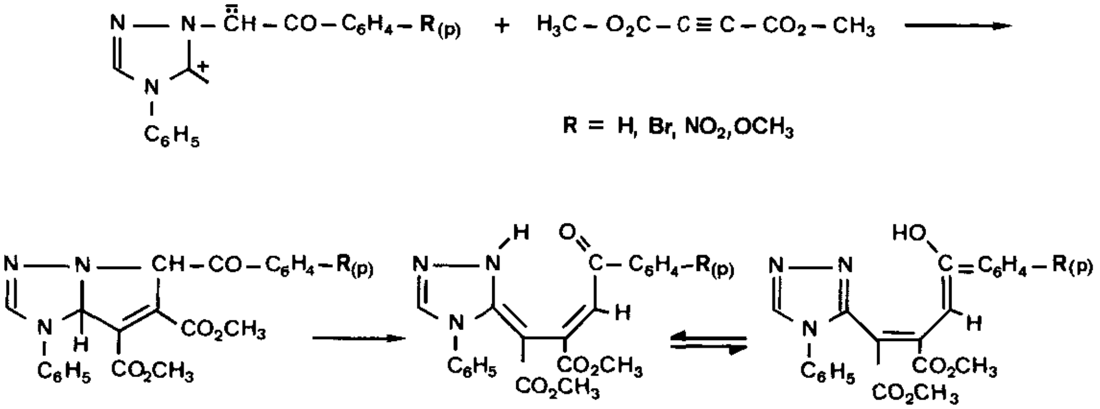
N°	Compound	Orbital	Energy (eV)	Atomic orbital coefficients	
				C_1	C_3
1		HOMO	-8.28001	-0.3583	+0.7019
		LUMO	+2.22009	+0.4411	+0.1008
				C_1	C_2
2	$H\overset{1}{C} \equiv \overset{2}{C} - CO_2Et$	HOMO	-14.10041	0	0
		N HOMO	-14.30000	+0.2677	+0.1922
		LUMO	-3.39982	-0.5074	+0.3004
		N LUMO	+6.14932	0	0

By these numerical date the interfrontier orbital representation in Figure 5.8 could be constructed[70].

Figure 5.8. The interfrontier orbital interactions (compounds in Tables 15 and 17).



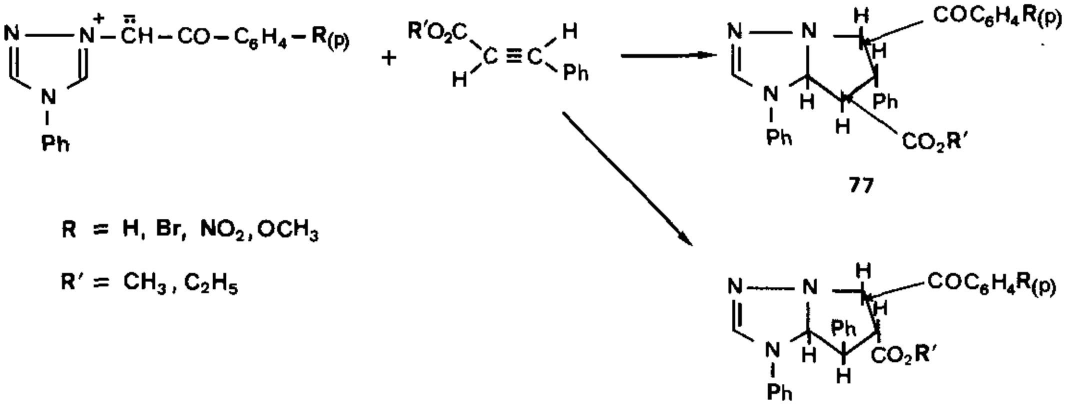
It is the opposed classical polarization of ylides and ethyl propiolate which leads to compound 67. Similarly, the reaction between 1,2,4-triazolium ylides and DMAD occur.



73 **74** **75**

5.3. Corochemistry of [3+2]cycloaddition

According to Epiotis, corochemistry includes both stereochemistry and regiochemistry. Such aspects appear in the cycloadditions between 1,2,4-triazolium ylides and ethyl or methyl cinnamates[71,72].



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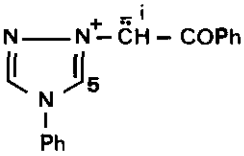
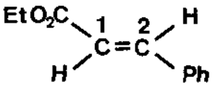
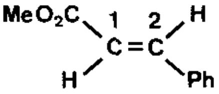
76

In previous Scheme 30 some possible cycloadducts are given. Their structures using NMR-H spectra and induced chemical shifts have been established.

A theoretical study on the corochemistry of these cycloadditions was realized. First, the frontier orbital energies, the total atomic charges and the atomic orbital coefficients of potential reaction centers of the compound in Table 18, using CNDO/2 procedure method, have been calculated.

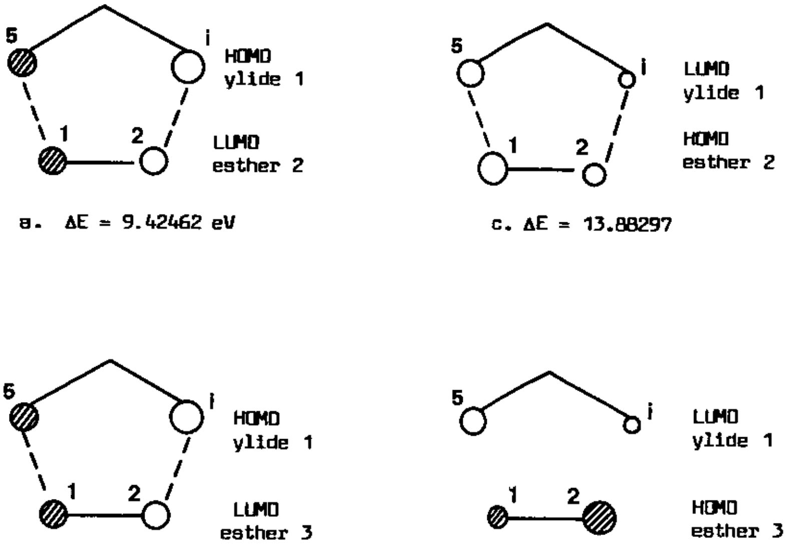
Table 18. The total atomic charges, energies and atomic orbital coefficients.

Nº	Compound	Orbital	Energy (eV)	Atomic orbital coefficients	
				C_5	C_1
1		HOMO LUMO Q	-8.28003 2.21998	-0.3583 +0.4411 +0.0576	+0.7019 +0.1008 -0.2929
				C_1	C_2
2		HOMO LUMO Q	-11.66297 1.14459	+0.4673 -0.4248 -0.1118	+0.3329 +0.4717 +0.0713
				C_1	C_2
3		HOMO LUMO	-11.72722 1.09531	-0.4695 -04232	-0.3306 +0.4738

These numerical data permitted us to draw up the interfrontier interactions in Figure 5.9.

By the above representations the 1,2,4-triazolium ylide 1 (Table 18) reacts coroselectivity with ethyl cinnamate giving a mixture of cycloadducts 76 and 77 (R' = C_2H_5). The same ylide in reaction with methyl cinnamate forms by a corospecific way only the cycloadduct 76 (R' = CH_3). In the Figure 5.10 some NMR spectral date of the cycloadduct 76 (R = H, R' = CH_3) are presented.

Figure 5.9. The interfrontier orbital interactions (compounds in Tables 15 and 18).



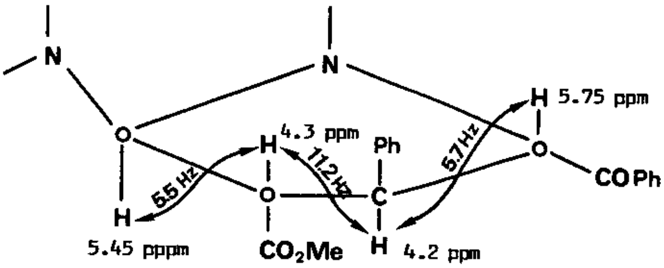
a. ΔE = 9.42462 eV

c. ΔE = 13.88297

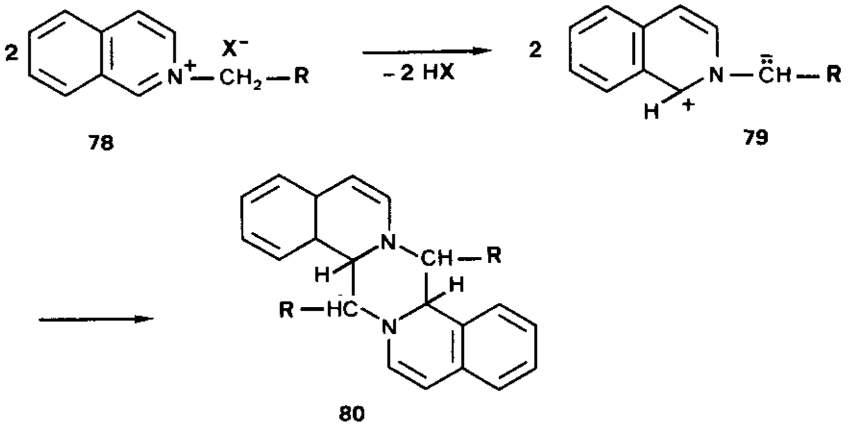
b. ΔE = 9.37534 eV

d. ΔE = 13.88295 eV

Figure 5.10. The NMR-H data of compound 76 (R = H, R' = CH_3).



There are no great structural differences between methyl and ethyl cinnamates but according to the theory theses two compounds would however have different chemical behaviour in cycloaddition. Some cycloimmonium ylides by dimerization, involving a[3+3] cycloaddition, form the compounds of the type 80.



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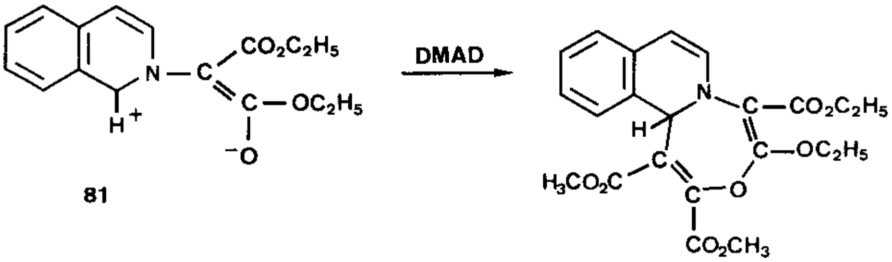
80

6. CYCLOIMMONIUM YLIDES AS 1,5-DIPOLE IN CYCLOADDITIONS

According to their resonance structures 41e, the cycloimmonium ylides could participate to the [5+2] cycloadditions. Thus, in the reaction of isoquinolinium dicarbethoxycarbonyl[77] and phthalazium dicarbethoxymethylide[78]. With DMAD, in chloroformic solution, the oxazepines of the type 82 have been obtained.



81

82

The structures of these compounds by their NMR and IR spectra have been established. In the literature to our knowledge there are not other examples of cycloadditions, where ylides react of 1,5-dipole.

7. CONCLUSIONS

In this paper the recent theoretical and experimental data on the chemical behaviour of cycloimmonium ylides have been presented.

Two general aspects : 1) nucleophilicity of cycloimmonium ylides of ylide carbon atoms and 2) the 1,3-dipole character of these molecular systems, have been analyzed. These two general chemical properties of cycloimmonium ylides using both molecular orbital theory and experimental results, were studied.

We may conclude that the monosubstituted carbanion cycloimmonium ylides have larger nucleophilic character than the disubstituted carbanion cycloimmonium ylides. That is verified by the protonation reactions and by the reactions between monosubstituted cycloimmonium ylides with acyl chloride, anhydrides, isocyanates and isothiocyanates.

Both monosubstituted and disubstituted carbanion cycloimmonium ylides participate as 1,3-dipoles to the [3+2]cycloadditions.

In this paper many examples of such cycloadditions between monosubstituted cycloimmonium ylides and dipolarophiles having double and triple bonds are given. Successively, stereochemistry, regiochemistry and corochemistry aspects of the [3+2] cycloadditions from experimental and theoretical point of view, have been studied. These cycloadditions by a concerted pericyclic mechanism occur. The orbital factors have the dominant role in such reactions. Generally, a good agreement between theoretical and experimental results is founded.

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