Tetrahedron. Vol 32, pp. 2647 to 2663. Pergamon Press 1976. Printed in Great Britain

TETRAHEDRON REPORT NUMBER 23

STRUCTURE AND REACTIVITY OF CYCLOIMMONIUM YLIDES

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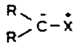
(*Received in the UK for publication* 15 *May* 1976)

INTRODUCTION

Ylides are zwitterionic compounds in which an anion is covalently bonded to a positively charged heteroatom. Ylides can be classified as carbanion ylides **1**: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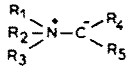
and as amidines ylides **2**, R being the electron withdrawing groups.

Type **1** ylides can themselves be classified by heteroatom[1] into nitrogen ylides **3**, sulfur ylides **4**, arsenic ylides **5** and phosphorus ylides **6**.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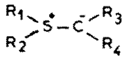
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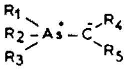
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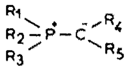
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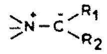
The type **3** ylides can be subdivided into ammonium **7**, cycloammonium **8**, immonium **9**, cycloimmonium **10**, nitrile **11**, and diazonium **12** ylides according to the nature of the nitrogen atom.[2]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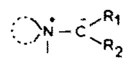
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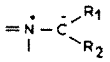
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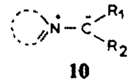
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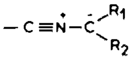
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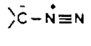
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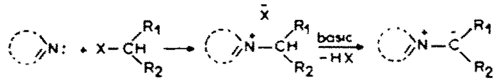
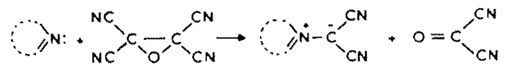
In this paper we differentiate between the ylide in which the carbanion is monosubstituted and the ylides in which it is disubstituted. The questions arising from the structure and reactivity of the type **10** ylides will be discussed. A summary of the methods of synthesis of these ylides is given below.

I. *The Kronhke salt method*[3,4]. The first step is the synthesis of the cycloimmonium salt **13**. In basic medium it loses an hydracid molecule and is converted into an ylide of type **10** by the following mechanism:

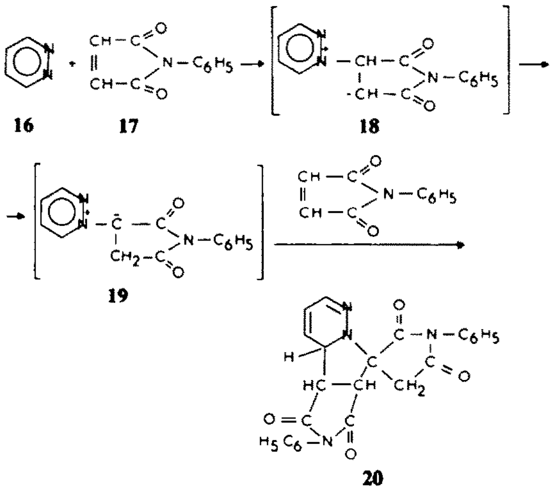

13 **10**

Many syntheses of type **13** salts are described in the literature.[5-8]

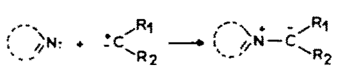
II. Many dicyano-methylides **15** can be formed by the reaction of tetracyanonethylene oxide **14** with azaheterocycles:[9,10]


14 **15**

III. Some stable[11,12] and unstable[13] ylides are formed by the reaction of philodienes with azaheterocycles:

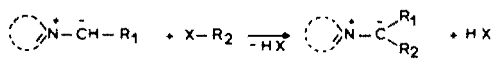

16 **17** **18** **19** **20**

IV. Ylides can also be formed by the reaction of carbenes **21** on azaheterocycles:[14]


21 **10**

V. Disubstituted ylides can be synthesised from monosubstituted ylides of type **22** by two different methods:

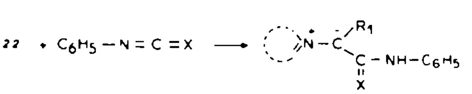
(a) by acylation:[15]


22 **10**

$R_2 = -COR, -COOCOR, R_1$
= electron withdrawing groups

and

(b) by reaction with isocyanates or thioisocyanates:[16,17]



23 **24**

X = O, S

Many heterocyclic syntheses which involve non-isolated ylides as intermediates have already been published.[18-22] In this paper we shall deal only with ylides stable enough to be isolated and characterized by their physical and chemical properties.

A. *Structure*

I. *Phosphonium ylides.* In general, phosphonium ylides are more stable than nitrogen ylides. Their stability is due to an overlap of the doubly-occupied 2p orbital of the ylide carbon with the unoccupied 3d orbital of the phosphorus atom **25b**[1] and can be represented by the following resonance structures:

$$\underset{a}{B-CH_2-\bar{C}H-\dot{P}R_3} \longleftrightarrow \underset{b}{B-CH_2-CH=PR_3}$$

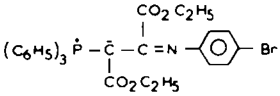
25

A similar conjugation however cannot be considered in the case of nitrogen ylides. The energy of the unoccupied 3s orbital of the nitrogen atom is too high to form a π bond. An ammonium group can stabilise an adjacent carbanion by electrostatic interaction; the C–N bond length (1.47 Å) is indeed, considerably shorter than that of the C–P (1.87 Å). According to this bond length difference, the electrostatic coulombic attraction is 30% higher in the case of the C–N bond than in the case of the C–P bond.[23] The polarisability effects are more important in the case of the phosphorus ylides than in the case of the nitrogen ylides but cannot counterbalance the difference of coulombic interaction. In fact, the stability of the phosphorus ylides is due mainly to the possibility of the 3d phosphorus orbitals forming actual π bonds.[24] This explains the fact that a great number of phosphorus ylides have been isolated and characterized as stable species.[25-34]

Authors, who studied the theoretical aspect of the p_π–d_π bonds, agree that they exist but have different opinions regarding the respective contributions of the p and d orbitals to the bond formation.

According to Jaffe,[35] and Craig *et al.*[36] the multiple bonds which involve the overlap of p and d orbitals provide the actual chemical stability to these molecules. Craig *et al.*[36] came to the conclusion that the replacement of a H-bonded to the phosphorus atom by a carbon atom increases the positive charge of the phosphorus and therefore favours the formation of the p_π–d_π bond.[37]

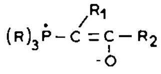
Mak and Trotter[38] found that the length of the phosphorus–carbanion bond, in compound **26** is of the order of 1.70 Å ± 0.03 Å.



$$(C_6H_5)_3\dot{P}-\underset{CO_2C_2H_5}{\bar{C}}-\overset{CO_2C_2H_5}{C}=N-C_6H_4-Br$$

26

This bond is much shorter than the sum of the atomic radii of the phosphorus and carbon atoms involved in a single bond (1.87 Å), and even shorter than the P–C bond of the triphenylphosphine (1.83 Å).[39] But it is slightly larger than the sum of the same radii of a P=C double bond (1.67 Å).[40] From these data it appears that the ylide C–P bond length is analogous with that of a C=P double bond. However, from recent ESCA data[41] it has been found that in the case of phosphonium ylides with strongly electron-withdrawing substituents, the formal negative charge written on the ylide carbon is actually highly delocalized on substituents of type **27**.

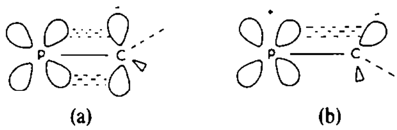


$$(R)_3\dot{P}-\overset{R_1}{C}=\underset{-O}{C}-R_2$$

27

This conclusion is supported by X-ray studies of the triphenylphosphine phenacylide D⁻ crystal.[42]

The carbon ylide hybridisation forms an sp^2 orbital with the non-bonding doublet in the 2pz (Fig. 1a), or forms a tetrahedral orbital a doublet in an sp^3 hybridised orbital (Fig. 1b).



(a) (b)

Fig. 1.

The carbanion structure is usually sp^2, but some examples are known in which the C atom is of sp^3 hybridisation.[1]

The phosphorus ylide atom is hybridised bipyramidally (dsp^3).[43] The C atom can be in an axial position (Fig. 2a) or at the base of the pyramid (Fig. 2b).

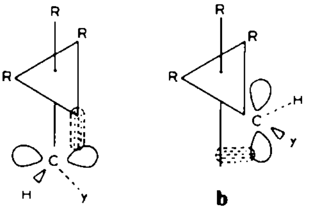


Fig. 2. (a) Ylide carbanion at axial position of trigonal bipyramidal phosphorus. (b) Ylide carbanion at basal position of trigonal bipyramidal phosphorus.

Absar and Wazer[44] have performed *ab initio* computations on $H_3P^+–\bar{C}H_2$ and $H_2P–CH_3$ using fixed C–P bond lengths in each case. Inspection of their wave functions, Table 1, reveals that in the ylide, which has the shorter bond length, both the ionic bond order and the overlap

Table 1. Overlap population and ionic bond order of the C–P bond in $H_3P^+–\bar{C}H_2$ and $H_2P–CH_3$ as a function of basis set[46]

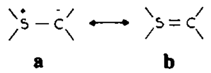
Molecule	r_{PC}(Å)	p'_{PC}†	p_{PC}
H_3PCH_2‡	1.66	0.29	0.88
H_2PCH_3‡	1.863	0.08	0.59
H_3PCH_2§	1.66	0.05	1.08
H_2PCH_3§	1.863	−0.01	0.69

†Bond lengths a expressed in Å in the calculation of P′.
‡Without d-type functions on phosphorus.
§With d-type functions on phosphorus.

population of the C–P bond are greater, whether d-type functions are present on phosphorus or not. In addition π-like interactions are present in the C–P bonds even when d character is not allowed.[45,46] Therefore, it seems unnecessary to rationalize the shorter C–P bond of the ylide in terms of $(p \rightarrow d)_\pi$ conjugation. One should, rather, emphasize the correlation with the ionic bond order.

Since the length of a chemical bond is the result of both ionic and covalent effects, the ionic interaction should not be ignored in the explanation of bond length variation of charged and zwitterionic systems.

II. *Sulphur ylides.* The possibility that a S atom may stabilize a negative charge born by an adjacent C atom is still in question.[47,48]



28

The stabilization of the sulphur ylide is probably achieved by electrostatic interactions and by the overlap of the d orbital of the S atom with the 2p doubly-occupied orbital of the carbon ylide.[49,50] The main problem is to determine in the actual structure the weight of forms **28a** and **28b**. To have the maximum overlap of a 2p carbon orbital with a 3d of the S atom, the molecule will have the tendancy to become coplanar (Fig. 3).

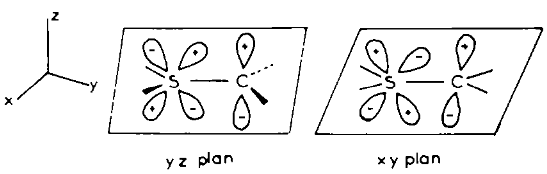
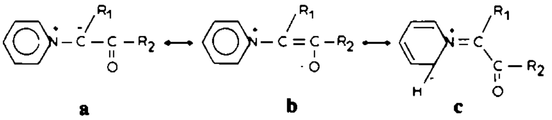


Fig. 3.

When the S atom is substituted by strongly electron-withdrawing groups or by groups linked to the sulphur by an O atom, the stability of sulphur ylides is greatly increased.[51–61]

III. *Cycloimmonium ylides.* The stability of cycloimmonium ylides is mainly determined by three factors, (1) Delocalization of the charge on the carbon ylide by the R_1 and R_2 electron withdrawing groups **29b**; (2) The coulombic attractive strength between the aromatic positive cyclic nitrogen and the negative carbon **29a**; (3) The resonance interaction between the heterocycle and the carbanion **29c**.



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The coulombic term probably has a strong influence in the case of ammonium ylides, where the positive charge on the nitrogen is important.

In all the cycloimmonium ylides the N atom ylide is sp^2 hybridised. sp^2 and sp^3 are the two limits of the hybridisation of the ylide C atom. When it is sp^2 (Fig. 4a) there is an important overlap between the doubly-occupied 2p orbital of this C atom and the π aromatic ring cloud. When it is sp^3 (Fig. 4) hybridised this overlapping becomes less important:

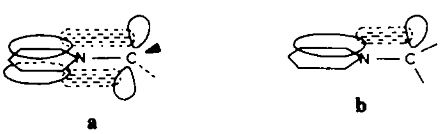
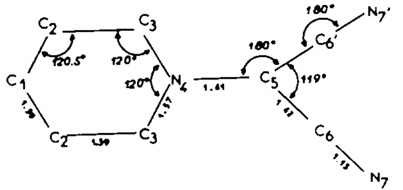


Fig. 4.

The theoretical data and the experiments which will be discussed below confirm that the first factor (delocalization of the negative carbon ylide charge on the substituents) is preponderant in the case of disubstituted ylides. The contribution of the two other factors seems to be less important for these ylides.

The data obtained from X-ray diffraction spectra of pyridinium dicyanomethylide below crystals **30**[62] are:



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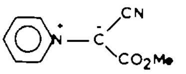
The pyridine ring is coplanar with the ylide C atom. The two cyano groups are both inclined in same plane at an angle of 3°.

All the distances measured in the molecule are known to an accuracy of ±0.01 Å. The ylide C–N bond length (1.41 Å) is smaller than that expected for a C_{sp^2}–N_{sp^2} bond. The exocyclic C–C bond length is 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),[63] but much smaller than the single C–C (sp–sp^3) bond in propionitrile (1.458 Å).[65]

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 pyridinic ring and the carbanion. The charge density CNDO calculations on this ylide with the geometry determined by X-ray analysis, diverge. It is impossible to obtain a convergence to an energy minimum by successive iterations. The energy reaches a minimum but rises when more iterations are done.[65]

Similar calculations have been carried out for a series of ylides with mixed substituents (compounds **31–36**)[66,67] using as geometry of the ylide C atom the one described for pyridinium dicyanomethylide. The geometry used for the carbomethoxy group is the one described for methyl



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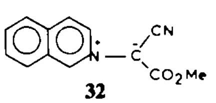

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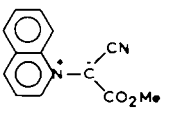

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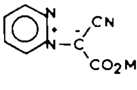

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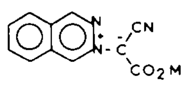

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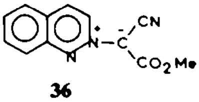

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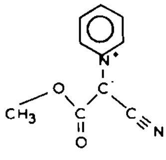
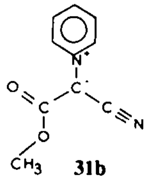
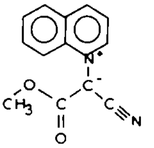
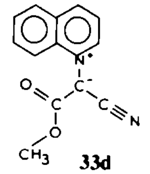
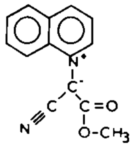
acetate.[68] For most of these compounds the calculations converge.[67] For the ylide **31**, calculations have been performed for the two configurations **31a** and **31b**


31a


31b


33c

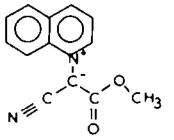

33d

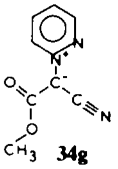

33e

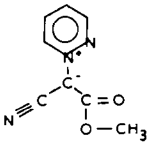
The energy is minimum for configuration **b**. In the case of the ylide derived from isoquinoline **32** the condensed ring cannot have a steric effect on the configuration of the ylide carbon substituents and therefore the more stable configuration is probably of type **b**. In the case of ylide **33** derived from quinoline, the condensed ring certainly has a steric effect on this configuration. We[68] have performed CNDO calculations for the four different configurations **c**, **d**, **e**, **f** of ylide **33** and the calculations diverge for all configurations.

In the case of ylide **34**, derived from pyridazine, the energy is minimum for configuration **h** and not for configuration **f**. Both are **b** type configurations. In the case of ylide **35** derived from phthalazine it is the **h** type configuration which is the more stable form. In the case of the ylide **36** derived from cinnoline it is the **g** configuration which has the minimum energy.

The charge densities on the nitrogens, carbonyl, oxygens, ylide C atoms and on the ring C atom α to the nitrogen, calculated for the configurations described above are presented in Table 2.


33f


34g


34h

From Table 2 it appears that the actual charges calculated for the carbon and the nitrogen of the ylide bond are very different from the value of the charges formally written for these atoms. (An important charge is localized on the oxygen of the carbomethoxy group and on the N atom of the cyanogroup). These data agree with the previous hypothesis.[65] To verify the validity of the theoretical data, binding energies E_A of the 1s electrons of the N atoms have been measured by ESCA (Table 3).[67]

The curve $E_A - V_A = f(Q_A\{\mathrm{CNDO}\})$ where V_A is the molecular potential of N atoms

$$V_A = \sum_{B \neq A} \frac{Q_B}{R_{AB}}.$$

Q_B are the charge densities of the other atoms B of the molecule, R_{AB} are the interatomic distances have been plotted.[69,70] The slope of this curve is $K = 18.6\,\mathrm{eV}$. Siegbahn[70] found 21.5 eV from a series of azacompounds using the equation: $E_A = K_{Q_A} + V_A + l$; K and l are two experimentally determined constants; K is the electrostatic repulsion term, l the binding energy of the 1s electron when $Q_A = V = 0$.

A simpler equation have been proposed, $\Delta E = KQ'_B$.[70] It is mainly used when the CNDO calculations are difficult to perform.

Table 2.

Ylides	N^+ Charge	N^+ Potential	N° Charge	N° Potential	N(CN) Charge	N(CN) Potential	C^- charge	O(C=O) charge	C_α charge
31	+0.1115	−1.08			−0.1555	+0.43	−0.2570	−0.4108	+0.0134
32	+0.0978	−0.99			−0.1493	+0.49	−0.2581	−0.4134	+0.0288
34	+0.1922	−1.88	−0.089	+1.9	−0.1537	+0.084	−0.2133	−0.3757	+0.0020
35	+0.1860	−2.08	−0.1111	+2.18	−0.1652	+0.85	−0.2253	−0.3945	−0.0034
36	+0.2793	−2.40	−0.1697	+3.35	−0.2406	+1.78	−0.1540	−0.4270	−0.0120

Charge densities and potentials calculated by the CNDO/2 method for ylides **31**–**36**.

N^+: nitrogen to which is bonded the ylide carbon atom; N°: other nitrogen of the ring; C^-: ylide carbon; O(C=O): carbonyl oxygen of the carbomethoxy group; C_α: Ring carbon atoms α to the nitrogen.

Table 3.

Ylides		Binding energies of the nitrogen 1s electrons (eV)						
		31	**32**	**33**	**34**	**35**	**36**	Pyridine-N oxyde
Binding energies (eV)	N^+	400.2	399.3	398.8	402.2	399.5	400.8	400.9
	N°				399.9	397.0	398.3	
	N^-	396.5	395.6	395.5	398.2	395.3	397.5	

N^+, N° and N^- have the same significations presented in Table 2.

From the charge densities of the nitrogen atoms (Table 2) it can be concluded that:

The classical representation of these ylides with formal charges localized on the nitrogen and on the carbon of the ylide bond is far from the reality.

The delocalization of the negative charge is the most important criterion of stability of cycloimmonium ylides. The coulombic interaction between the N and the C atoms of the ylide bond cannot be important, the value of the actual charges localized on the atoms of this bond being small. Similarly the resonance interaction term between the negative C and the positive N atoms is not significant because the α C atom of the ring, bears no significant negative charge.

The delocalization of the negative charge on the substituents of the ylide carbon seems, on the contrary, totally justified and agrees perfectly with the physical and chemical properties of the cycloimmonium ylides.

IV. *Some spectral properties of pyridinium ylides.* Data on the absorption spectra of pyridinium ylides are collected in Table 4. Some isolated reports on individual ylides have previously appeared.[71–80]

Table 4. UV and visible absorption spectra of N-pyridinium ylides

Substance	Solvent	λ_{max} (mμ)	log ϵ
$\mathrm{PhCO\bar{C}Hpy^+}$	B	454	4.31
	D	247, 450	4.00, 4.05
	A	246, 437	4.03, 4.22
	E	246, 420	4.10, 4.00
p-$\mathrm{BrC_6H_4CO\bar{C}Hpy^+}$	B	453	4.38
	D	246, 263, 451	40.1, 3.89, 4.50
	A	246, 256, 437	4.05, 3.99, 4.44
	E	247, 260, 424	4.02, 4.03, 4.19
(1) $\mathrm{PhCO}\underset{\substack{\vert\\ \mathrm{py^+,H_2O}}}{\bar{\mathrm{C}}}\mathrm{COMe}$	B	425	3.31
	D	238, 246, 270, 423	4.05, 4.04, 3.84, 2.89
	C	284, 404	4.12, 3.20
	A	226, 281, 404	4.05, 4.12, 3.18
	E	283, 364	4.20, 3.10
	DMF	283, 411	4.05, 3.18
	W	285	4.24
	W/HCl	255	4.20
(2) $\mathrm{PhCO}\underset{\substack{\vert\\ \mathrm{py^+,H_2O}}}{\bar{\mathrm{C}}}\mathrm{COEt}$	D	229, 281, 425	4.14, 4.05, 3.26
	A	227, 282, 413	4.07, 4.12, 3.23
	E	283, 367	4.21, 3.12
(3) $\mathrm{PhCO}\underset{\substack{\vert\\ \mathrm{py^+,H_2O}}}{\bar{\mathrm{C}}}\mathrm{CO(CH_2)_{14}Me}$	D	279, 420	4.01, 3.20
	A	282, 416	4.09, 3.26
	E	284, 368	4.13, 3.07
(4) p-$\mathrm{MeC_6H_4CO}\underset{\substack{\vert\\ \mathrm{py^+,H_2O}}}{\bar{\mathrm{C}}}\mathrm{COMe}$	D	243.5, 263, 422	4.07, 4.00, 2.97
	A	235, 282, 410	4.11, 4.11, 3.20
	E	285, 365	4.20, 3.12
	W	287	4.23
	W/HCl	262.5	4.28
(5) p-$\mathrm{BrC_6H_4CO}\underset{\substack{\vert\\ \mathrm{py^+,H_2O}}}{\bar{\mathrm{C}}}\mathrm{COMe}$	D	244.5, 267, 417	4.20, 4.02, 3.07
	A	237, 284, 403	4.24, 4.10, 3.21
	E	236.5, 285, 363	4.16, 4.18, 3.16
(6) $\mathrm{PhCO}\underset{\substack{\vert\\ \mathrm{py^+}}}{\bar{\mathrm{C}}}\mathrm{COPh}$	B	322, 429	3.95, 3.39
	D	247, 320, 420	4.07, 3.97, 3.32
	C	317, 402	4.03, 3.32
	A	246, 313, 390	4.10, 3.95, 3.25
	E	316	4.09
	E/HCl	257	4.34
	DMF	317, 390	3.98, 3.28
	W	226.5, 317	4.20, 409
	W/HCl	255	4.25
(7) o-$\mathrm{C_6H_4(CO}\underset{\substack{\vert\\ \mathrm{py^+}}}{\bar{\mathrm{C}}}\mathrm{COPh)_2}$	D	312, 412	4.20, 3.99
	A	316, 411	4.30, 3.71
	E	316	4.39
(8) p-$\mathrm{MeC_6H_4CO}\underset{\substack{\vert\\ \mathrm{py^+}}}{\bar{\mathrm{C}}}\mathrm{COPh}$	D	281, 320, 420	3.91, 3.98, 3.34
	A	315, 395	4.02, 3.31
	E	227, 250, 318	4.29, 4.08, 4.09
(9) p-$\mathrm{BrC_6H_4CO}\underset{\substack{\vert\\ \mathrm{py^+}}}{\bar{\mathrm{C}}}\mathrm{COPh}$	D	320, 414	4.94, 3.32
	A	316, 390	3.99, 3.29
	E	231, 317	4.31, 4.07

Table 4. (*Contd.*).

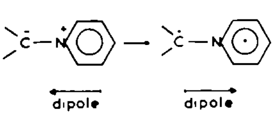
Substance	Solvent	l_{max} (mμ)	log ε
(10) $\underset{\mathrm{py^{+}}}{\mathrm{PhCO\bar{C}CN}}$	B	415	4.11
	D	241, 276, 410	4.06, 3.66, 405
	C	272, 408	3.74, 4.03
	A	238, 279, 296	4.13, 3.65, 4.05
	E	240, 272, 391	4.09, 3.84, 3.90
	DMF	401	3.96
	W	238.5, 264, 370	4.09, 3.95, 3.70
	W/HCl	230.5, 258, 365	4.04, 3.95, 3.41
(11) $\underset{\mathrm{py^{+}}}{\mathrm{EtOOC\bar{C}CN}}$	D	228, 404	4.29, 4.26
	A	227, 391	4.31, 4.25
	E	229, 390	4.26, 4.08
	W	232, 376	4.31, 3.81
(12) $\underset{\mathrm{py^{-}}}{\mathrm{EtOOC\bar{C}COOEt}}$	B	441	3.59
	D	246, 439	4.16, 3.19
	C	430	3.46
	A	245, 420	4.42, 3.37
	E	247, 398	4.03, 3.09
	DMF	420	3.37
	W	249, 370	4.43, 3.10
	W/HCl	261	3.74
(13) $\underset{\mathrm{py^{+}}}{\mathrm{PhCH{=}CHCO\bar{C}COPh}}$	D	273, 290, 343, 413	4.15, 4.17, 4.09, 3.52
	A	223, 285, 342	4.30, 4.17, 4.10
	E	243, 296, 308, 343	4.19, 4.13, 4.13, 4.25
(14) $\underset{\mathrm{py^{+}}}{\mathrm{PhCO\bar{C}CONHPh}}$	D	252, 298, 440	4.16, 4.09, 3.46
	A	249, 293, 412	4.13, 4.09, 4.34
	DMF	295, 415	4.14, 3.45

A: Acetonitrile; B: Benzene; C: Chloroform; D: Dioxan; DMF: Dimethylformamide; E: 95% ethanol; W: Water. λ_{max} values in italic indicate shoulders.

Kröhnke and Bohlmann[78] classified as C-betaines the ylides having maxima at 440–460 mμ and as O-betaines those with maxima at 300–330 mμ. They concluded that the O-betaines included pyridinium dibenzoylmethylide and the C-betaines included all phenacylides. The spectra of pyridinium cyclopentadienylide in several solvents have been studied.[79]

The longest wavelength absorption band of this compound was assigned to an intramolecular charge-transfer transition because of its solvent sensitivity.

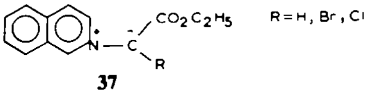
Similarly,[81] the visible absorption band of pyridinium ylides is attributed to an intramolecular charge-transfer transition (Scheme 24).



The deepening of the colour of pyridinium ylides accompanying a decrease in the degree of hydration has previously been noted by Krohnke[3] and commented on by Stafford.[75–82]

The changes in the visible absorption band observed in solvents of different Z value (a measure of polarity)[83] as set out in Table 4, clearly support its assignment to the intramolecular charge-transfer transition. Boyd[80] has also observed this bathochromic shift of the visible band with decrease in solvent polarity in the case of pyridinium 2-benzimidazolide. From an examination of the spectra of pyridinium dibenzoylmethylide in various solvents, it is evident that the band at 320 mμ as characteristic of O-betaines,[78] is not the ylide charge-transfer band because of its relative insensibility to change with solvent polarity; the ylide charge-transfer band appears at 429 mμ in benzene. In addition, the classification of enol betaines as C or O betaines is unsatisfactory[81] as many ylides show bands in both region even in polar solvents.[74–77]

Surpateanu *et al.*[84] have determined the electronegativity of some groups from absorption spectra of some isoquinolinium and pyridinium ylides in which one of the substituents of the ylide C atom is always a carbethoxy group. They assumed that the visible absorption band is due to the same intramolecular charge transfer.[85,86] First, these authors established a linear relationship between the Pauling scale atomic electronegativity of H, Cl, Br{χ} and the difference ΔE_T between the energy of the visible maximum of absorption of such isoquinolinium ylides **37** in which R=Cl or Br and this energy when R = H,



37

$\chi = 0.07\,\Delta E_T + 2.3.$

Using this relation and some literature data[81] they then determined the group electronegativity of the second substituents of the ylide C atom.

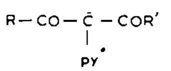
The group electronegativity found by this method is in good agreement with the one found by other techniques.[87–93] The knowledge of the group electronegativity can help to see *a priori* the stability of cycloimmonium ylides and the delocalization possibilities in these compounds.

Table 5.

No.	Ylides	χ
1	$\text{Is}^+\text{—}\bar{\text{C}}\text{—CO}_2\text{Et}$ H	2.20
2	$\text{Is}^+\text{—}\bar{\text{C}}\text{—CO}_2\text{Et}$ CSNHC_6H_5	2.52
3	$\text{Is}^+\text{—}\bar{\text{C}}\text{—CO}_2\text{Et}$ $\text{SO}_2\text{C}_6\text{H}_4\text{CH}_3$	2.74
4	$\text{Is}^+\text{—}\bar{\text{C}}\text{—CO}_2\text{Et}$ CONHC_6H_5	2.82
5	$\text{Is}^+\text{—}\bar{\text{C}}\text{—CO}_2\text{Et}$ $\text{SO}_2\text{C}_6\text{H}_5$	2.86
6	$\text{Is}^+\text{—}\bar{\text{C}}\text{—CO}_2\text{Et}$ CSSH	2.87
7	$\text{Is}^+\text{—}\bar{\text{C}}\text{—CO}_2\text{Et}$ $\text{CO}_2\text{C}_2\text{H}_5$	2.93
8	$\text{Is}^+\text{—}\bar{\text{C}}\text{—CO}_2\text{Et}$ COCH_3	3.07
9	$\text{Is}^+\text{—}\bar{\text{C}}\text{—CO}_2\text{Et}$ $\text{COC}_3\text{H}_7\text{(n)}$	3.08
10	$\text{Is}^+\text{—}\bar{\text{C}}\text{—CO}_2\text{Et}$ COC_6H_5	3.10
11	$\text{Is}^+\text{—}\bar{\text{C}}\text{—CO}_2\text{Et}$ CN	3.14
12	$\text{Is}^+\text{—}\bar{\text{C}}\text{—CO}_2\text{Et}$ $\text{COC}_6\text{H}_4\text{NO}_2$	3.20
13	$\text{Py}^+\text{—}\bar{\text{C}}\text{—COC}_6\text{H}_5$ COCH_3	3.07
14	$\text{Py}^+\text{—}\bar{\text{C}}\text{—COC}_6\text{H}_5$ COC_6H_5	3.10
15	$\text{Py}^+\text{—}\bar{\text{C}}\text{—COCH}_6\text{H}_5$ CN	3.16

Is = Isoquinoline; Py = Pyridine.

The IR spectra of the ylides have been measured in Nujol and in chloroform solution. The spectra are complex but all show strong ylide carbonyl absorption [94–100] at low frequency. Thus the ylide **38** (R = R′ = Ph) absorbs near 1490 cm^{-1} and the ylide **39** (R = Ph) near 1500 cm^{-1}. This presumably indicates that structure **40** contributes importantly to the resonance hybrid:[101]



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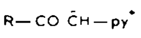

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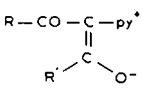

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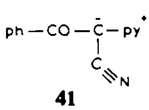
The ylides **41** and **43** absorbed strongly at 2166 cm^{-1} and 2185 cm^{-1}, respectively, which may also be interpreted as evidence that the structures **42**–**44**, respectively, contribute to the resonance hybrids.[99]



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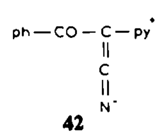

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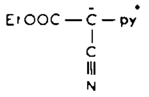

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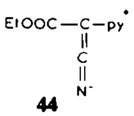
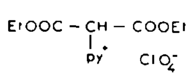


44

The most interesting feature of the NMR spectra of the pyridinium ylides is the variation in the chemical shift of the α protons of the pyridinium ring. In the perchlorate salt of **45** these protons absorb at $\delta = 9.21$ (d_6-dimethyl sulphoxide), but at $\delta = 8.63$ (deuterochloroform) in the corresponding ylide. Similar values were observed for the α protons in the ylides **38** (R = Me, R′ = Ph) and **38** (R = R′ = Ph). This shift is to be expected because of the overall increase in electron density. However, in the cyano ylides **41** and **43** the α protons absorb well downfield at $\delta = 9.23$ and $\delta = 9.31$ respectively (deuterochloroform), but the β and γ protons are not deshielded. This effect may also be explicable in terms of contributions of the structures **42** and **44**.



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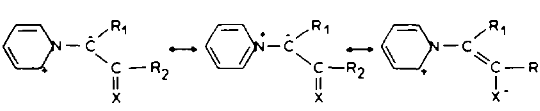
From the results we discussed previously, it can be deduced that the chemical reactivity of the disubstituted cycloimmonium ylides will not be explained only by the 1 – 3 dipolar structure usually assigned to these molecules.[67] The (3 + 2) cycloaddition (pyrolidines formation) or the (3 + 3) cycloaddition (dimer ylides formation) reactions can be explained assuming that the disubstituted ylides react in the resonance structure **46a**.



a b c

46

The CNDO calculation results and the spectroscopic data (mainly the ESCA and IR) show clearly that the negative charge of the ylide C atom is strongly delocalized on the heteroatoms of the electron withdrawing substituents. The weight of the resonance structure form **46b** is therefore important. Disubstituted cycloimmonium ylides would therefore lead to (5 + 2) or (2 + 2) (at the C=C exocyclic double bond) **46c**, cycloaddition reactions.

In the next part of this paper we shall try to rationalize chemical properties of disubstituted cycloimmonium ylides as follows:

Cleavage of the ylidic bond $N^+–C^-$.

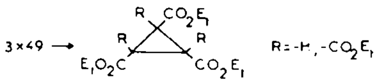
Cycloaddition reactions involving the resonance structure **46a**: (3 + 2) cycloadditions; (3 + 3) cycloadditions.

Reactions involving the resonance structure **46c**: (5 + 2) cycloadditions; (2 + 2) cycloadditions and substituent exchange reactions.

B. *Reactivity*

I. *Thermal reactions.* (1) *Cleavage of the* C–N *bond.* Zugravescu *et al.*[102] have studied the thermal decomposition of two isoquinolinium ylides, one monosubstituted, (**47**, R = H) the other one disubstituted (**47**, R = CO_2Et). Isoquinoline **48** and cyclopropanic derivatives **50**

47 **48** **49**



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are formed in both cases. The formation of **50** proceeds via carbene **49** formation.

Cook *et al.*[103] obtained dibenzoyl ethylene **54** by sublimation under high vacuum of ylide **51** at 150°.

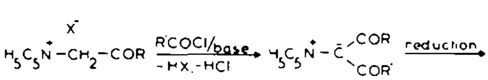
$$C_2H_5\overset{+}{N}-\overset{-}{C}H-COC_6H_5 \rightarrow C_5H_5N + [C_6H_5CO-CH] \rightarrow$$

51 **52** **53**

$$H_5C_6-COCH=CH-COC_6H_5$$

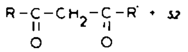
54

Cornforth[104] acylated some type **55** salts and ylides **56** were obtained. They were converted to β-diketones **57** by reduction with (Zn/CH_3CO_2H) (Table 6).



$$H_5C_5\overset{+}{N}\overset{X^-}{}-CH_2-COR \xrightarrow[-HX,\,-HCl]{R'COCl/base} H_5C_5\overset{+}{N}-\overset{-}{C}\begin{smallmatrix}COR\\COR'\end{smallmatrix} \xrightarrow{reduction}$$

55 **56**



$$R-\underset{O}{\underset{\|}{C}}-CH_2-\underset{O}{\underset{\|}{C}}-R' + 52$$

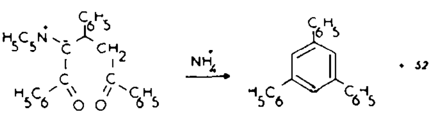
57

When the intermediate ylides **56** were not sufficiently stable to be isolated, the reduction was performed directly in the reaction mixture.

In some cases this ylide bond cleavage can be used to synthesize new heterocyclic compounds.[105-107]

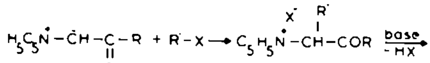
$$H_5C_5\overset{+}{N}-\overset{-}{C}H-COC_6H_5 + H_5C_6-CH=CH-COC_6H_5 \rightarrow$$

58 **59**



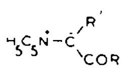
60 **61**

(2) *Nucleophilic character of cycloimmonium ylides.* (a) *Monosubstituted ylides.* The monosubstituted carbanion ylides are nucleophilic reagents. In the introduction we have reported that monosubstituted ylides can be transformed into disubstituted ylides by reaction with acid chloride, anhydride and chloroformide.[3,108-111] An S_N2 mechanism has been proposed to explain these reactions.[2] Alkylation reactions of monosubstituted ylides proceed probably by a similar mechanism.



$$H_5C_5\overset{+}{N}-\overset{-}{C}H-\underset{O}{\underset{\|}{C}}-R + R'-X \rightarrow C_5H_5\overset{+}{N}\overset{X^-}{}-\overset{R'}{\overset{|}{C}H}-COR \xrightarrow[-HX]{base}$$

62 **63** **64**



$$H_5C_5\overset{+}{N}-\overset{-}{C}\begin{smallmatrix}R'\\COR\end{smallmatrix}$$

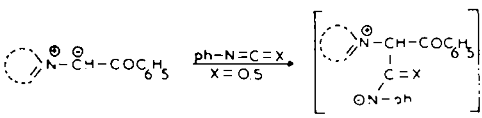
R = ph, OCH_3, OC_2H_5

R' = alkyl

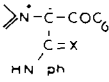
65

This reaction is not important for the synthesis of type **65** ylides because the replacement of an hydrogen by an alkyl group decreases the stability of the ylide.[12] The intermediate salts **64** have been used for the synthesis of a great variety of organic compounds (ketones, diketones, esters, thioesters).[103,112,113]

The first step of the reaction of monosubstituted ylides on isocyanates, isothiocyanates[3,114,115] and carbon disulphide[116] is a nucleophilic attack on the carbon of the double bond C=N or C=S by the ylide C atom. This attack is followed by a migration of a proton to the negative nitrogen, and by the formation of the disubstituted ylides **68**.



66 **67**



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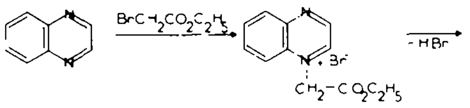
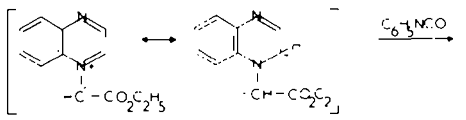
When the carbon α to the nitrogen of the aromatic ring bears significant positive charge, a cyclization reaction can occur.[117]



69 **70**



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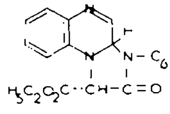
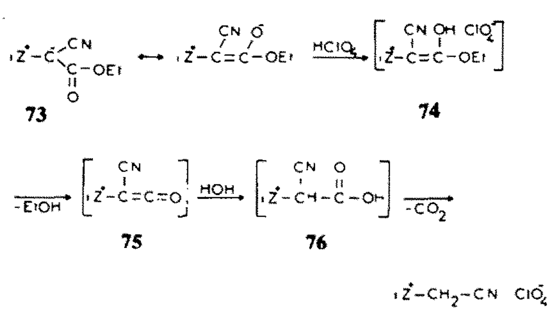


72

Table 6.

Salt 55		Acyl chloride	β diketones 57
R = p-Cl–C_6H_4,	X = Br	R' = C_6H_5	ClC_6H_4–CO–CH_2–CO–C_6H_5
R = CH_3,	X = Cl	R' = C_6H_5	CH_3–CO–CH_2–CO–C_6H_5
R = $(CH_3)_3C$,	X = Br	R' = C_6H_5	$(CH_3)_3C$–CO–CH_2–CO–C_6H_5
R = $(CH_3)_3C$,	X = Br	R' = $(CH_3)_3C$	$(CH_3)_3C$–CO–CH_2–CO–$C(CH_3)_3$

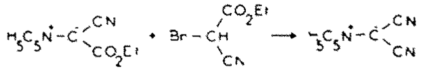
(b) *Disubstituted ylides*. Disubstituted ylides are less basic than the mono ylides. Their nucleophilic behaviour can be explained by the influence of the ylide C atom substituents. In some cases the negative charge can be localized on a heteroatom substituent. For example Kröhnke[111] has shown that cyanocarbethoxy isoquinolinium methylide **73** reacts in aqueous solution with perchloric acid giving the salt **77**.



73 **74** **75** **76** **77**

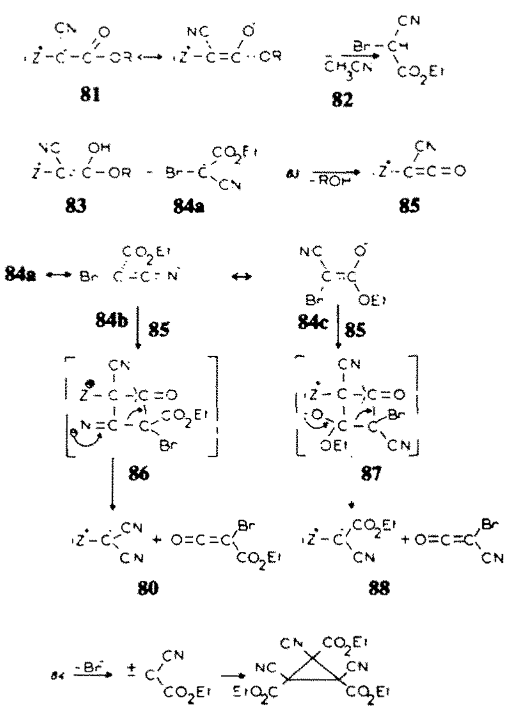
The same ylide in trifluoroacetic acid: MeOH leads by a transesterification reaction to the ylide **73** (Et = CH_3).[66] The intermediate ketene **75** is also implied in this reaction.

Leonte and Zugravescu[118] have shown that the reaction of cyanocarbethoxypyridinium or isoquinolinium methylide with ethyl bromocyanacetate in acetonitrile gives the corresponding dicyanomethylide **80**.



78 **79** **80**

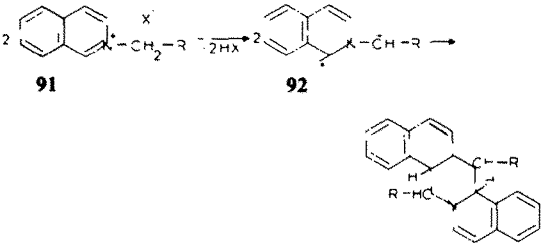
During this reaction, the formation of the ketene intermediate is proposed[66] by analogy with the reactions performed on isoquinolinium cyanocarbethoxymethylure either in aqueous solution with perchloric acid or in methanolic solution with trifluoroacetic acid.[66]



81 **82** **83** **84a** **85** **84a** **84b** **84c** **86** **87** **80** **88** **89** **90**

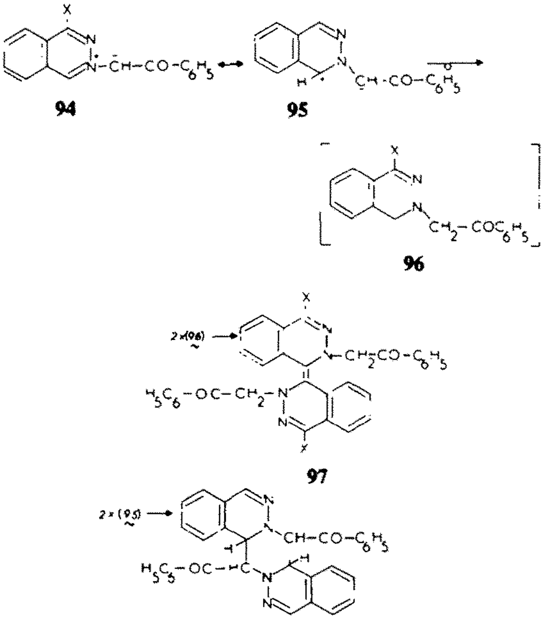
The first step which leads to the ketene formation **85** is carbethoxy oxygen protonation. The intermediate carbanion **84** loses a bromine anion leading to the carbene **89** which by trimerization gives the isolated cyclopropanic derivative **90**. The cyclopropanic compounds **90** is always derived from bromocyanacetate.

(3) *Ylides inactivation*. It is known that disubstituted methylides are more easily isolated from a reaction mixture than the monosubstituted.[7] Inactivation of these latter compounds is attributed to structural factors (structure of the heterocycle and of the carbanion substituent) and to the composition of the reaction mixture. In basic tetrahydrofuran or chloroform N-acyl isoquinolinium salts **91** are converted into dimers **93** (R = COPh), $COCH_3$. Their formation is attributed to a (3 + 3) cycloaddition of the intermediate ylides **92**.[119,120] Analogous dimers **93** were isolated with R = $COC_6H_4NO_2p$, $COC_6H_4CH_3p$, $COC_6H_4OCH_3p$, $COCH_3$ and CO_2CH_3.[119]



91 **92** **93**

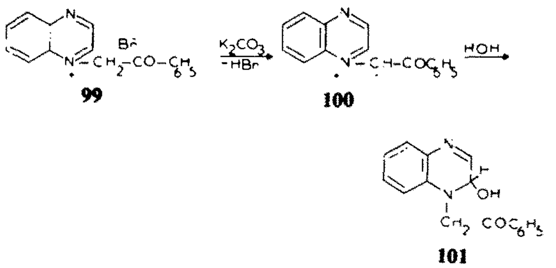
Phthalazinium phenacylide **94**(X = H) and 1-methylphthalazinium phenacyclide **94** (X = CH_3) obtained *in situ* by reaction of triethylamine with their salts in benzene solution are inactivated during purification.[121,122] In the latter case dimer **97** is the only reaction product.[122] In the former, the dimer **98**, a (3 + 3) cycloaddition product



94 **95** **96** **97** **98**

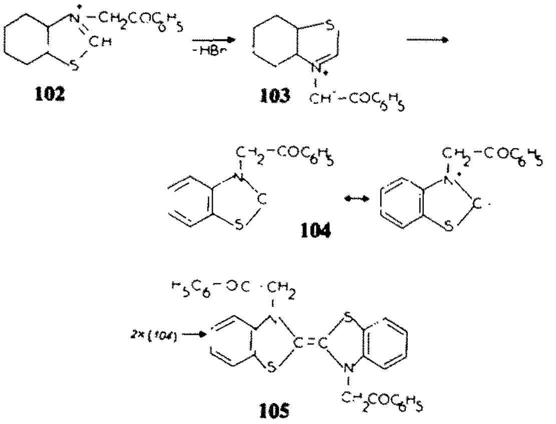
is formed together with the dimer **97**. Similar dimers have been isolated in the case of 3*p*-tolylpyridazinium-phenacylide.[123]

Quinoxalinium phenacylide **100** obtained *in situ* by reaction of its salt **99** with potassium carbonate, adds water and is converted into **101**.[124]



99 **100** **101**

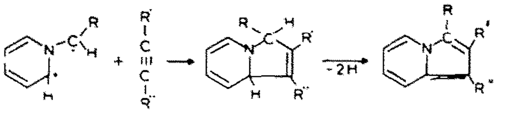
Kröhnke and Friedrich[125,126] have studied the behaviour of N-phenacyl benzothiazolium salts **102** in alkaline solution at various pH values in different solvents. They explained the formation of the ethylenic dimer **105** by the following mechanism established by analogy with that proposed in the literature.[127,128]



102 **103** **104** **105**

(4) (3 + 2)*Cycloaddition*. (a) *Monosubstituted ylides with acetylenic derivatives.* CNDO calculations show that these compounds have a more important a (1 − 3) dipolar structure,[129] than the disubstituted ylides.[67]

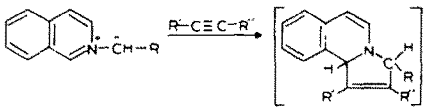
Monosubstituted pyridinium methylides undergo cycloaddition with acetylenic philodienes giving indolizines **109**. The primary reactions products **108** easily aromatise either by hydrogen transfer to the philodiene[130–132] or by dismutation.[133]



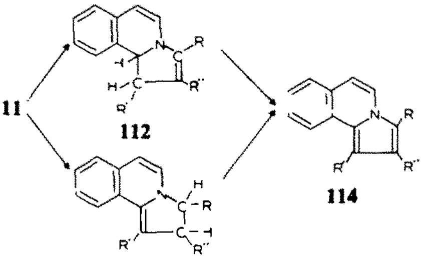
106 **107** **108** **109**

In some cases the hydrogenated philodiene has been detected in the reaction mixture.[113] Acetylene dimethyldicarboxylate (DMAD) is one of the most common acetylenic philodiene. Table 7 summarizes the indolizinic derivatives **109** already synthesized by this method.

Isoquinolinium methylides react similarly with acetylenic dipolarophiles and lead to benzoindolizines **114** formed by aromatisation of the intermediate dihydroindolizines **111**, **112**, **113**.



110 **111**



111 **112** **113** **114**

Quinolinium methylides behave similarly (Table 9):

Table 7.

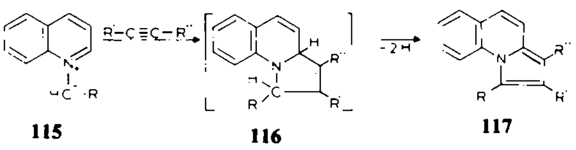
Ylide **106** R =	Dipolarophile reagent **107**	Indolizines **109** R	R'	R''	Ref.
$-COC_6H_5$	DMAD	COC_6H_5	CO_2Me	CO_2Me	134
$-COC_6H_5$	$HC{=}CC_6H_5$	COC_6H_5	H	C_6H_5	134
$-COMe$	DMAD	COMe	CO_2Me	CO_2Me	134
$-CO_2Et$	DMAD	CO_2Et	CO_2Me	CO_2Me	134
$-C_6H_4NO_2p$	DMAD	$C_6H_4NO_2p$	CO_2Me	CO_2Me	134
$-CN$	DMAD	CN	CO_2Me	CO_2Me	134
$-COC_6H_5$	$HC{\equiv}C{-}CN$	COC_6H_5	H	CN	135
$-COC_6H_5$	$ClC{\equiv}CCN$	COC_6H_5	Cl	CN	135

Table 8.

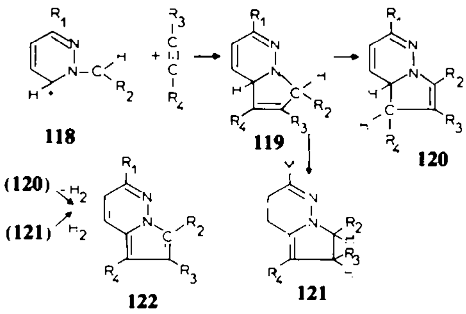
Ylides **110** R =	Dipolarophile reagents	Benzoindolizines R	R'	R''	Ref.
COC_6H_5	$H{-}C{\equiv}C{-}CN$	COC_6H_5	CN	H	132
COC_6H_5	$Cl{-}C{\equiv}C{-}CN$	COC_6H_5	CN	Cl	132
CO_2CH_3	DMAD	CO_2CH_3	CO_2Me	CO_2Me	136
$CO_2C_2H_5$	DMAD	$CO_2C_2H_5$	CO_2Me	CO_2Me	137

Table 9.

Ylides **115** R =	Dipolarophile reagents	Benzoindolizines **117** R	R′	R″	Ref.
COC_6H_5	HC≡C–CN	COC_6H_5	H	CN	132
COC_6H_5	Cl–C≡C–CN	COC_6H_5	Cl	CN	132
COC_6H_5	DMAD	COC_6H_5	CO_2Me	CO_2Me	113
$COCH_3$	DMAD	$COCH_3$	CO_2Me	CO_2Me	113

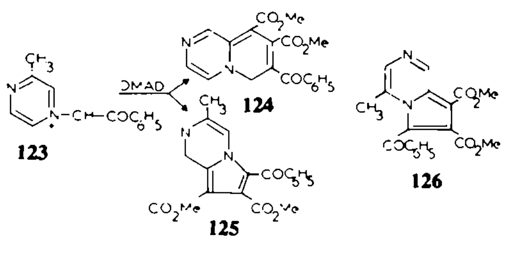


The reaction of pyridazinium methylides with DMAD leads to the heterocycles **121** and **122**:



When : R_1 = tolyl, R_2 = CO–Ph, $R_3 = R_4$ = CO_2Me,[123,138,139] R_1 = tolyl, R_2 = CO–PhNO$_2$p, $R_3 = R_4$ = CO_2Me,[138] R_1 = p-isopropylphenyl, R_2 = CO-Ph, $R_3 = R_4$ = CO_2Me[141] **122** is the only formed compound. When R_1 = p-isopropylphenyl, R_2 = CO-Ph, $R_3 = R_4$ = CO_2Me both **120** and **122** are formed.[140,141]

3-Methylpyrazinephenacylide **123** reacts in acetonitrile with DMAD and gives **124** with a 4% yield.[142]

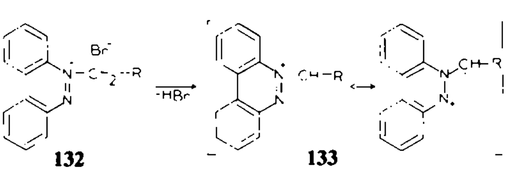


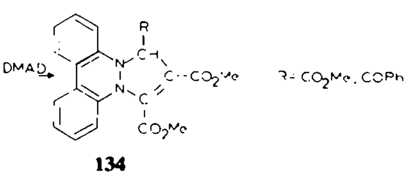
When the reaction mixture is heated under reflux in chloroform the yields of **122** and **125** are 8% and 4% respectively. **126** is also formed in very low yield.[142]

Ylide **128** formed *in situ* reacts with DMAD[134] and leads to **130** and **131**.

This last compound is formed by elimination of a hydrogen and a benzoyl group from the initial adduct **129**.

Azabycyclic derivatives **134** have also been synthesized from benzocinnoline monosubstituted ylides.[143,144]

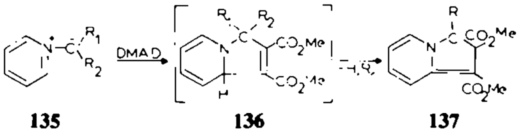


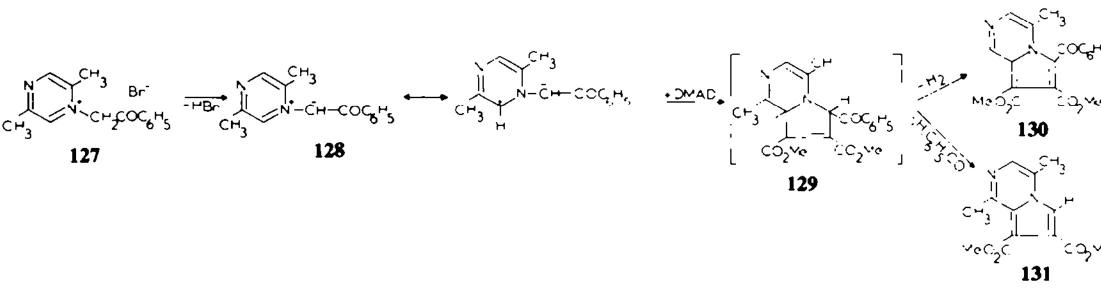


In all the described reactions in this chapter the monosubstituted ylides are formed in the reaction mixture.

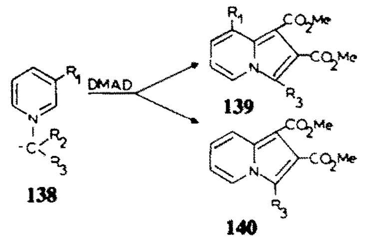
(b) ***Reactions of disubstituted ylides with acetylenic derivatives.*** We have reported that the negative charge of the ylide C atom, in disubstituted ylides is delocalized on the substituents. But, according to theoretical calculations some negative charge remains on this atom.[67] This explains why such ylidic compounds give (3 + 2) cycloadditions.

Pyridinium methylides **135** react with DMAD and leads to indolizines **137**. This reaction proceeds by loss of an hydrogen and an ylide substituent:





Linn *et al.*[10] have shown that in the case of dicyanopyridinium methylide **135** ($R_1 = R_2 = CN$) the indolizine **137** ($R_2 = CN$) is formed by a (1 – 4) cyanhydric acid elimination from intermediate **136** ($R_1 = R_2 = CN$). Similarly **137** ($R_2 = CO_2Et$, COPh) is formed from dicarbethoxypyridinium methylide **135** ($R_1 = R_2 = CO_2C_2H_5$) and dibenzoylpyridinium methylide **135** ($R_1 = R_2 = COPh$) respectively.[145] Similar cycloadditions have been performed with ring substituted pyridinium methylides (Table 10).



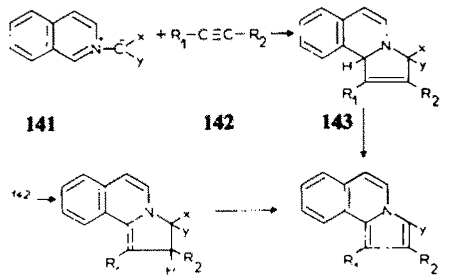
138 **139** **140**

Table 10.

138			139	140
R_1	R_2	R_3	R_1	R_3
Me	CN	CN	Me	CN
Me	H	COPh	Me	COPh
CN	CN	CN	CN	CN
CN	H	COPh	CN	COPh

In this case the mixture of indolizines **139** and **140** is formed, **139** being obtained in the higher yield.[142]

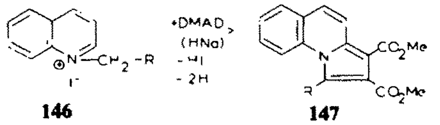
Isoquinolinium methylides **141** react also with acetylenic derivatives giving the indolizines derivatives **145**. Dihydroindolizines **143** and **144** are the usually isolated reaction intermediates.[146,147]



141 **142** **143** **144** **145**

Table 11 gives the structures of compounds **142**, **143**, **144** which have been isolated and characterized.[14,132,142,143,147,148]

Quinolinium methylides can also give (1 – 3) dipolar cycloaddition. From mixtures of ylides, formed *in situ*, DMAD and sodium hydride cycloadducts **147** were obtained.[145]



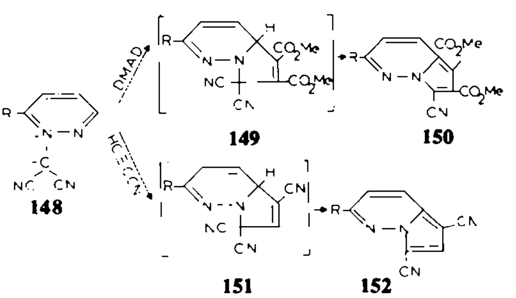
146 **147**

R=COMe, COPh

Pyridazine dicyanomethylides **148** lead to the cycloadducts **150** and **152** similar to those obtained from pyridine methylides.[142]

Table 11.

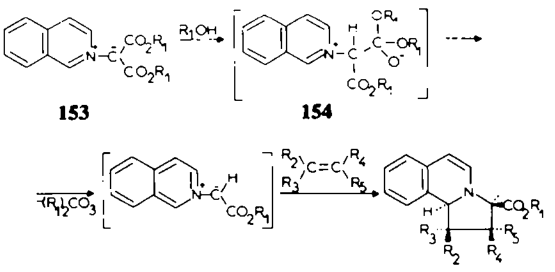
	Compounds														
	141		142		143				144				145		
Indices	X	y	R_1	R_2	X	y	R_1	R_2	X	y	R_1	R_2	y	R_1	R_2
(a)	CO_2Me	CO_2Me	CO_2Me	CO_2Me	CO_2Me	CO_2Me	CO_2Me	CO_2Me	CO_2Me	CO_2Me	CO_2Me	CO_2Me	CO_2Me	CO_2Me	CO_2Me
(b)	CO_2Me	CN	CO_2Me	CO_2Me	CO_2Me	CN	CO_2Me	CO_2Me	CO_2Me	CN	CO_2Me	CO_2Me	—	—	—
(c)	CO_2Me	CO_2Me	CO_2Me	H	CO_2Me	CO_2Me	CO_2Me	H	—	—	—	—	CO_2Me	CO_2Me	H
(d)	CN	CN	CO_2Me	CO_2Me	—	—	—	—	CN	CN	CO_2Me	CO_2Me	CN	CO_2Me	CO_2Me
(e)	CO_2Me	CO_2Me	CN	CN	—	—	—	—	CO_2Me	CO_2Me	CN	CN	CO_2Me	CN	CN
(f)	CN	CN	CN	CN	—	—	—	—	—	—	—	—	CN	CN	CN
(g)	CO_2Me	CN	CN	CN	—	—	—	—	CO_2Me	CN	CN	CN	CO_2Me	CN	CN



148 149 150 151 152

(R = H, OMe, OEt)

(c) *Reactions with ethylenic compounds.* Mono and dicarbethoxy isoquinolinium methylides react with olefines and lead to tetrahydroindolizines **156**.[126] Similar compounds have been isolated from enamines.[149]



153 154 155 156

Table 12.

Compounds 156 R_1 = CH_3 or Et				
Indices	R_2	R_3	R_4	R_5
(a)	CO_2Me	H	CO_2Me	H
(b)	CO_2Me	H	H	CO_2Me
(c)	CO_2Me	H	H	Ph
(d)	CN	H	H	H
(e)	CO_2Me	Me	H	H
(f)	CO_2Me	CO_2Me	CO_2Me	CO_2Me

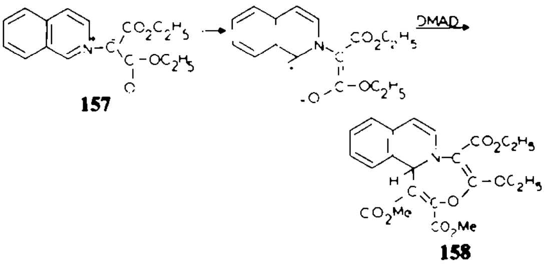
The methylide **155** formed *in situ* from the corresponding salt leads, by reaction with olefines in methanol, to the same series of cycloadducts **156a–f** (Table 12). During this reaction the disubstituted ylide **153** can first be transformed into the monosubstituted ylide **155**. This first step can proceed by addition of the methanol, used as solvent on the ylide **153** and elimination of alkyl carbonate; in absence of dipolarophile, in methanol, ylide **155** gives dimer **93** (R = CO_2CH_3) and alkyl carbonate, whereas in acetonitrile it remains unchanged. The same dimer **93** (R = CO_2CH_3) can also be formed directly by heating the monosubstituted ylide **155** in methanol.[150]

The olefine geometry remains unchanged during the formation of the cycloadducts **156**; methyl maleate and fumarate lead only to one pair of isomers.

Similar results are described in the reaction of phenylpyridazinium phenacylide with fumaric and maleic esters.[140] These results confirm that most of the 1,3-dipolar compounds react stereospecifically with dipolarophiles and that the addition is *cis*-stereospecific.[151–156]

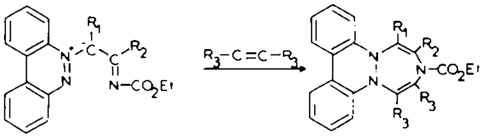
Some reactions of mono and disubstituted ylides with ethylazodicarboxylate and N-phenylmaleinamide have been described in the literature.[2]

(5) (5 + 2) *Cycloadditions.* The charge distribution of highly electron withdrawing disubstituted ylides is such that they can be considered as 1,5-dipoles **157**.



157 158

Zugravescu *et al.*[137,157] have isolated oxazepinic derivatives **158** during the reaction of dicarbethoxyisoquinolinium or phthalazinium methylides with DMAD in benzene solution. Their structures have been established by proton NMR: two different ethyl groups appear: ylide **159** ($R_1 = CO_2Me$, $R_2 = H$) formed by cycloaddition of N-ethoxycarbonyl imide benzocinnoline with methyl propiolate[158] gives cycloadducts **160** ($R_1 = R_3 = CO_2Me$, $R_2 = H$) and ($R_1 = CO_2Me$, $R_2 = H$, $R_3 = CO_2Et$) when it reacts with DMAD:[159]

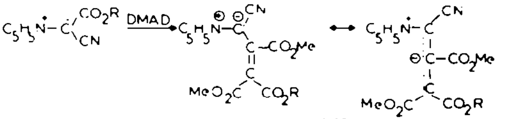


159 160

The structure of the triazepines **160** has been proved by X-ray analysis. Similar thermal (5 + 2) cycloaddition of cumulenes with a diazepine[160] and of diphenylketene with benzenediazonium 2-carboxylate[161] are known. They are supposed to be concerted thermal reactions.

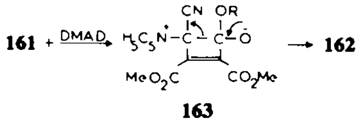
(6) (2 + 2) *Cycloadditions.* In this chapter some cycloimmonium ylides reactions will be described which can be explained by the action of the intermediate (2 + 2) adducts on the ylide carbanion.

In the previous part we have shown that mono and disubstituted pyridinium methylides reacting with DMAD lead to indolizines. Cyanocarbethoxy or carbomethoxy pyridinium ylides **161** reacting in acetonitrile, with this acetylenic derivative lead to ylide **162** (R = CH_3 or Et):[162]



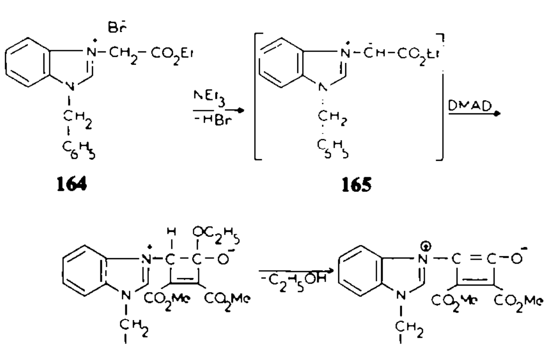
161 a 162 b

During this reaction the elimination of the ylide C atom substituent is not observed. In a previous paper,[65] the reaction mechanism proposed by Zugravescu and Petrovanu[2] was confirmed by ESCA studies. It involves a nonisolated cyclobutenic intermediate **163**:



163

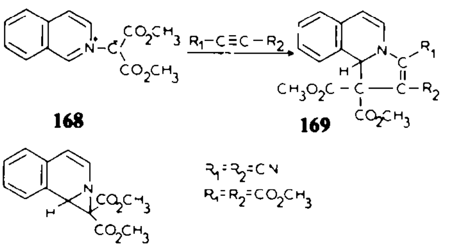
Similar cyclobutenic (2 + 2) adducts have been isolated during the reaction of benzimidazole salt **164** with DMAD in presence of triethylamine:[163]



164 **165**

166 **167**

(7) *Cycloaddition involving intermediate formation of an aziridine.* During the reaction of dicarbomethoxy isoquinolinium methylide **168** with dicyanoacetylene or DMAD, the product **169** is formed in very low yield besides the main reaction products **145a**, **145e**:[148,164,165]

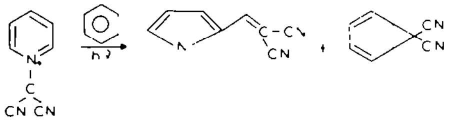


168 **169**

170

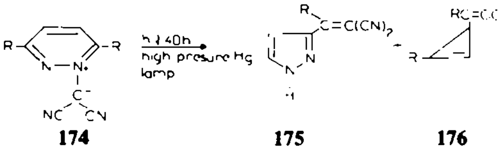
The structures of these two adducts can be explained by assuming that the aziridine **170**[165] is the primary reaction product which adds to the unsaturated compounds, following a general mechanism proposed in the literature.[167,168]

(II) *Photochemistry of cycloimmonium ylides.* The photoreactions of disubstituted methylides in diluted benzene are of two types: (1) The cleavage of C^-–N^+ ylide bond with formation of the heterocycl and the disubstituted carbene. This is usually the main reaction.[66,168] (2) The photoisomerization of cycloimmonium ylides. In this reaction the contraction or expansion of the heterocyclic ring occurs:[168]



171 **172** **173**

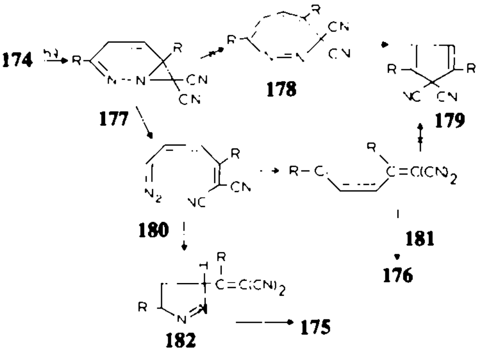
The photolysis of a benzenic solution of pyridazinium dicyanomethylide **174** leads to the three products **175**, **176** and 7,7-dicyanonorcaradiene **173** formed by addition of



174 **175** **176**

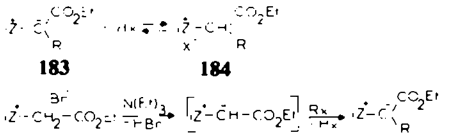
R=H,Me

the corresponding carbene on the solvent.[169] In dichloromethane the yield of the pyrazole **175** is increased whereas the yield of the cyclopropenic derivative **376** is decreased. A reaction mechanism analogous to the one proposed for the photolysis of pyridazine N-oxides[170,171] has been proposed in this case.



(III) *Applications of cycloimmonium ylides.* It has been shown that cycloimmonium ylides can be used in the synthesis of numerous heterocycles. Many papers deal with the use of these compounds in analytical chemistry.

Surpateanu and Rucinschi[172] have shown that some colored ylides of structure **183** are highly sensitive acido-basic indicators, taking into account the following reversible reaction:



183 **184**

185 **186** **187**

colored colourless

Isoquinolinium disubstituted methylides are stable compounds. They absorb in the visible range having high extinction coefficients. Their solutions follow the Beer–Lambert law. Taking into account these properties and the fact that a series of the disubstituted isoquinolinium ylides **187** can be synthesized from the isoquinolinium carbethoxy methylide **186** by reaction with acid chlorides, anhydrides and isocyanates, Surpateanu *et al.*[173-175] proposed a quantitative spectrophotometric method for the determination of these reagents:

It is well known that the electrical conductivity of organic semi-conductors is described by the relation:

$$\sigma = \sigma_0 e^{-(\epsilon_T/kT)}$$

where σ is the electrical conductivity corresponding to the absolute temperature T at which measurement was performed, σ_0 is electrical conductivity for $T \rightarrow \infty$, k is Boltzmann's constant, ϵ_T is so-called thermal activation energy.[176] The dependence of the electrical conductivity upon temperature for a series of ylidic compounds proves the semiconducting character.[177,178] The values of the thermal activation energy for a series of isoquinoline ylides is given in the Table 14.

CONCLUSION

From the results summarized in this report some fundamental features of cycloimmonium ylides can be emphasized.

Table 13.

183 R =	λ_{max} (nm)	ϵ_{max} (mole^{-1}cm^{-1})	pK_a	pH range of colour change	Change of colour
H	552	37,818	6.47	—	—
–CONHPh	467	36,856	4.58	4.8–5.2	colourless–orange
–CO_2Et	452	37,350	4.00	4.3–5.0	colourless–yellow
–CSNHPh	493	19,400	3.82	4.2–4.9	colourless–pink
–CN	436	16,800	3.74	1.3–1.4	colourless–yellow

Table 14.

Ylides	ϵ_T (eV)
Isoquinolinium-benzoyl-carbethoxymethylide	0.90
Isoquinolinium-acetyl-carbethoxymethylide	1.57
Isoquinolinium-cyano-carbethoxymethylide	1.37
Isoquinolinium-N-phenylthyoamido-carbethoxymethylide	1.10

The positive charge formally written on the ylide N atom is never high. The negative charge of the ylide C atom is also small in the case of disubstituted ylides. These two points are confirmed by theoretical calculations and by ESCA spectroscopic data. In the case of monosubstituted ylides the negative charge of the ylide C atom remains higher than for the disubstituted ylides. This point, which is supported by the high nucleophilicity of the monosubstituted ylide C atom, has not yet been studied from the theoretical and ESCA points of view. These studies are in progress.

We think that the classification established in this report will enable one to predict the difference in reactivity of mono and disubstituted ylides; cycloimmonium ylides are highly polarisable molecules. Therefore the reaction conditions (solvent, reagents) must strongly influence the reaction course.

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