*Chimia 45 (1991) 65–76*
*© Schweiz. Chemiker-Verband; ISSN 0009–4293*

# The Photochemistry of *N*-Iminopyridinium Ylides in Retrospect. From a Simple Concept to Some Applications

**Jacques Streith***

Dedicated to Prof. *G. Ourisson* on the occasion of his 65th birthday

*Abstract.* Azomethine-imines are well known to undergo ground-state 1,3-dipolar cycloaddition reactions with olefins or acetylenes, leading thereby to five-membered heterocyclic systems. When excited by UV light, some of these 1,3-dipolar azomethine-imines lead to the isomeric three-membered diaziridines *via* disrotatory electrocyclisation. The following review article shows that many *N*-iminopyridinium ylides – which are aromatic analogues of azomethine-imines – also lead to electrocyclisation from their photo-excited electronic (singlet) state to give the expected non-aromatic and boat-shaped 1*H*-1,2-diazepine isomers. Diazanorcaradienes – *i.e.* bicyclic diaziridines – are the postulated intermediates for these photoinduced ring-expansion processes.

Ylides **Y** (*Scheme 3*) being mesoionic compounds have a large dipole moment; as a consequence, they are hydrophilic/lipophobic species, whereas diazepines **D** are poorly polar and, therefore, lipophilic/hydrophobic molecules. This very pronounced change of polarity triggered off the synthesis of some novel negative photoresists which are based on the photoisomerisation of water-soluble polymeric pyridinium ylides to the corresponding hydrophobic polymeric diazepines.

Thermal activation of diazepines **D** led to ring contraction back to the corresponding ylides **Y** – obviously *via* norcaradiene intermediates **N** – and permitted to establish the kinetic and thermodynamic parameters for this process. Diazepines **D** are higher-energy (by *ca.* 85 kJ/mol) isomers of ylides **Y**. They react smoothly and chemospecifically as dipolarophiles with diazoisopropane to give pyrazoline cycloadducts. From these latter ones, novel small-ring compounds could be prepared, *e.g.* homodiazepines (cyclopropane derivatives), their tricyclic staircase-like isomers (fused cyclopropane/cyclobutane derivatives) as well as the first example of a cyclopropapyridine (a cyclopropene derivative).

## 1. Introduction

Several photoinduced interconversions of $4\pi$ electron 1,3-dipolar species with their three-membered heterocyclic isomers have been described during the last three decades and by now present well-understood phenomena [1]. Along these lines, *Calvin* performed the pioneering work by demonstrating the photochemical electrocyclisation of nitrones **1** into the corresponding oxaziridines **2** [2]. He showed, furthermore, that this ring closure follows a disrotatory mode [3], obeying thereby the orbital-symmetry conservation rules [4] (*Scheme 1*). Likewise, *Huisgen* and coworkers showed that the aziridines **3** and **4** undergo photoinduced disrotatory ring opening to the corresponding azomethine ylides **6** and **5**, respectively, whereas thermally induced ring opening followed a conrotatory mode which leads to **5** and **6**, respectively [5] (*Scheme 1*). These results agree well with the *Woodward-Hoffmann* rules [4]. Last but not least, *Moore* and coworker demonstrated the photoisomerisation of the cyclic azomethine-imine **7** to the diaziridine **8** [6]. Such a wedge-shaped bicyclic isomer was expected to be formed by photo-excitation of **7**, presumably *via* a concerted disrotatory mode (*Scheme 1*).

## 2. From a Simple Concept...

The photoinduced interconversion of the three types of 1,3-dipolar species **A** which are under consideration – *i.e.* azomethine oxides (usually called nitrones) **1**; azomethine ylides **5** and **6**; type **7** azomethine imines (*Scheme 1*) – with the corresponding three-membered ring isomers **B**, can be represented in a unified manner as depicted in *Scheme 2* (non-aromatic azomethine-ylides). It should be noted that the direction of the photoinduced electrocyclisation – *i.e.* ring formation starting from a 1,3-dipolar species, or ring cleavage of three-membered heterocycles to the corresponding 1,3-dipoles – is solely dependent upon the relative thermodynamic stabilities of these pairs of cyclic *vs.* acyclic isomeric partners [5].

The idea then cropped up that analogous 1,3-dipolar species, in which the azomethine moiety is fully incorporated into a pyridine ring, could show a photochemical behaviour similar to the one described above for the non-aromatic 1,3-dipoles **A**. We speculated that upon UV excitation the pyridinium ylides **A'** would lead – *via* an electrocyclic process – to the heteroatomic norcaradienes **B'**, which, by virtue of a fast thermal valence

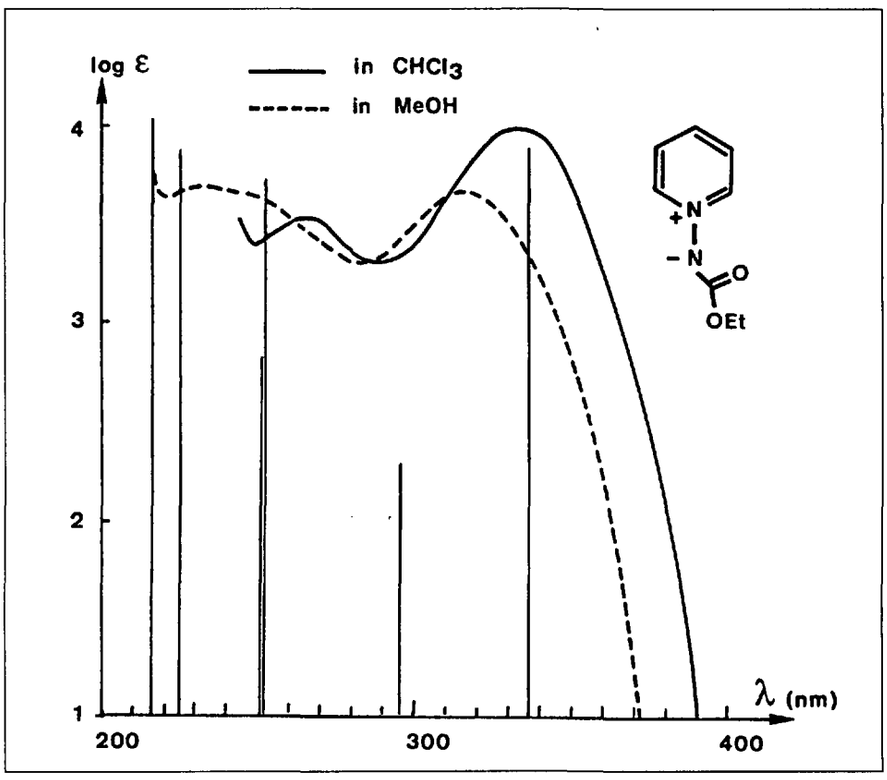



Fig. 1. *UV Spectrum and calculated electron transitions of pyridinium ylide* **17** *using a PPP model* [17]

*Correspondence*: Prof. Dr. Jacques Streith
Ecole Nationale Supérieure de Chimie
Université de Haute-Alsace
3, rue Alfred Werner, F–68093 Mulhouse Cedex

tautomerism, would produce the seven-membered rings **C**. These pyridinium ylides **A'**, which are aromatic species, are thermodynamically more stable entities than the postulated norcaradiene photoisomers **B'**. Clearly UV excitation would be needed to achieve de-aromatisation of the pyridinium ylides **A'**, a process which was expected to be strongly endothermic (*Scheme 2*).

### ...to Some Experimental Results

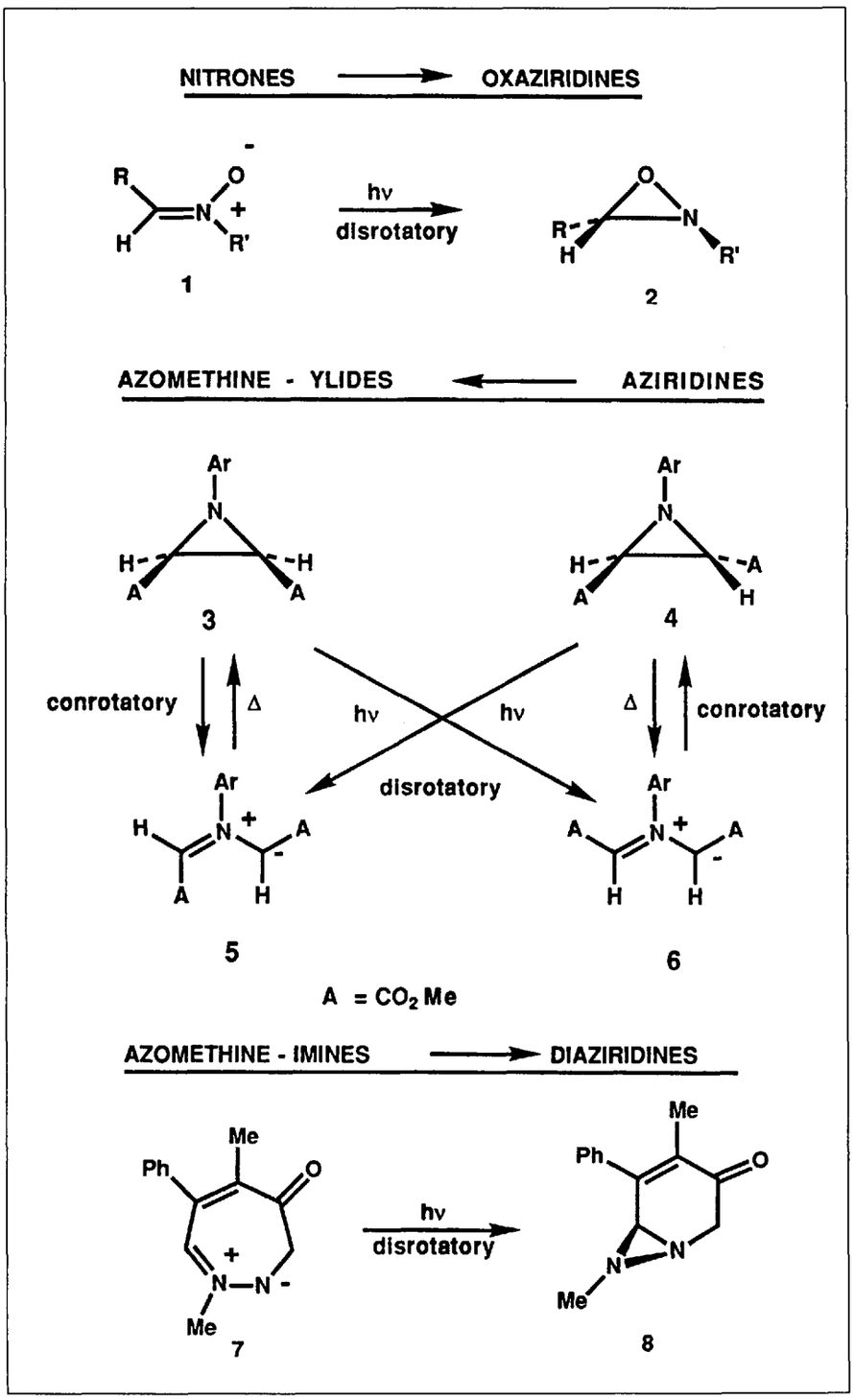
The photochemistry of pyridine *N*-oxides and of polycyclic aromatic *N*-oxides has been studied and reviewed extensively [7][8]. Most authors explain the formation of the isolated photoisomers by assuming the occurrence of short-lived oxaziridines as the primary photoproducts, although such intermediates have never been detected, not even by ns flash photolysis [9]. To quote but one example, the photoinduced rearrangement of pyridine *N*-oxide (**9**) led in poor yield to pyrrole-2-carbaldehyde (**12**) [10], presumably *via* the bicyclic oxaziridine **10** and some additional short-lived intermediates, including an open-chain nitrene [11][12] (*Scheme 3*).

The photochemistry of pyridinium ylides has only been studied sparsely. In one instance, the UV-initiated rearrangement of pyridinium dicyanomethylide (**13**) led to the 2-(dicyanovinyl)pyrrole (**16**) whose structure is reminiscent of **12** [12]. The postulated primary photoproduct is the azanorcaradiene **14** (*Scheme 3*).

*N*-Iminopyridinium ylides **Y** turned out to be the most interesting among the pyridinium ylides studied so far, since UV excitation of these zwitterionic ylides led in excellent yields to the expected seven-membered diazepines **D**, diazanorcaradienes **N** being the postulated intermediates [13] (*Scheme 3*). Since our first findings [13], these photoinduced ring enlargements have been generalized and reviewed extensively [14–16].

This article is devoted to the photoinduced reactions of type **Y** *N*-iminopyridinium ylides (*Chapt. 3*), as well as to the chemistry of their major photoisomers, *i.e.* the 1*H*-1,2-diazepines **D** (*Chapt. 4*). We shall select and discuss some results most of which have been obtained during the last decade.

*Scheme 1*



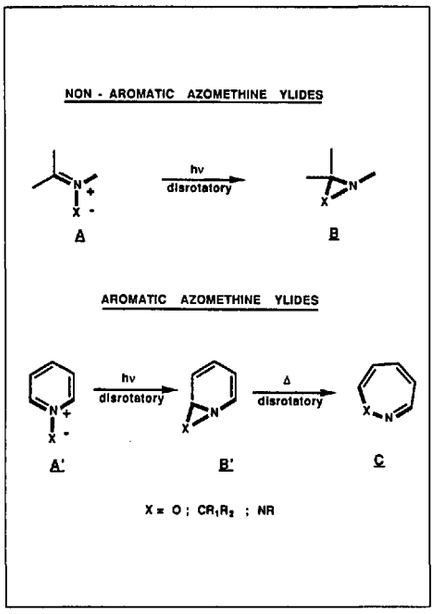

## 3. From *N*-Iminopyridinium Ylides to 1,2-Diazepines and the Reverse Thermal Ring Contraction

The mesoionic pyridinium ylides **Y** have a large dipole moment which accounts for the fact that they are soluble in $H_2O$, and only poorly soluble in lipophilic solvents. The diazepine photoisomers **D** have a small dipole moment; as a consequence they are lipophilic and hydrophobic species. This rather drastic change of polarity, when the ylides **Y** undergo photoisomerisation to the diazepines **D**, led to some practical applications, *i.e.* the preparation of liposomes and the making of photoresists starting from amphiphilic- and from polymeric *N*-iminopyridinium ylides, respectively (see below *Chapt. 3–5*).

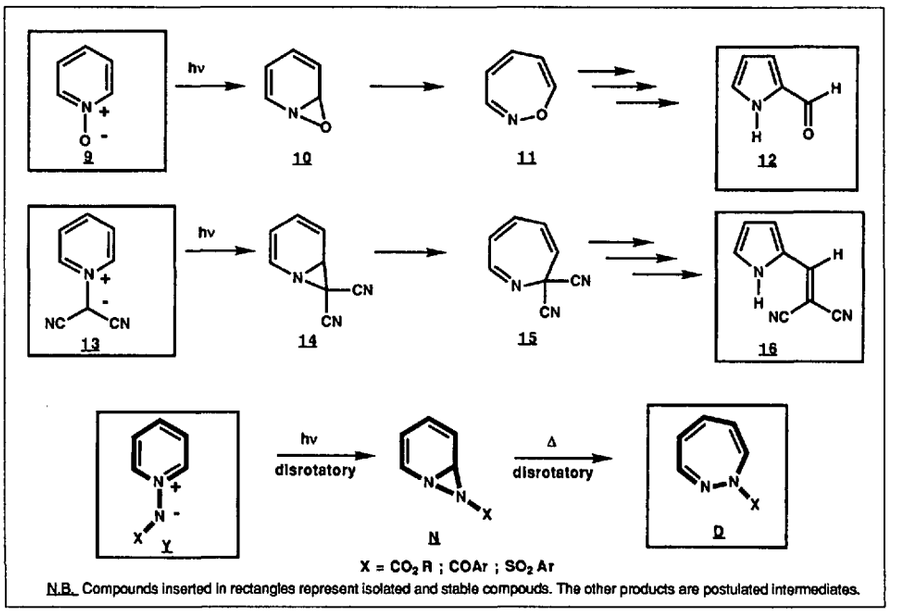
### 3.1. *Photophysical Data of the* N-*Iminopyridinium Ylides* Y

The UV-absorption spectrum of ylide **17** is reproduced in *Fig. 1*. To interpret the electronic spectrum of **17**, *Gleiter* measured the dichroism of **17** oriented in a stretched, polyvinyl alcohol film [17] according to *Eggers* method [18]. Since it proved possible to reduce the perpendicular component of the first band but not the parallel component (for a discussion of this methodology, see [18]), he inferred that the vector of the first transition is approximately parallel to the long axis of **17** whose most probable conformation is represented in *Fig. 1*. Assuming some reasonable geometric parameters, a PPP model was applied and led to the calculated absorption spectrum as represented in *Fig. 1* (vertical lines represent the calculated electronic transitions) [17]. The theoretical predictions concerning the angles, relative intensities and polarization directions agree well with the experimental results. This model predicts $\pi^* \leftarrow \pi$ transitions for the first two absorption bands, the lowest-

*Scheme 2*




*Scheme 3*




energy band being the photoactive one [17].

In *Fig. 2* are listed the changes in charge distribution $\delta q\mu = q\mu^* - q\mu$ for the first two transitions of **17**. The symbols $q\mu$ and $q\mu^*$ characterize the charge in the ground and first excited states. Inspection of *Fig. 2* leads to the conclusion that on excitation *negative charge is transferred from the ylide-N-atom to the pyridine ring* [17]. In other words, these $\pi^* \leftarrow \pi$ transitions have a pronounced *charge-transfer character*, which accounts also for the *negative solvatochromism* as represented in *Fig. 1* (*i.e. a hypsochromic shift is observed when going from a less polar to a more polar solvent*). Studies performed by ESCA with **17** confirmed that a strong negative charge is localized on the exocyclic ylide N-atom of 17 in its ground state ($q\mu$ = –0.7) [19].

The fluorescence spectrum of **17** proved to be weak; it was determined at low temperature in EPA ($\lambda_{max}$ 440 nm) and plotted against the absorption spectrum of 17 ($\lambda_{max}$ 320 nm). The intersection of the two curves appears at *ca.* 365 nm *i.e.* at 78 kcal/mol (O–O transition of $S_1$) [20]. The total luminescence of 17 was determined in EPA at 77 K. The use of a chopper permitted the deduction of the phosphorescence spectrum whose O–O transition ($T_1$) occurs at 65 kcal/mol (the phosphorescence lifetime at 77 K is 220 ms) [21].

### 3.2. *Photochemical Results*

#### 3.2.1. *1,2-Diazepines*

As indicated above UV irradiation of *N*-iminopyridinium ylides **Y** led in excellent chemical yields to the isomeric 1,2-diazepines **D** (*Scheme 3*). For example, when ylide **17** was irradiated in benzene solution, it gave diazepine **19** in 95% yield as well as trace amounts of pyridine (**20**) (3%) and (ethoxycarbonyl)nitrene **21** which was trapped instantaneously by benzene, leading to *N*-(ethoxycarbonyl)azepine (*ca.* 2%) (*Scheme 4*) [22]. These photoreactions were scaled up (20–30 g) using a falling film photoreactor equipped with a high-pressure Hg vapour lamp [11].

#### 3.2.2. *Quantum Yields*

The quantum yields $\Phi$ of these photoinduced ring-enlargements were determined at room temperature using an apparatus whose prototype had been conceived and built by *Schaffner* and coworkers [23]. Whatever the ylides **Y** and whatever the solvents, these quantum yields were in the order of 3% (the molar concentrations varying between $10^{-2}$ and $10^{-4}$), as measured for the formation of diazepines **D**. It was found, furthermore, that these $\Phi$ values were independent of the UV wavelengths which were used between 290 and 370 nm. That the photoinduced rearrangement is a monophotonic process was demonstrated by the fact that $\Phi$ is independent of the intensity of the incipient UV light. *However, the temperature had a pronounced effect upon $\Phi$, since its magnitude was decreased about 5-fold when determined at –100°, whereas at +50° it increased slightly to* ca. *5%* [20].

#### 3.2.3. *Photoinduced Fragmentation of N-Iminopyridinium Ylides*

As stated above photofragmentation of ylide **17** is but a minor reaction pathway which leads to pyridine (**20**) and to (ethoxycarbonyl)nitrene (**21**). In the presence of a triplet sensitizer, the formation of diazepine **19** was suppressed, and photoinduced fragmentation became the only reaction pathway [21][24]. From these experiments, one may infer that the photoinduced ring enlargement proceeds from an excited singlet state, whereas photofragmentation occurs from an excited triplet state, the $S_1 \rightarrow T_1$ intersystem crossing (ISC) being a poor yield process. This assumption could be confirmed by trapping experiments: UV irradiation of **17** in $CH_2Cl_2$ in the absence of any photosensitizer in the presence of *trans*-4-methyl-2-pentene led in poor yield to a mixture of *cis*- and *trans*-aziridines **22** and **23**, respectively (*Scheme 5*). The **22/23** ratio proved to be constant, whatever the relative concentration of the ylide **17** and of the olefin was [25][26]. The mechanistic interpretation

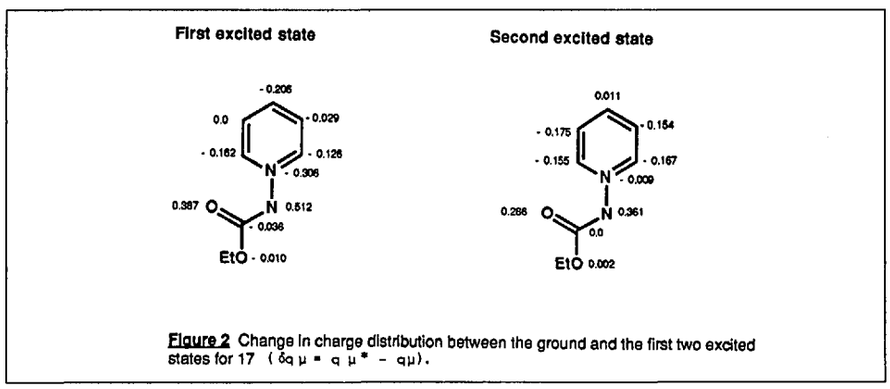



**Figure 2** Change in charge distribution between the ground and the first two excited states for 17 ( $\delta q\mu = q\mu^* - q\mu$ ).

Fig. 2. *Change in charge distribution between the ground and the first two excited states for pyridinium ylide* **17**

of these experimental data is straightforward. If the photochemically produced nitrene were in its excited singlet state, one would observe that the ratio **22/23** changes as a function of olefin concentration [27]. Since there is no change in this ratio, one concludes that the incipient nitrene **21** occurs photochemically in close to 100% yield in its triplet ground state. Furthermore, *Lwowski* had shown that (ethoxycarbonyl)nitrene (**21**) in its *singlet state* gave insertion reaction into the C–H bonds of cyclohexane, leading to the corresponding cyclohexylurethane; whereas the same nitrene in its *triplet state* reacted by H abstraction with cyclohexane, leading thereby to the urethane **24** and to cyclohexene (**25**) [28]. When the UV irradiation of ylide **17** was performed in cyclohexane/$CH_2Cl_2$ – and under experimental conditions similar to those described by *Lwowski* and *Mattingly* [28] – the urethane **24** was the only by-product (the major photoproduct is diazepine **19**) detected by GPC after evaporation of the solvents [26] (*Scheme 5*). Similar results were obtained by *Abramovitch* and *Takaya* [ 24] and by *Bird et al.* [29]. Both groups irradiated some iminopyridinium *N*-ylides in a variety of solvents and observed homolytic fragmentation of the N–N bonds. In all these cases the intermediate nitrenes led to H abstraction only, which demonstrates that *these reactive species occurred in their triplet ground state.*

3.2.4. *The Directing Effect of Substituents at Pyridine upon the Photoinduced Ring-Enlargement*

In a previous review article, a survey was given about directing effects of substituents on the pyridine ring upon the photoisomerisations [16]. We shall discuss a few results pertaining to regiospecific- and non-regiospecific, ring enlargements as observed during the photochemical isomerisation of C(2)- and C(3)-substituted *N*-imino-pyridinium ylides of type **Y**.

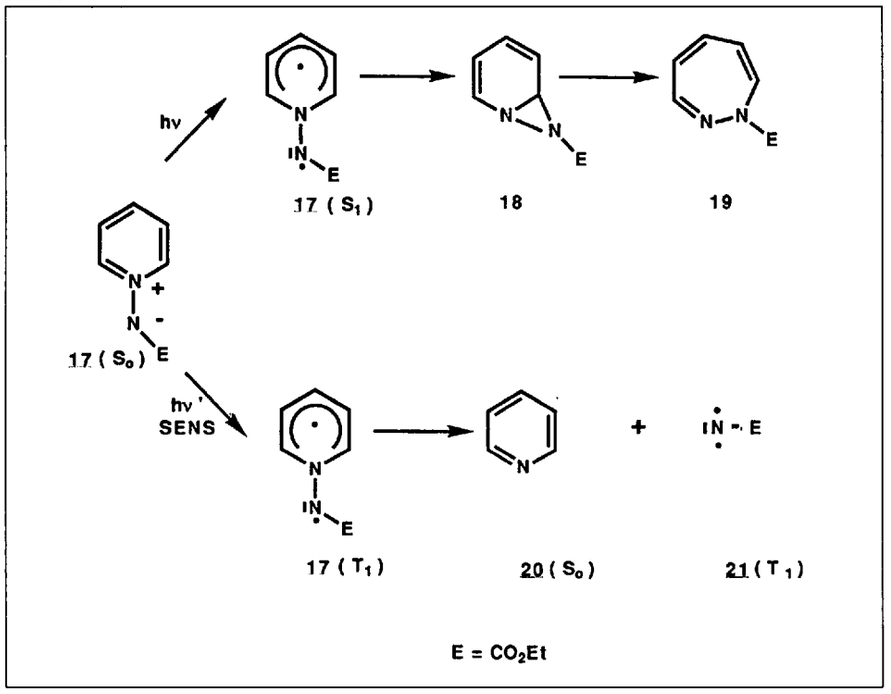
*Substituents at C(2).* Alkyl, MeO, and CN substituents at C(2) orient the primary photochemical process exclusively toward C(6), leading thereby to 3-substituted 1,2-diazepines [16]. These regiospecific ring enlargements, which are obviously independent of the 2-substituents electronic effects, suggest that these latter ones are overruled by steric effects. The optically active steroidal pyridinium ylide **26**, which was synthesized starting from 19-nortestosterone, photoisomerized regiospecifically to diazepine **27** (90% yield) [30]. A series of 2-methoxy-pyridinium ylides **28** led regiospecifically to the 3-methoxydiazepines **29** whose demethylation gave the diazepinones **30** [31] (*Scheme 6*).

*Substituents at C(3).* Irradiation of pyridinium ylides **31** with electron-withdrawing groups at C(3) ($CO_2Et$, $CONH_2$, CN) leads in high yield to regiospecific ring expansion towards the 4-substituted diazepines **32**. On the other hand, electron-donating groups (Me, F, Cl, Br, OCOPh) of ylides **33** act indiscriminately, affording both 4- and 6-substituted diazepines **34** and **35** in good overall yields [32] (*Scheme 7*). These regiospecific *vs.* non-regiospecific ring enlargements can be interpreted by using a HMO model. While the wave function and energy of the highest occupied molecular orbital (HOMO, $\pi_1$) is essentially unaffected by any substituent in position C(3), there is a considerable effect concerning the wave function in case of the two lowest unoccupied molecular orbitals $\pi_{-1}$* and $\pi_{-2}$* as shown in *Fig. 3*. Clearly two series of substituents must be distinguished : *1*) substituents with low-lying $\pi$* orbitals (X = $CO_2R$, $CONH_2$, CN) in position C(3), and *2*) substituents with (high-lying) occupied orbitals (Me, F, Cl, Br, OCOPh).

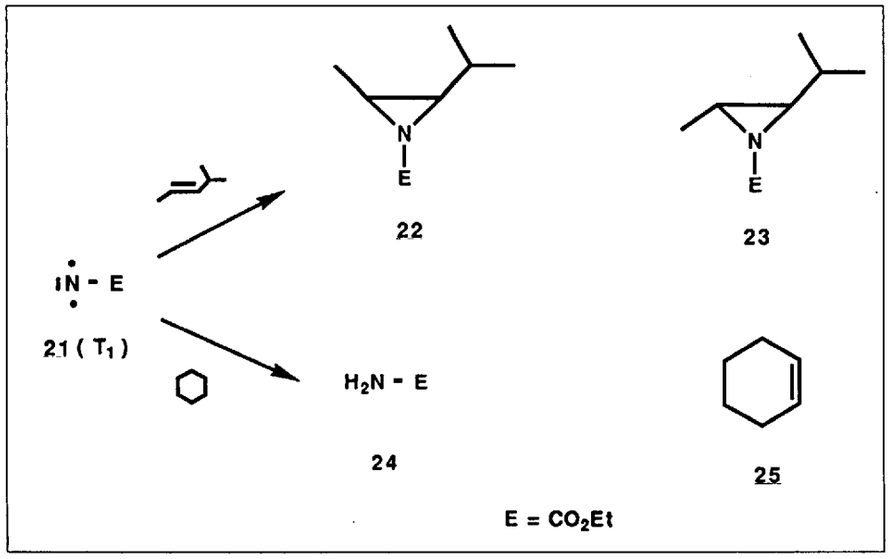
In *Case 1* the substituents overrule the perturbation of the pyridinium N-atom and in a first approximation the plane of symmetry of $\pi_{-1}$* and $\pi_{-2}$* is aligned with the C–X bond as shown in *Fig. 3*. In *Case 2* where the perturbation is weak compared to the pyridinium N-atom the plane of symmetry of $\pi_{-1}$* and $\pi_{-2}$* is aligned with the N–N bond (*Fig. 3*, right).

Consider *Case 1*: exciting an electron from $\pi_1$ into $\pi_{-1}$* (*Fig. 3*, left) will increase the bonding character between the exocyclic N-atom and the C-atom in the $\alpha$-position considerably more than between the exocyclic N- and the C-atom in the $\alpha'$-position (*Fig. 3*, left). This model explains the preferential formation of 4-substituted 1,2-diazepines **32** in the case of electron-withdrawing substituents. In *Case 2* (*Fig. 3*, right), the C-atoms in $\alpha$- and $\alpha'$-positions are equivalent and, thus, no regiospecificity should be found. Therefore, halogen atoms

*Scheme 4*




*Scheme 5*



and alkyl groups were not expected to lead to any significant regiospecificity [32].

When diazepines **34** and **35** (X=Cl; Y=COPh) were irradiated individually with UV light for a prolonged period of time, no interconversion between these two isomers could be detected. Instead, the bicyclic isomers **36** and **37**, respectively, were formed in moderate yields [33] (*Scheme 7*). These two experiments clearly rule out a photoinduced [1,7]-sigmatropic shift of the PhCO moiety which would have led to the interconversion of **34** and **35** [34].

### 3.3. *Thermally Induced Ring Contraction of 1,2-Diazepines and the Postulated Energy Diagram for the Photochemical and Thermal Processes*

3.3.1. *Thermal Ring Contraction of 1,2-Diazepines* **D**

Thermally induced ring contraction of several 1,2-diazepines **D** towards the isomeric pyridinium ylides **Y** (*cf. Scheme 3*) have been described to occur in poor-to-moderate yields, ring cleavage to open-chain isomers being the major reaction pathway [22][35]. Nevertheless some 1,2-diazepines which bear an alkyl (Me) group at C(3) undergo this type of ring contraction in close to 100% yield [36] inviting, therefore, a quantitative treatment, *i.e.* to establish the kinetic parameters as well as the reaction enthalpy of this process.

The kinetic measurements were performed with diazepines **38** at different temperatures in $C_6D_6$ (non-polar solvent) and in ($D_6$) DMSO (polar solvent) using $^1$H-NMR spectroscopy. After completion of each run, the ylides **40** were characterized by IR and NMR (comparison with authentic samples). All ring contractions follow first order reaction kinetics. The rate constants $k$ were obtained at various temperatures $T$. Using then *Eqn. 1* which derives from the transition state theory [37] $\Delta H^*$ and $\Delta S^*$ values were determined (*Table*)

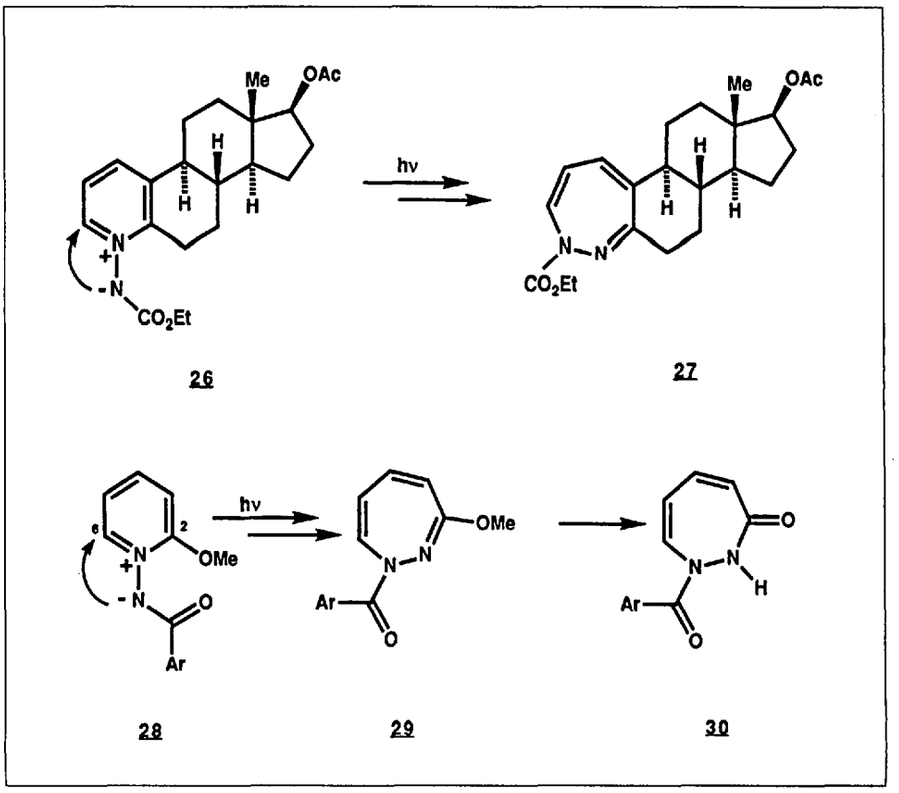
$$\ln \frac{k}{T} = \ln \frac{k_B}{h} + \frac{\Delta S^*}{R} - \frac{\Delta H^*}{R} \cdot \frac{1}{T} \qquad (1)$$

($k_B$ = *Boltzmann*'s constant ; $h$ = *Planck*'s constant)

Whether determined in DMSO or in benzene, these values turned out to be very similar, and, therefore, almost independent of solvent polarity [36]. The values of $\Delta S^*$ would be expected to be negative, if the conformationally *flexible* diazepines **38** lead to the postulated *rigid* norcaradiene isomers **39**.

When the crystalline diazepines **38a–c**, which are orange-coloured compounds, were heated up at a slow rate, a sharp melting point was observed. At a slightly higher temperature, decolouration occurred which corresponds to the ring contraction. These thermal processes were repeated using differential scanning calorimetry (DSC).

*Scheme 6*




*Scheme 7*

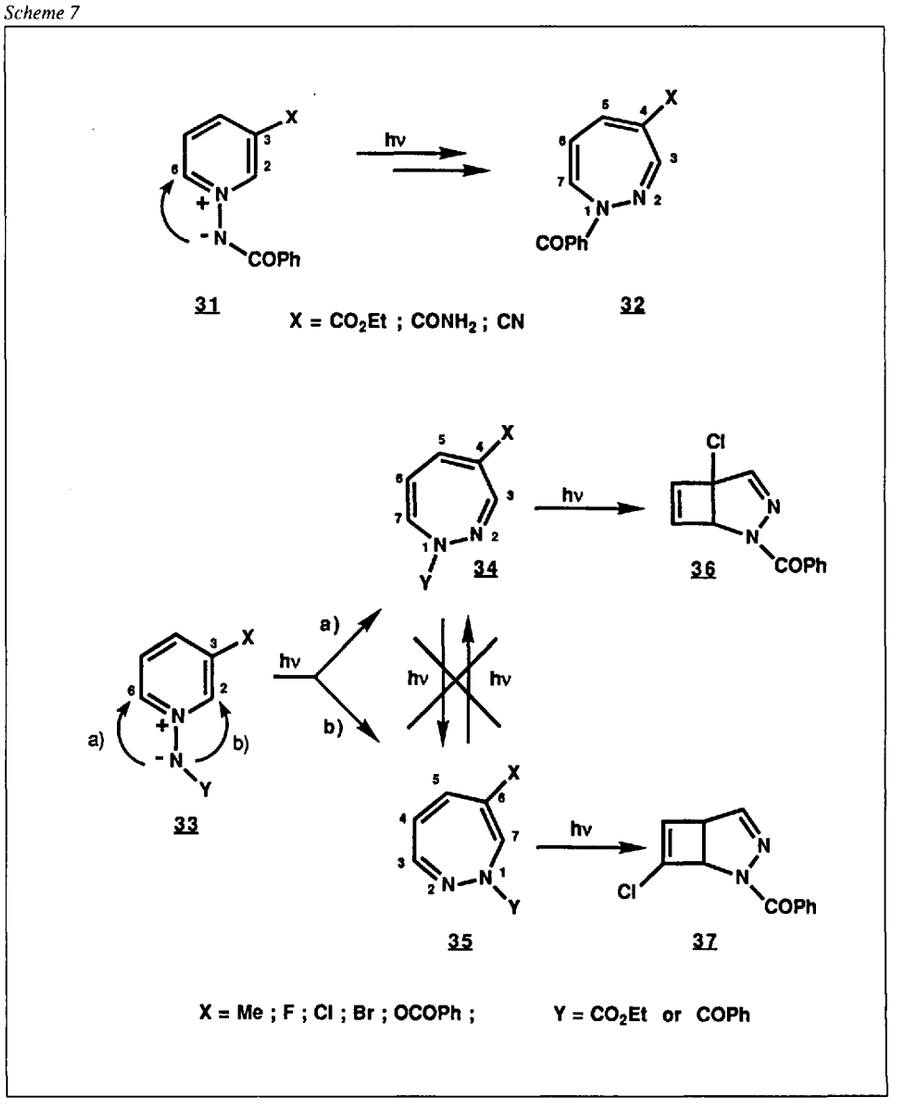


Table. *Kinetic Parameters* (determined from isothermal modes for 0.35 molar solutions in ($D_6$)DMSO) *and Reaction Enthalpies* (as obtained by DSC in DMSO) *for the* **38** → **40** *Ring Contractions*

| | $\Delta H^*$ [kcal/mol] | $\Delta S^*$ [cal/K/mol] | $\Delta H$ [kcal/mol] |
|---|---|---|---|
| **38a** →**40a** | 26.5 ± 0.4 | −7.7 ± 1.8 | −22.2 ± 1 |
| **38b** →**40b** | 26.5 ± 0.6 | −7.6 ± 2.0 | −22.2 ± 1 |
| **38c** →**40c** | 23.7 ± 0.5 | −7.2 ± 2.0 | −18.6 ± |

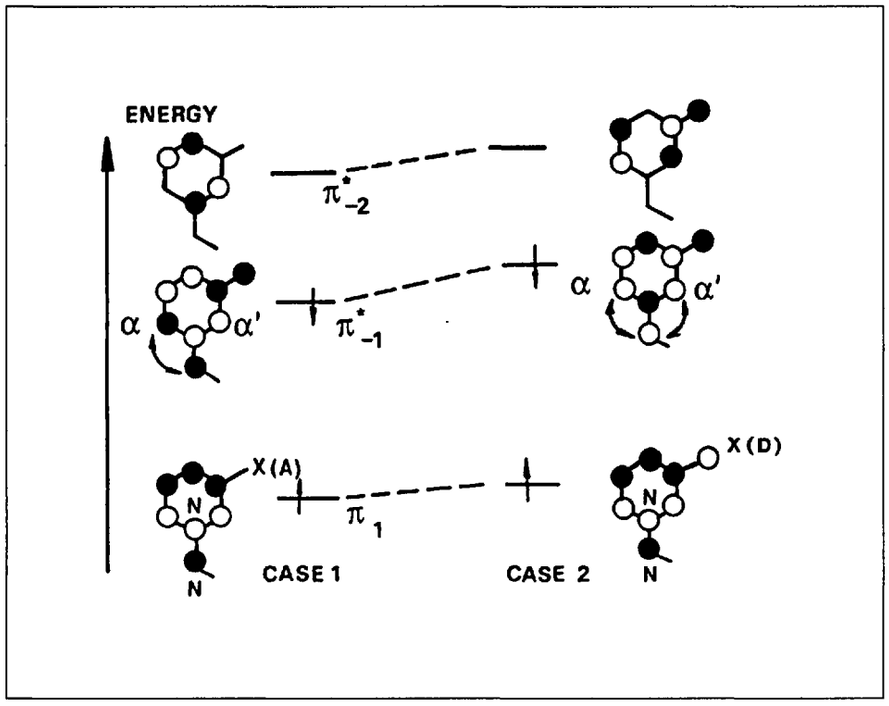



Fig. 3. *Qualitative HMO diagram for C(3)-substituted* N-*iminopyridinium ylides.* At left, the perturbation (low-lying $\pi^*$ orbitals, electron acceptor) of the substituent dominates (*Case 1*). At right, the perturbation (high-lying $\pi$ *orbitals, electron* donator) is assumed to be weak (*Case 2*)

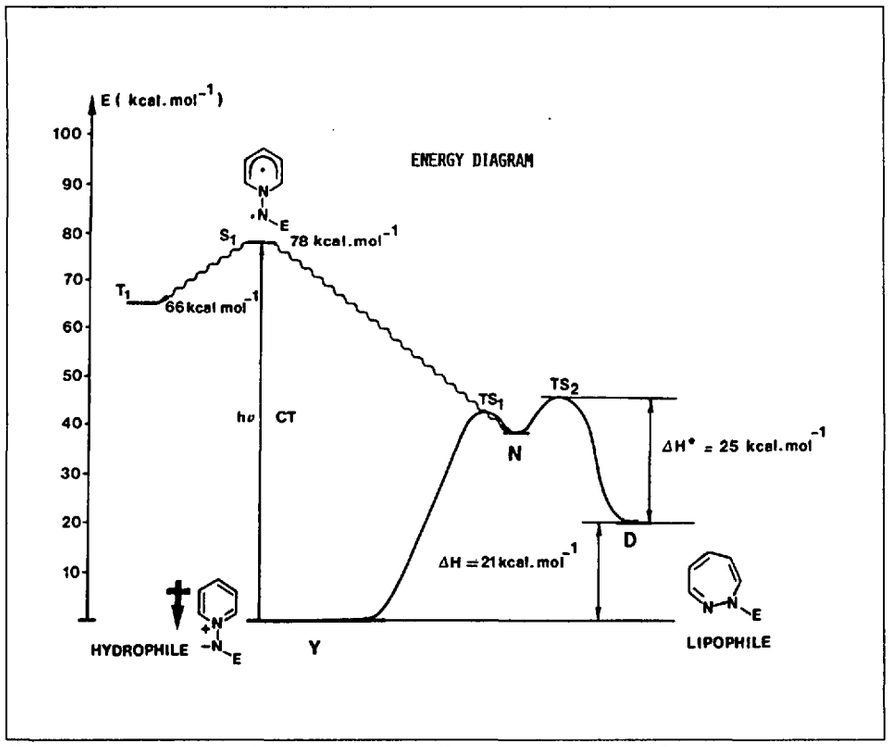



Fig. 4. *Energy diagram of the photoinduced reactions of 1-iminopyridinium ylides* **Y** (the $S_1$ and $T_1$ energy levels have been determined for ylide **17** (E = $CO_2Et$)) *and of the thermal induced ring contraction of diazepines* **D** (**38**, *i.e.* E = PhCO, *p*-(*t*-Bu)$C_6H_4CO$, $SO_2Ph$ and Me at C(3))

DSC led sequentially to a sharp endothermal peak (corresponding to the melting point) and to a large exothermal hump whose integration led directly to the enthalpy of the rearrangement process; the magnitude of these $\Delta H$ values is about −20 kcal/mol (*Table*) [36].

3.3.2. *The Energy Diagram of the Thermal and Photochemical Processes* (*Fig. 4*)

From the thermochemical data, it appears clearly that diazepines **38** – which had been obtained by photoinduced ring enlargement of the corresponding ylides **40** – are storing, in the form of chemical energy, part of the photonic energy which had been absorbed by the ylides **40**. This chemical energy is released in the form of (degraded) thermal energy during the **38** → **40** ring contraction process. The values of $\Delta H$ and of $\Delta H^*$, whose magnitudes have been determined above, permit the drawing of an energy profile for the **38**→**40** ring contraction (*Fig. 4*), norcaradienes **39** being once again postulated as the obvious but short-lived intermediates. The fact that the $\Delta S^*$ values are negative is best interpreted by assuming that the geometry of the transition state $TS_1$ is very close to the norcaradiene **39** whose structure is quite rigid as compared to the one of the very flexible diazepine **38**. The energy level of the norcaradiene intermediates could not be estimated.

In our opinion, the disrotatory valence tautomerism of diazepines **38** which lead to the norcaradienes **39** must be the rate-determining step, because the rate constants of the overall ring contractions are nearly independent of solvent polarity (both diazepines **38** and the corresponding norcaradienes **39** are poorly polar substances). Otherwise, there would have been a pronounced effect of solvent polarity upon the rate of ring contraction, ylides **40** being very polar substances [36]. In other words, we reasonably assume that the second step is much faster than the first one, since the reaction to **Y** is much more exothermal than to **D** (*Fig. 4*). It should be noted that this assumption is contrary to the result of a recent AM1 calculation [38]. However, this calculation also predicted **D** and **Y** to be nearly isoenergetic ($\Delta H$ = 1.1 kcal/mol) which is contradicted by our thermochemical results ($\Delta H$ = *ca.* 20 kcal/mol) (see *Chapt. 3.2.2*). It may, therefore, be expected that this error in the AM1 calculation will also be reflected in the relative magnitudes of $TS_1$ and $TS_2$.

The assumption that $TS_1$<$TS_2$ allows to rationalize the small absolute values of the quantum yields $\Phi$ and their temperature dependence as follows ($\Phi_N$ which is the quantum yield for the formation of **N**, is independent of T):

$$\Phi = \Phi_N \frac{k_D}{k_D + k_Y} \qquad (2)$$

or $$\frac{1}{\Phi} = \frac{1}{\Phi_N}\left(1 + \frac{k_Y}{k_D}\right)$$

The quantum yields of fluorescence and intersystem crossing of the ylides **Y** are very low (add up to less than 4%). This suggests that their lowest singlet state is rapidly depopulated by an efficient primary photochemical process which we attribute to the formation of the norcaradiene intermediates **N**. We, therefore, assume that $1/\Phi_N \approx 1$. If we further assume that the preexponential factors governing the decay rates of the intermediate **N** *via* $TS_1$ and $TS_2$ are of similar magnitude, *i.e.* $A_1 \approx A_2$, it follows that

$$\frac{1}{\Phi} = 1 - e^{-\Delta E/RT}$$

or

$$\ln\left(\frac{1}{\Phi} - 1\right) = -\Delta E/RT \qquad (3)$$

where $\Delta E$ is the energy difference between $TS_1$ and $TS_2$ (*Fig. 4*). The quantum yields for the photoconversion of **17**→**19** were determined as 0.6 % (at −100°), 3% (at +20°), and 5% (at +50°). *Eqn. 3* then allows us to estimate that $\Delta E$ has a magnitude of *ca.* 2 kcal/mol.

The fact that **N** could be detected neither by ns flash photolysis at room temperature, nor by low temperature photolysis, suggests that the activation energy $TS_1$ for **N**→**Y** is less than 5–8 kcal/mol.

Some seven-membered cyclic trienes – which are close structural analogues of diazepines **38** – are known to lead to thermal equilibrium with the corresponding norcaradienes by virtue of an allowed ground state disrotatory electrocyclisation process (*Scheme 8*):

– *Ciganek* showed that some specifically substituted ($R^1$ and $R^2$) cycloheptatrienes **41a** occur in equilibrium with their norcaradiene valence isomers **42a** [39].

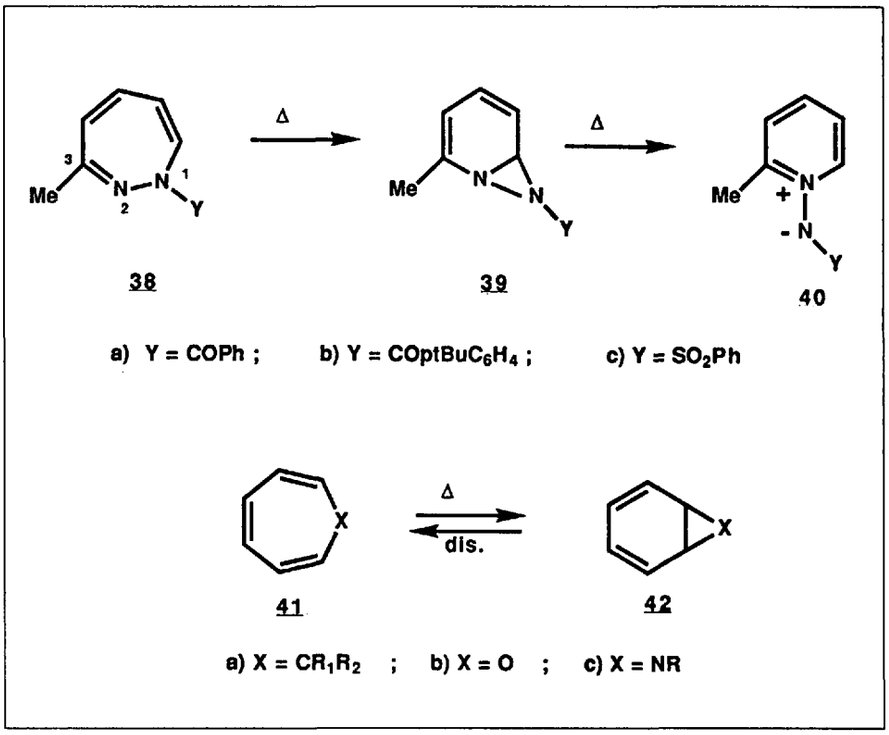
– *Vogel et al.* demonstrated the existence of an equilibrium between some substituted oxepines **41b** and their epoxybenzene isomers **42b** [40].

– *Prinzbach et al.* demonstrated in two instances the occurrence of an equilibrium between at C-polysubstituted azepines **41c** and their 7-azanorcaradiene isomers **42c** [41].

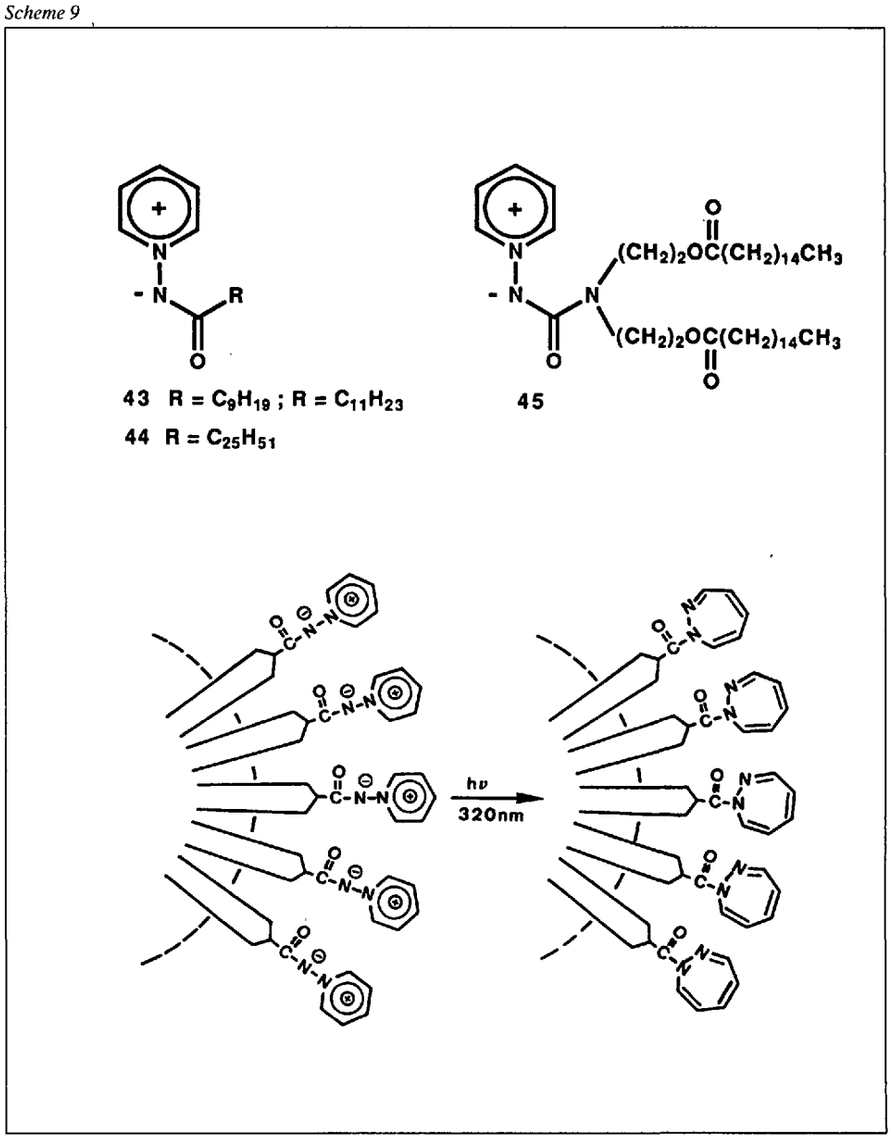
By analogy with these data, an equilibrium could have been expected to occur at room temperature between the diazepines **D** (**38**) and their [1,7]-diazanorcaradiene isomers **N** (**39**) (*Schemes 3* and *8*). This is ruled out by the thermodynamic parameters as reported above. *A posteriori*, then, it becomes obvious that many cycloadditions which had been performed to trap the postulated norcaradienes **N** at room temperature were bound to fail (see below *Chapt. 3*).

For further probes into the nature of this elusive norcaradiene intermediate **N**, experiments using deuterated and $^{13}C$-labeled *N*-imides were carried out in collaboration with *Kwart et al.* [42][43]. Photoconversion of 2-deuteriopyridine *N*-benzoylimide into

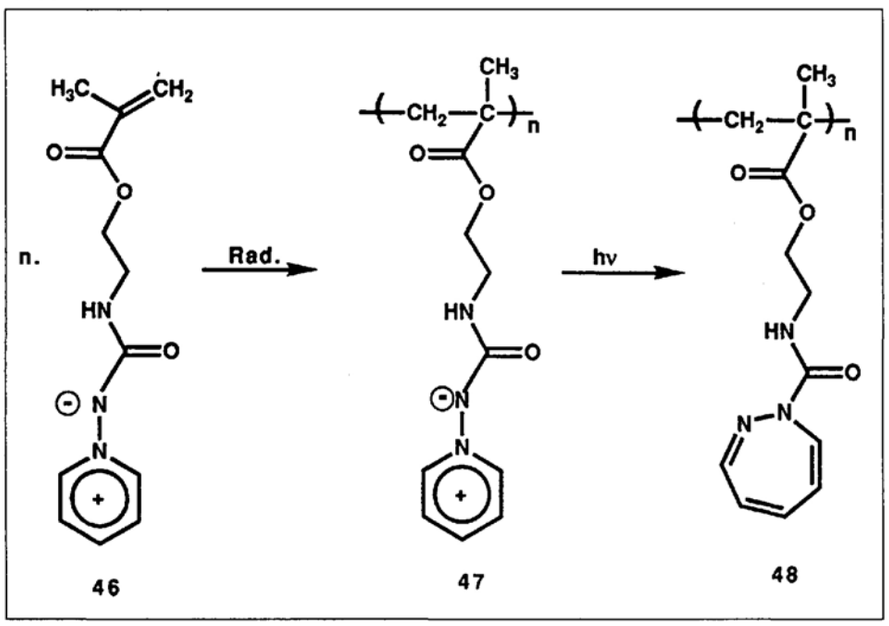
*Scheme 8*



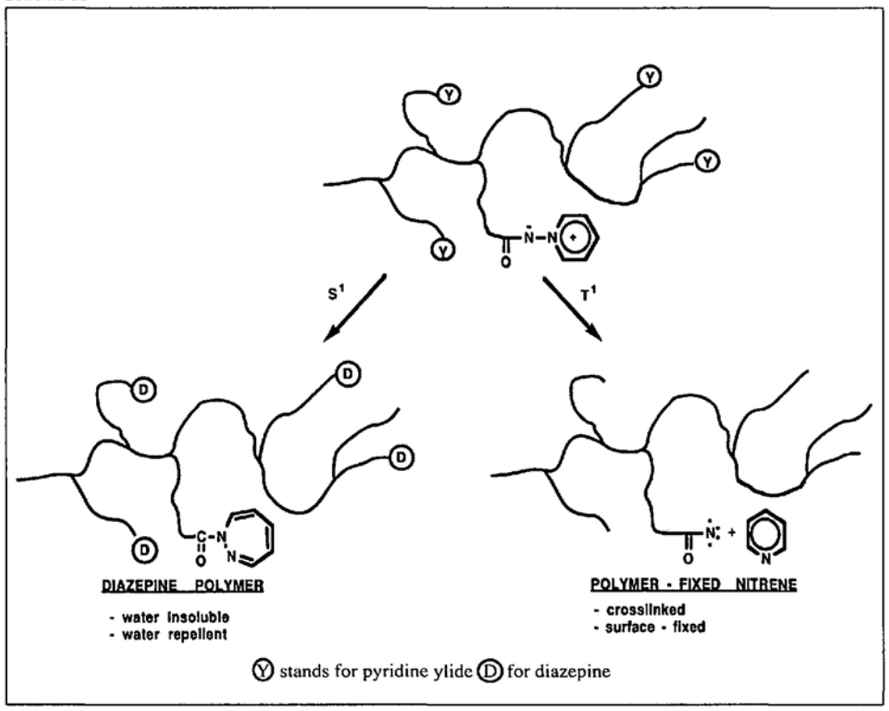

*Scheme 9*



*Scheme 10*




*Scheme 11*




a mixture of 3- and 7-deuterated diazepines showed a large inverse secondary D-isotope effect : $k_H/k_D$ = 0.911 [42]. This result indicates a thermal transition state in which C(2) of the *N*-imide is undergoing rehybridization from $sp^2$ to $sp^3$. A second set of experiments – involving competitive UV irradiation of a mixture of unlabeled and 2,6-$^{13}$C-labeled pyridine *N*-benzoylimides to give the corresponding unlabeled and 2,7-$^{13}$C-labeled diazepines – also showed an inverse isotope effect: $k_{12C}/k_{13C}$ = 0.9876 [43]. This result implies a greater bonding preference for the heavier isotope, and can be reconciled only with a transition state of an associative mechanism in which C(2) is fully bonded to each of the two N-atoms. Since inverse heavy-atom isotope effects are rarely observed, these results must be regarded as strong evidence for the intermediacy of the 1,7-diazanorcaradiene **N** in the photochemical transformation **Y**→**D** (*Schemes 3* and *4*).

### 3.4 *Some Applications: Photoinduced Isomerisation of Amphiphilic and of Polymeric* N-*Iminopyridinium Ylides*

*Ringsdorf* was the first to grasp the potential usefulness of the photoinduced ring enlargement of the polar ylides **Y** towards the less polar 1,2-diazepines **D**, by putting it into the context of supramolecular chemistry. He surmised that long-chain lipophilic molecules bearing type **Y** polar (mesoionic) headgroups would exhibit amphiphilic character and lead to self-organisation. Depending on the nature (length) of the lipophilic chain, self-organisation could lead either to (monolayered) micelles or to liposomes (double layered membranes). More importantly, *Ringsdorf* surmised that photoisomerisation of such pyridinium-ylide liposomes would lead to the suppression of the amphiphilic character of the individual molecules, *i.e.* to a change in solubility, and, therefore, to the probable collapse of the isomeric liposomes [44].

#### 3.4.1. *Amphiphilic Pyridinium Ylides and the Formation of Micelles and of Liposomes*

These speculations proved to be correct. For example, the single chain ylides **43** bearing $C_9$- and $C_{11}$-alkyl chains dissolve in $H_2O$ to form micelles. The foaming solutions dissolve hydrophobic dyes in $CHCl_3$ which precipitate or are released upon UV irradiation [44][45]. The single-chain ylides **44** with $C_{25}$-alkyl chains and the double chain ylides **45** self-assemble to liposomes as

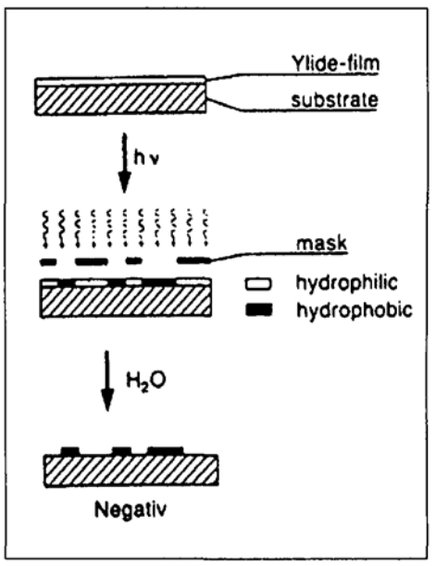



Fig. 5. *Scheme of the photolithographic process sequence in pyridinium-ylide-resists*

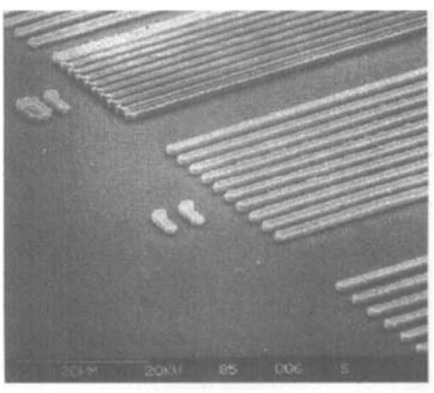


Fig. 6. *Negative image contact-printed in ylide-resist* (1µ, 600 mJcm$^{-2}$) *at 313 nm* (with courtesy of *BASF*)

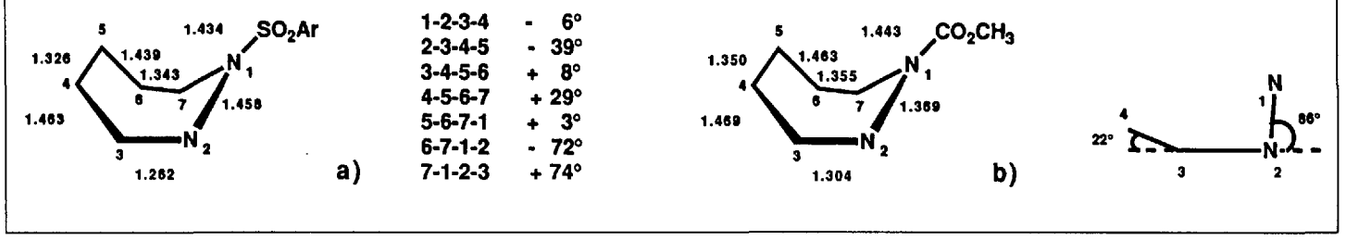



Fig. 7. a) *Geometric parameters of 1-tosyldiazepine as determined by X-ray analysis* [50]; b) *conformation and geometrical parameters of 1-(methoxycarbonyl)-1,2-diazepine obtained by the MNDO-method with complete geometric optimization* [49]

shown by electron microscopy and dye inclusion experiments (*Scheme 9*).

The photoreaction of these lipids in the liposomal membrane leads to the 1,2-diazepines in high yield (*Scheme 9*). Investigations on such giant liposomes under the phase-contrast light microscope revealed that these liposomes with diazepine surface are metastable and collapse irreversibly on mechanical stress [45][46].

3.4.2. *Polymeric Ylides as Photoresists*

The application of photochemistry to polymer science seemed to be particularly interesting when the photochemical alteration of solubility is extremely pronounced. *Ringsdorf* surmised that the large change in polarity, which accompanies the photoreaction of pyridinium ylides **Y** to diazepines **D** (*Scheme 3*) might lead to a large solubility change in polymeric systems which include such chromophores [45]. Here too, he proved to be right. The pioneering experiments were performed by two groups and led to a new type of negative photoresist [47][48].

Let us take but one illustrative example: *i.e.* the pyridinium-ylide monomer **46** whose mesoionic chromophore is connected *via* a spacer to a methacrylic ester function [45]. Ylide **46** is polymerized in $H_2O$ by a radical initiator to yield the $H_2O$-soluble homopolymer **47**. The photoconversion of the pyridinium-ylide polymer **47** to the 'polydiazepine' **48** is accompanied by a large change in solubility (*Scheme 10*). Polymer **48** is not soluble in $H_2O$ and is also not soluble in common organic solvents. This may be due to some cross-linking *via* polymer bound nitrenes from the triplet reaction. This nitrene formation is also expected to promote the very good adhesion to substrates such as quartz, silicon, and copper. The photoreactions of 'polyylide' **47** are depicted in *Scheme 11*.

On the basis of these photoeffects, polymeric pyridinium ylides can be applied as negative photoresists [45][47][48]. After irradiation of the spincoated polymer film through an imaging mask, the film can be developed by simple immersion in pure $H_2O$. The unexposed area, being very soluble in $H_2O$, rapidly dissolves, leaving the exposed area as a hydrophobic, negative image (*Fig. 5*). Due to the photochemically induced polarity change the product of irradiation is not just $H_2O$-insoluble but is actually $H_2O$-repellant and does not swell. Therefore, the images have sharp edges compared to images made with other negative resists. Structures in the 1μ range have been resolved on silicon wafers (*Fig. 6*).

## 4. From 1,2-Diazepines to Small Ring Compounds

Initially, we expected a thermal valence tautomeric equilibrium to occur between diazepines **D** and their norcaradiene isomers **N** (see *Chapt. 3.3*). Consequently, a series of cycloadditions were initiated with diazepines **D** in order to trap their elusive norcaradiene isomers **N**. For example, *N*-phenyltriazolinedione and TCNE, which acted as dienophiles, as well as diphenylisobenzofuran, a diene, did react in the presence of diazepines **D** at room temperature, but only cycloadducts of these latter heterocycles could be isolated [16][49]. The kinetic and thermochemical parameters, which we had determined in the meantime for the ring contraction of diazepines **D** (*Chapt. 3.3* and *Fig. 4*), clearly *rule out the occurrence of such an equilibrium at room temperature.*

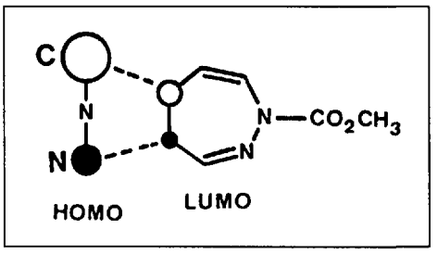
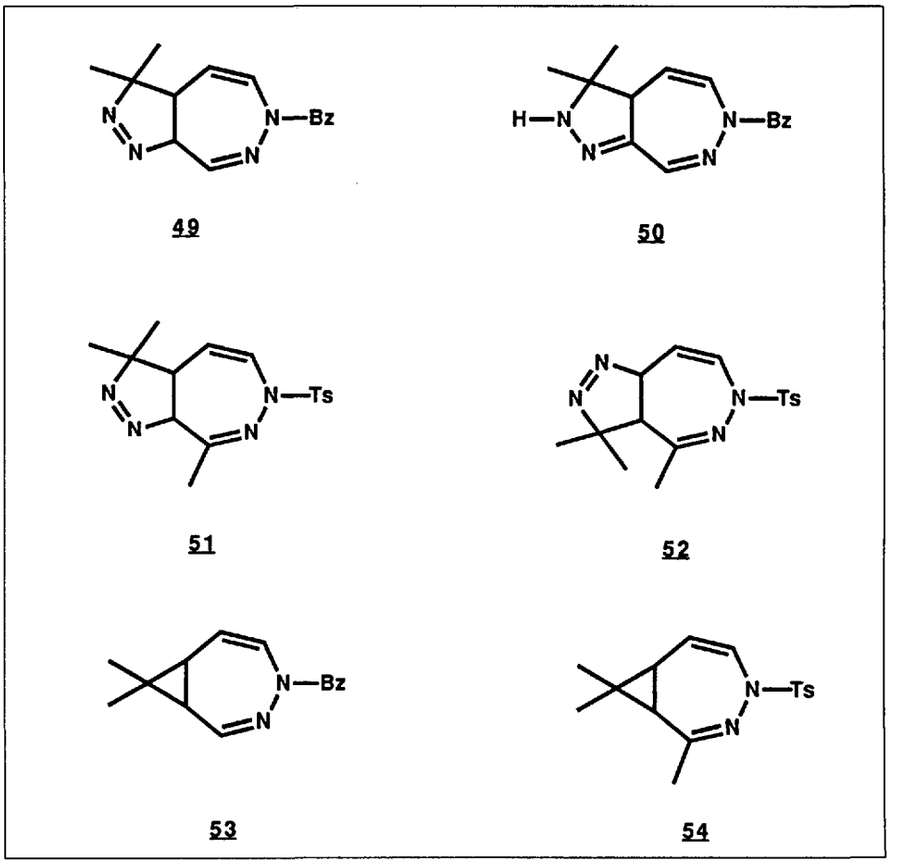



Fig. 8. *Schematic HOMO-LUMO interaction during the cycloaddition of 1-(methoxycarbonyl)-1,2-diazepine with diazoalcanes* [49]

Nevertheless some primary cycloadducts, which we had obtained when



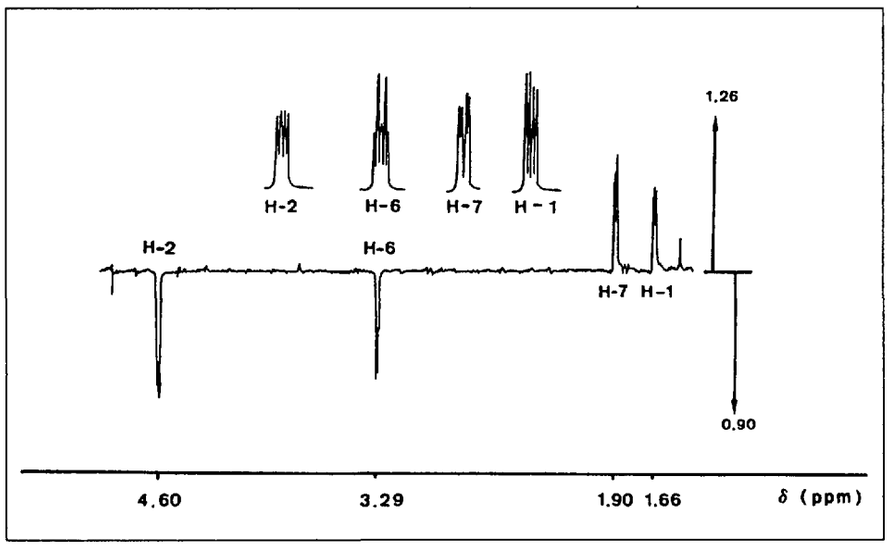
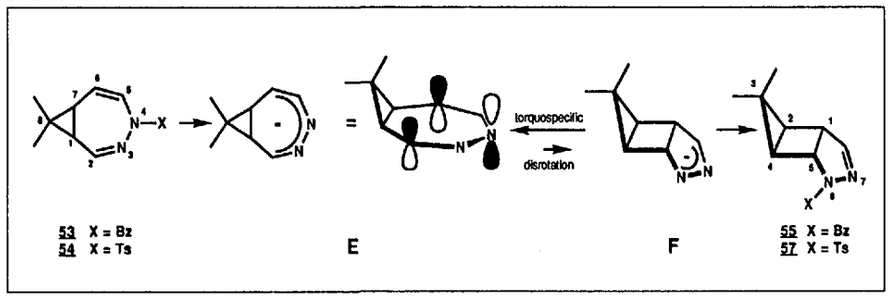



Fig. 9. *Nuclear* Overhauser *effects* (360 MHz, $CDCl_3$) *measured during irradiation of the* $Me_{exo}$ *group* (0.90 ppm) *and of* $Me_{endo}$ *group* (1.26 ppm), *followed by substraction of the two enhanced spectra from the reference spectrum of* **55**. The enlarged *m* of the 4 cyclobutane protons are superimposed upon the substraction spectra. $\delta$ in ppm; internal standard HMDS.

*Scheme 12*




diazepines **D** were reacted with diazoalkanes, proved to be of great interest, since they permitted the preparation of novel types of small-ring compounds [49][51][52][55].

### 4.1. *1H-1,2-Diazepines: Geometric Parameters*

The X-ray analysis of 1-tosyl 1*H*-1,2-diazepine showed this compound to be boat-shaped, as expected for a cyclic-conjugated non-aromatic 8$\pi$-electron system [50]: the atoms N(2), C(3), C(6), and C(7) are approximately coplanar, whereas the 'bow' atoms (N(2)–N(1)–C(7)) make an angle of *ca.* 73° with this latter plane, and the 'stern' atoms (C(3)–C(4)–C(5)–C(6)) an angle of *ca.* 35° (*Fig. 7*). A *Dreiding* model shows a very similar geometry. MNDO calculations of 1-(methoxycarbonyl)-1,2-diazepine were performed with complete geometrical optimization, and led to a boat-shaped conformation whose geometric parameters are similar to those determined by X-ray analysis (*Fig. 7*) [49]. In solution diazepines **D** undergo a fast conformational inversion as could be demonstrated with an optically active diazepine by using variable temperature circular dichroism [50].

### 4.2. *1,3-Dipolar Cycloaddition Reactions of 1,2-Diazepines with Diazoisopropane*

All 1,2-diazepines **D** which we tested did undergo cycloadditions with diazoisopropane (DAP), in most instances already at –78°. In all cases cycloadditions, occurred in a sitespecific (chemospecific) manner with the C(4)=C(5) bond, whereas regiospecificity was observed in a few instances only [49]. To cite but two examples, 1-benzoyldiazepine reacted with DAP to give in good yield **49** as the only regioisomer, whereas 3-methyl-1-tosyldiazepine gave both the 'direct' adduct **51** and the 'inverse' adduct **52** [49]. It should be noted that the primary cycloadducts – *e.g.* **49** – are 1-pyrazolines which, when heated in solution, lead to their 2-pyrazoline tautomers, *e.g.* **50** (*Scheme 12*).

Considering the AO coefficients of the frontier MO's which come into interaction during the concerted cycloadditions – *i.e.* the HOMO of DAP and the LUMO of diazepines – it appears that these cycloadditions should not occur in a regiospecific manner, the difference of the AO coefficients (LUMO of the diazepines) being rather small (*Fig. 8*).

As a consequence only a small regioselectivity was predicted in favour of the direct adducts, and indeed observed in most instances [49].

### 4.3. *From 1-Pyrazolinodiazepines to Cyclopropanes and Cyclobutanes*

Pyrolysis of the 1-pyrazolinodiazepines gave the expected homodiazepines in good yield [51]. For example, *instant pyrolysis* of **49** at 150° in a 'bombenrohr' led to **53**; a similar treatment of the regioisomers **51** and **52** gave homodiazepine **54** in both cases.

Saponification of homodiazepine **53** with NaOMe in $C_6D_6$ led to an orange-coloured product, whose NMR spectrum was very similar to the one of **53**: the three olefinic protons were still present and retained their coupling constants, but H–C(5) underwent a shielding effect of *ca.* 1.8 ppm [52]. We believe that this spectrum is best accounted for by the delocalized anion **E**. According to the NMR data, this base-induced reaction seemed to be quantitative. Nevertheless, when benzoyl chloride was added to the reaction mixture, compound **53** could not be obtained. Instead, the tricyclic isomer **55** formed rather unexpectedly. Its structure was confirmed by NMR, and particularly by NOE measurements (*Fig. 9*). A similar reaction sequence – starting from **53** and using $Na_2CO_3$ in MeOH followed by addition of TsCl and pyridine – led to the homodiazepine **56** (20%) and to its isomer **57** (42%) whose tricyclic structure was confirmed by an X-ray analysis [52].

From these results, as well as from more detailed investigations [52], it appears clearly that a second anionic intermediate **F** must be in equilibrium with **E**, in order to account for the formation of the staircase-like compounds **55** and **57**. Since **F** could not be detected by NMR, the postulated equilibrium between the anionic species **E** and **F** lies strongly on the side of **E**. That products **55** and **57** are formed nevertheless predominantly, is due to the fact that N(6) of **E** (an *allylic anion*) is by its very nature more nucleophilic and, therefore, much more reactive than N(4) of **E** (a *pentadienyl anion*). It was indeed expected that the equilibrium would be strongly in favour of **E**, since the gain of energy for the conversion of a $\pi$ bond into a $\sigma$ bond (*ca.* –20 kcal/mol) does not compensate the added ring strain which is due to the formation of the cyclobutane ring (*ca.* +27 kcal/mol). For a similar example, albeit of a reversed reaction pathway (disrotatory ring opening of 2,3-diazabicyclo[3.2.0]hept-2-ene, leading to the corresponding monocyclic diazacycloheptadiene), see [53].

Considering the HOMO of **E** and applying the *Woodward-Hoffmann* rules to it [4], it follows that a 1,5-*electrocyclization* had to proceed according to a *disrotatory* mode (*Scheme 12*) [54]. This electrocyclization occurs in a *torquospecific* manner, *i.e.* in such a way as to avoid any steric interference between the $Me_{endo}$ group and the five-membered ring which is in the build-up stage. As a consequence, only the *transoid* tricyclic compounds **55** and **57** form, *via* anion **F** [52].

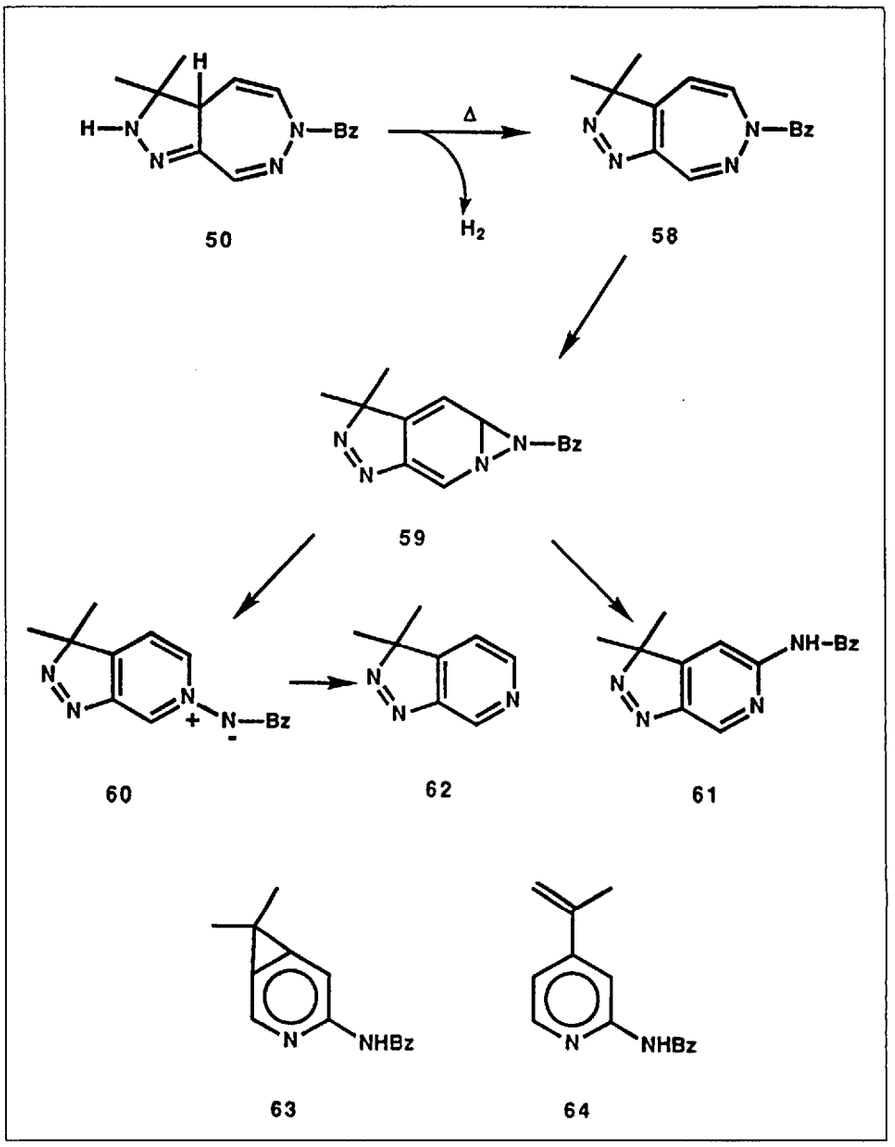
### 4.4. *From 2-Pyrazolinodiazepines to Cyclopropapyridines*

In most cases, the formation *via* prototropy of type **50** 2-pyrazolines could not be avoided in solution. To obtain homo-

diazepines from these 2-pyrazolinodiazepines, they had to be pyrolized at higher temperature (170–180°) and over a longer period of time. As a consequence, formation of tar increased, and the yields of homodiazepines decreased. Quite interestingly, pyrazolopyridines **60**, **61**, and **62** were formed, in poor yields though. It should be noted that these three compounds did not appear during the short pyrolysis periods of 1-pyrazolinodiazepines [51]. Structural determinations of these pyrazolopyridines follow in a straightforward manner from their $^1$H- and $^{13}$C-NMR data, and were corroborated by an X-ray analysis of **61**. The formation of pyridines **60–62** is best explained by assuming the occurrence of the following reaction cascade (*Scheme 13*): *i*) orbital symmetry allowed 1,4-elimination of $H_2$ of **50** leading to the pyrazolodiazepine **58**; *ii*) ring contraction of the diazepine moiety of **58** to the diazanorcaradiene **59**, a reaction which has been already described [15][16]; *iii*) **59** may then undergo ring opening to **60** and **61**, **60** being subsequently thermolyzed to **62** [51].

UV photolysis (broad-band filter, medium-pressure Hg vapor lamp) of pyrazolopyridine **61** led to the formation of the corresponding cyclopropapyridine **63** and of the isomeric isopropenylpyridine **64** in moderate yields. The broad-band filter permitted selective excitation of the N=N $\pi$ electrons ($\lambda_{max}$ *ca.* 350 nm) without excitation of the aromatic $\pi$ electrons of **61**, **63**, or **64** [55]. The formation of **63** and **64** is best explained by assuming the occurrence of a short-lived diradical intermediate [56] after the photoinduced expulsion of a nitrogen molecule. An X-ray structure analysis of **63** (*Fig. 10*) [55] showed that the geometric parameters of the cyclopropene moiety and of its immediate surroundings were very similar to those that had been measured previously for a cyclopropabenzene derivative [57]. The pyridine ring of **63** appears to have a normal geometry, an observation that is reminiscent of the structural similarity between benzene and cyclopropabenzene. Compound **63** is the first cyclopropapyridine to have been synthesized [58].

*Scheme 13*




## 5. The Photochemistry of *N*-Imino-pyridinium-Ylides in Retrospect

*There are only two types of research: applied research and the not-yet-applied research.* *Sir George Porter*

The photoinduced electrocyclisation of some 1,3-dipolar azomethine-imines to the corresponding three-membered diaziridines led us to investigate the photochemical behaviour of their aromatic analogues, *i.e.* of 1-iminopyridinium ylides. It turned out that many of these ylides photoisomerised in good yield to the corresponding 1*H*-1,2-diazepines, the bicyclic diazanorcaradienes being the most likely intermediates. Photophysical studies of this ring-expansion reaction as well as kinetic and thermochemical investigations of the reverse thermal ring contraction, permitted to draw an energy diagram for both processes. From this diagram, two salient features emerge: *i*) the non-aromatic 1,2-diazepines appear at higher energy (*ca.* 20 kcal/mol) – *i.e.* they are less stable – than the corresponding aromatic pyridinium ylides; *ii*) the postulated short-lived norcaradiene intermediates react at a much faster rate to the pyridinium ylides than to their diazepine isomers. It should be noted, furthermore, that pyridinium-ylides are highly polar and, therefore, hydrophilic species whereas the poorly polar diazepine photoisomers are lipophilic substances.

The application of photochemistry to polymer science is especially interesting,

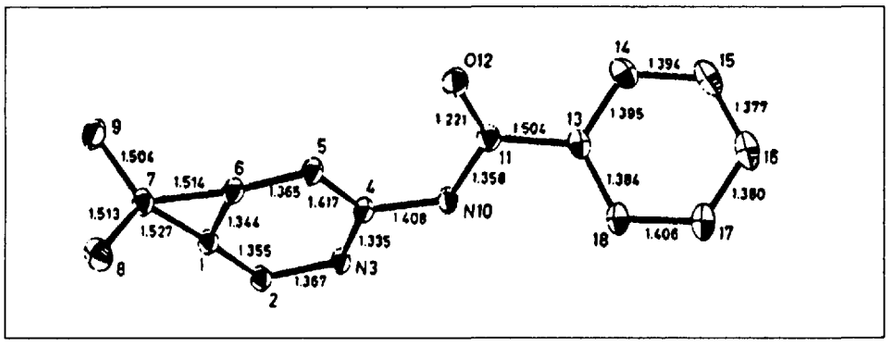



Fig. 10. *Crystal structure of* **63**. Bond lengths in Å; angles of the cyclopropene moiety [°]: C(1)–C(7)–C(6) **52**, C(1)–C(6)–C(7) **64**, C(6)–C(1)–C(7) **63**.

when the photoinduced alteration of solubility is extremely pronounced as observed in the present instance. Indeed, the large change in polarity, which accompanies the photoisomerisation of polymeric pyridinium ylides to the corresponding 'polydiazepines', led to a large solubility change in the polymer system which permitted the making of novel negative photoresists.

On the other hand, the non-aromatic, and non-planar diazepines represent a new vista in heterocyclic chemistry [16]. First of all, they store in the form of chemical energy part of the photonic energy which had been absorbed by the pyridinium-ylide precursors. Secondly, they lead easily to cycloaddition products – *e.g.* with diazoisopropane – from which small-ring systems could be prepared both thermally and photochemically. New reactions were triggered off with these diazepines and have been well documented by several research groups [16].

Much of the work cited from this laboratory was performed by a number of skilled students and talented post-doctoral fellows whose names appear in the references and in those of a previous review-article [16]. I am indebted to them for their dedicated engagement and endurance. I gratefully acknowledge the financial support of the *Centre National de la Recherche Scientifique (URA-135)*, and the *Rhône-Poulenc Company* for some PhD-grants, and express my sincere thanks to Prof. *J. Wirz*, University of Basel, for the determination of luminescence spectra and for the measurement of the quantum yields as a function of temperature, as well as for the interpretation he proposed in order to account for these phenomena. My thanks are due also to Prof. *R.A. Raphael*, University of Cambridge, and to Dr. *R. Schwalm*, *BASF*, Ludwigshafen, for a critical reading of the manuscript, to Mrs. *R. Baron* who typed it, and to Mrs. *C. Strehler* for the drawing of figures and schemes.

Received: October 22, 1990

[1] M. Nastasi, J. Streith, in 'Rearrangements in Ground and Excited States' Ed. de Mayo, Academic Press, New York, 1980, Vol. 3, p. 445-499.
[2] J.S. Splitter, M. Calvin, *J. Org. Chem.* **1958**, *23*, 651.
[3] J.S. Splitter, T. Su, H. Ono, M. Calvin, *J. Am. Chem. Soc.* **1971**, *93*, 4075.
[4] R.B. Woodward, R. Hoffmann, 'The Conservation of Orbital Symmetry', Verlag Chemie, Weinheim, 1970.
[5] H. Hermann, R. Huisgen, H. Mäder, *J. Am. Chem. Soc.* **1971**, *93*, 1779.
[6] M.G. Pleiss, J.A. Moore, *J. Am. Chem. Soc.* **1968**, *90*, 4738.
[7] G.G. Spence, E.C. Taylor, O. Buchardt, *Chem. Rev.* **1970**, *70*, 231.
[8] F. Bellamy, J. Streith, *Heterocycles* **1976**, *4*, 1391.
[9] K.B. Tomer, N. Harrit, I. Rosenthal, O. Buchardt, P.L. Kumler, D. Creed, *J. Am. Chem. Soc.* **1973**, *95*, 7402.
[10] J. Streith, C. Sigwalt, *Tetrahedron Lett.* **1966**, 1347.
[11] F. Bellamy, J. Streith, H. Fritz, *Nouv. J. Chim.* **1979**, *3*, 115; F. Bellamy, J. Streith, *J. Chem. Res. (S)* **1979**, 18; *ibid. (M)* **1979**, 101–116.
[12] J. Streith, J.M. Cassal, *C.R. Hebd. Séances Acad. Sci.* **1967**, *264*, 1307.
[13] J. Streith, J.M. Cassal, *Angew. Chem.* **1968**, *80*, 117; *ibid. Int. Ed.* **1968**, *7*, 129.
[14] W.J. McKillip, E.A. Sedor, B.M. Culbertson, S. Wawzonek, *Chem. Rev.* **1973**, *73*, 255.
[15] M. Nastasi, *Heterocycles* **1976**, *4*, 1509.
[16] V. Snieckus, J. Streith, *Acc. Chem. Res.* **1981**, *14*, 348.
[17] R. Gleiter, D. Schmidt, J. Streith, *Helv. Chim. Acta* **1971**, *54*, 1645.
[18] J. Michl, E.W. Thulstrup, J.H. Eggers, *J. Phys. Chem.* **1970**, *74*, 3878.
[19] J.P. Catteau, A. Lablache-Combier, J. Grimblot, M. Nastasi, J. Streith, *Tetrahedron* **1975**, *31*, 2909.
[20] J. Wirz, University of Basel, private communications.
[21] H. Strub, Ph.D. thesis, Université de Haute-Alsace, Mulhouse, 1983.
[22] J. Streith, J.M. Cassal, *Bull. Soc. Chim. Fr.* **1969**, 2175.
[23] W. Amrein, J. Gloor, K. Schaffner, *Chimia* **1974**, *28*, 185.
[24] R.A. Abramovitch, T. Takaya, *J. Org. Chem.* **1973**, *38*, 3311.
[25] M. Nastasi, H. Strub, J. Streith, *Tetrahedron Lett.* **1976**, 4719.
[26] H. Strub, C. Strehler, J. Streith, *Chem. Ber.* **1987**, *120*, 355.
[27] W. Lwowski, 'Nitrenes', Wiley-Interscience, New York, 1970.
[28] W. Lwowski, T.W. Mattingly, Jr., *J. Am. Chem. Soc.* **1965**, *87*, 1947; J.M. Simon, W. Lwowski, *J. Am. Chem. Soc.* **1969**, *91*, 5107; J.S. McConaghy, Jr., W. Lwowski, *ibid.* **1967**, *89*, 4450.
[29] C.W. Bird, I. Partridge, D.Y. Wong, *J. Chem. Soc., Perkin Trans. 1* **1972**, 1020.
[30] A. Frankowski, J. Streith, *Tetrahedron* **1977**, *33*, 427.
[31] T. Kigushi, J. L. Schuppiser, J.C. Schwaller, J. Streith, *J. Org. Chem.* **1980**, *45*, 5095.
[32] H. Fritz, R. Gleiter, M. Nastasi, J.L. Schuppiser, J. Streith, *Helv. Chim. Acta* **1978**, *61*, 2887.
[33] M. Martigneaux, C. Strehler, J. Streith, *Tetrahedron Lett.* **1983**, *24*, 3327.
[34] A photoinduced [1,7]-sigmatropic shift had been postulated merely as a working hypothesis by Prof. *R. Huisgen* (private communication).
[35] G. Kan, M.T. Thomas, V. Snieckus, *J. Chem. Soc. (D)* **1971**, 1022; J. Streith J.P. Luttringer, M. Nastasi, *J. Org. Chem.* **1971**, *36*, 2962.
[36] J. Streith, J.R. Frost, H. Strub, P. Goursot, *Nouv. J. Chim.* **1984**, *8*, 223.
[37] W. Drenth, H. Kwart, 'Kinetics applied to organic reactions', Marcel Dekker Inc., New York-Basel, 1980.
[38] A.E. Ames, A.M. Halpern, C.J. Ruggles, *J. Phys. Chem.* **1990**, *94*, 4464.
[39] E. Ciganek, *J. Am. Chem. Soc.* **1965**, *87*, 1149.
[40] E. Vogel, W.A. Böll, H. Günther, *Tetrahedron Lett.* **1965**, 609.
[41] H. Prinzbach, H. Babsch, H. Fritz, P. Hug, *Tetrahedron Lett.* **1977**, 1355.
[42] H. Kwart, D.A. Benko, J. Streith, D.J. Harris, J.L. Schuppiser, *J. Am. Chem. Soc.* **1978**, *100*, 6501.
[43] H. Kwart, D.A. Benko J. Streith, J.L. Schuppiser, *J. Am. Chem. Soc.* **1978**, *100*, 6502.
[44] M. Haubs, H. Ringsdorf, *Angew. Chem.* **1985**, *97*, 880; *ibid. Int. Ed.* **1985**, *24*, 882.
[45] M. Haubs, H. Ringsdorf, *Nouv. J. Chim.* **1987**, *11*, 151.
[46] H. Ringsdorf, B. Schlarb, J. Venzmer, *Angew. Chem.* **1988**, *100*, 118; *ibid. Int. Ed.* **1988**, *27*, 114.
[47] L.D. Taylor, H.S. Kolesinski, B. Edwards, M. Haubs, H. Ringsdorf, *J. Polym. Sci. C: Polym. Lett.* **1988**, *26*, 177; L.D. Taylor, M. Haubs, U.S. Patent 4, 617, 253, 1986; US Patent 4, 670, 528, 1987.
[48] R. Schwalm, A. Böttcher, H. Koch, 'Advances in Resist Technology and Processing V' (SPIE Vol 920), 1988, 21; R. Schwalm, H. Koch, G. Schulz, A. Böttcher, T. Loerzer, *BASF* EP 0212 374.
[49] P. Gesche, F. Klinger, W. Müller, J. Streith, H. Strub, R. Sustmann, *Chem Ber.* **1985**, *118*, 4682.
[50] R. Allmann, A. Frankowski, J. Streith, *Tetrahedron* **1972**, *28*, 581.
[51] F. Klinger, M. Foulon, P. Gesche, H. Strub, J. Streith, *Chem. Ber.* **1987**, *120*, 1783.
[52] P. Gesche, F. Klinger, A. Riesen, T. Tschamber, M. Zehnder, J. Streith, *Helv. Chim. Acta* **1987**, *70*, 2087.
[53] H. Prinzbach, H.-D. Martin, *Chimia* **1969**, *23*, 37.
[54] R. Huisgen, *Angew. Chem.* **1980**, *92*, 979; *ibid. Int. Ed.* **1980**, *19*, 947.
[55] R. Bambal, H. Fritz, G. Rihs, T. Tschamber, J. Streith, *Angew. Chem.* **1987**, *99*, 710; *ibid. Int. Ed.* **1987**, *26*, 668.
[56] B. Halton, *Chem. Rev.* **1973**, *73*, 113; *Ind. Eng. Chem. Prod. Res. Dev.* **1980**, *19*, 349; W.E. Billups, *Acc. Chem. Res.* **1978**, *11*, 245.
[57] E. Carstensen-Oeser, B. Müller, H. Dürr, *Angew. Chem.* **1972**, *84*, 434; *ibid. Int. Ed.* **1972**, *11*, 422.
[58] S. J. Buckland, B. Halton, B. Stanovnik, *Tetrahedron Lett.* **1986**, *27*, 1309.