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Laser flash photolysis studies of nitrogen ylides generated by the reaction of arylchlorocarbenes with substituted vinylpyridines and 1-azabuta-1,3-dienes

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Abstract

Laser Flash Photolysis of arylchlorodiazirines in isooctane/CH_2Cl_2 in the presence of substituted vinylpyridines yields substituted vinylpyridinium ylide ($\lambda = 540$ nm). As the ylide decays a concomitant growth causes an absorption at 330 nm, attributed to the formation of substituted indolizine. The reaction experiences the intramolecular 1,5-cyclization of the ylide intermediate. The kinetic parameters for the ylide formation and the 1,5-cyclization have been obtained. The activation energy for the latter process is reduced by 3–4 kcal mol^{-1} when the vinylpyridine has a phenyl ring as a substituent in β-position of the ethylenic group. Laser Flash Photolysis of phenylchlorodiazirine in isooctane in the presence of 1-azabuta-1,3-diene yields azomethine ylide ($\lambda = 550$ nm) as an intermediate. The kinetic parameters for the ylide formations and further intramolecular 1,5-cyclization to pyrrole have been determined. The results resemble those obtained for the 1,5-cyclization of vinylpyridinium ylide.

Keywords: Laser flash photolysis; Kinetics; Diazirine; Carbene; Vinylpyridine; Azomethine; Indolizine; Pyrrole; Vinylpyridinium ylide; Azomethine ylide

1. Introduction

Reactions of carbenes and metal carbenoids with nitrogen-containing compounds which produce nitrogen ylides as an intermediate have been shown to be a useful synthetic technique to a variety of biologically active nitrogen-containing heterocycles [1–4]. Investigation of the mechanisms of these reactions containing ylides as highly reactive intermediates has been attracting the constant interest of physical chemists. Pyridinium and azomethine ylides have been known for a long time and their reactions have been thoroughly studied and reviewed [1–4], but the kinetic studies on these systems are limited [5].

Previously we reported the Laser Flash Photolysis (LFP) studies of pyridinium ylide generated from the reaction of phenylchlorocarbene with pyridine. Further intermolecular cycloaddition of pyridinium ylides to dimethylacetylene dicarboxylate and α-chloroacrylonitrile yielded indolizines as the final products [6,7]. We also demonstrated by LFP that vinylpyridinium ylide can be generated from the reaction of *p*-chlorophenylchlorocarbene with vinylpyridine. Further intramolecular 1,5-dipolar cyclization of ylide formed in this manner produced 3-(*p*-chlorophenyl) indolizine [8,9]. As indolizine is an important class of heterocycles from theoretical and practical perspectives, [10] we wish to extend our studies on the reaction of arylchlorocarbenes with substituted vinylpyridines under photolytic or thermal conditions to produce 2,3-disubstituted indolizines. Inasmuch as intramolecular 1,5-cyclization of pyridinium ylides has shown to be a useful approach to the synthesis of heterocycles, we decided to apply this method to the reaction of arylchlorocarbenes with 1-azabuta-1,3-dienes, where such a possibility also exists. The literature reveals only a few examples where azomethine ylides have undergone intramolecular 1,5-cyclization [11–13]. No pyrroles could be detected in the reaction of dichlorocarbene with 1-azabuta-1,3-dienes, where dichloroaziridines were isolated in high yield [14,15]. This report investigates the formation of 1,2,3-trisubstituted pyrroles based on the reaction of arylchlorocarbenes with 1-azabuta-1,3-dienes under photolytic or thermal conditions. Since the reactions of arylchlorocarbenes with substituted vinylpyridines and 1-azabuta-1,3-dienes involve ylide intermediates, we wish to focus on

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the LFP studies of these systems especially on the kinetics of ylide formation, substituent effect, and the rates of 1,5-dipolar cyclization.

2. Experimental

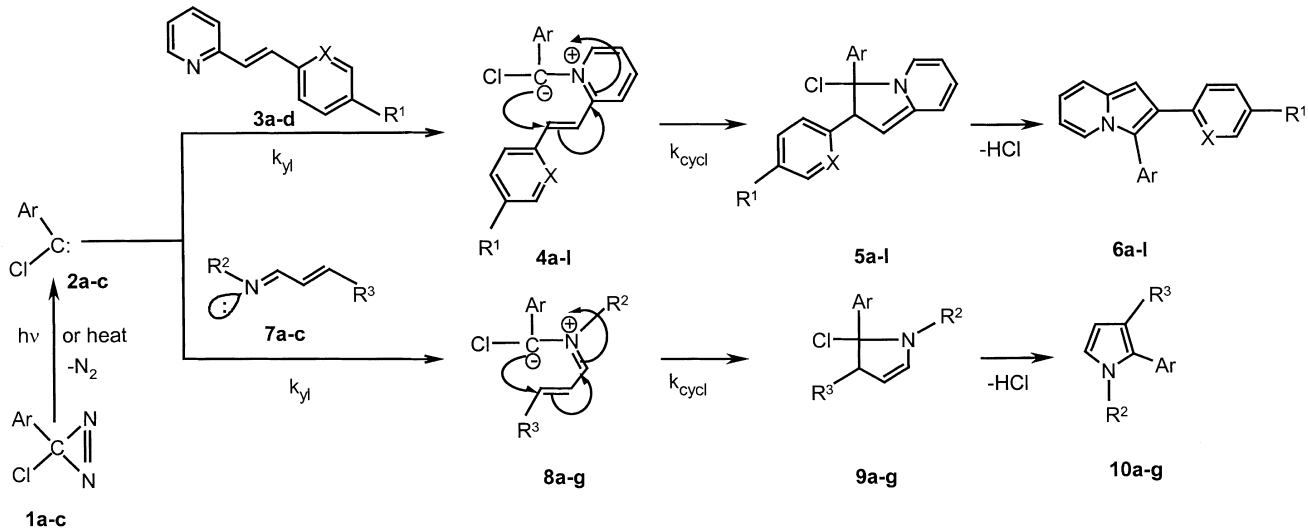
2.1. Synthesis

All arylchlorodiazirines **1a–c** were prepared [16] by oxidation of the corresponding benzamidine hydrochloride with sodium hypochlorite in DMSO and purified by column chromatography on Silica Gel. Arylchlorocarbenes **2a–c** were generated from arylchlorodiazirines **1a–c** by photolysis or thermolysis. 2-Phenyl-1-(2-pyridyl)ethylene **3a**, 2-(4-methylphenyl)-1-(2-pyridyl)ethylene **3b**, and 2-(4-chlorophenyl)-1-(2-pyridyl)ethylene **3c** were prepared from 2-picoline and aromatic aldehydes [17]. 1,2-Bis(2-pyridyl)ethylene **3d** and 1-(2-pyridyl)-2-(4-pyridyl)ethylene **3e** were purchased from Aldrich. We prepared 1-azabuta-1,3-dienes **7a–c** from cinnamaldehyde or crotonic aldehyde and methyl or benzyl amines. We purified them by distillation under a reduced pressure. Irradiation was performed with a battery of 350 nm lamps in a Rayonet photoreactor (Scheme 1).

Photolyses were carried out by irradiation (350 nm) of solutions of chlorodiazirine **1a–c** (1 mmol), substituted vinylpyridine **3a–d** or 1-azabuta-1,3-diene **7a–c** (2.5 mmol), and hexane (50 ml) at 25°C for 24 h. For thermolysis reactions solutions of arylchlorodiazirine **1a–c** (1 mmol) and substituted vinylpyridine **3a–d** or 1-azabuta-1,3-diene **7a–c** (2.5 mmol) in absolute benzene (10 ml) were refluxed for 6 h. After workup, indolizines **6a–l** and pyrroles **10a–g** were purified by column chromatography on Al_2O_3 with eluent Hexane/Ether = 10 : 1, followed by crystallization from i-Propanol/Hexane = 1 : 3. Yields and melting points of obtained indolizines **6a–l** and pyrroles **10a–g** are presented in Table 1 and Table 2. NMR spectral data, which compare well with those previously reported for **10a,d** [18–21] are given in Table 3. We detected no indolizines in photolysis or thermolysis of 1-(2-pyridyl)-2-(4-pyridyl)ethylene **3e** in the presence of chlorodiazirines **1a–c**.

2.2. Spectroscopy

The LFP setup uses a crossed-beam arrangement. The sample in a 10 mm × 10 mm cell was excited at 355 nm by single light pulses (200 ps; 5–30 mJ) provided by a frequency tripled mode-locked Nd-YAG laser (Quantel). The detection system (pulsed Xe-arc, monochromator, photo-



1, 2 a: Ar = Ph; **b**: Ar = *p*-MeC_6H_4; **c**: Ar = *p*-ClC_6H_4;
3 a: R^1 = H, X = CH; **b**: R^1 = Me, X = CH; **c**: R^1 = Cl, X = CH; **d**: R^1 = H, X = N;
4-6 a: Ar = Ph, R^1 = H, X = CH; **b**: Ar = *p*-MeC_6H_4, R^1 = H, X = CH; **c**: Ar = *p*-ClC_6H_4, R^1 = H, X = CH;
d: Ar = Ph, R^1 = Me, X = CH; **e**: Ar = *p*-MeC_6H_4, R^1 = Me, X = CH; **f**: Ar = *p*-ClC_6H_4, R^1 = Me, X = CH;
g: Ar = Ph, R^1 = Cl, X = CH; **h**: Ar = *p*-MeC_6H_4, R^1 = Cl, X = CH; **i**: Ar = *p*-ClC_6H_4, R^1 = Cl, X = CH;
j: Ar = Ph, R^1 = H, X = N; **k**: Ar = *p*-MeC_6H_4, R^1 = H, X = N; **l**: Ar = *p*-ClC_6H_4, R^1 = H, X = N;
7 a: R^2 = Me, R^3 = Ph; **b**: R^2 = Ph-CH_2, R^3 = Ph; **c**: R^2 = Ph-CH_2, R^3 = Me;
8-10 a: Ar = Ph, R^2 = Me, R^3 = Ph; **b**: Ar = *p*-MeC_6H_4, R^2 = Me, R^3 = Ph; **c**: Ar = *p*-ClC_6H_4, R^2 = Me, R^3 = Ph;
d: Ar = Ph, R^2 = Ph-CH_2, R^3 = Ph; **e**: Ar = *p*-MeC_6H_4, R^2 = Ph-CH_2, R^3 = Ph; **f**: Ar = *p*-ClC_6H_4, R^2 = Ph-CH_2, R^3 = Ph;
g: Ar = *p*-MeC_6H_4, R^2 = Ph-CH_2, R^3 = Me

Scheme 1.

Table 1
Isolated yields of 2,3-disubstituted indolizines **6**

Product 6	Ar	R^1	X	m.p. °C	Yield	
					hv	Heat
a	Ph	H	CH	95–96	8	10
b	*p*-MeC_6H_4	H	CH	87–88	7	20
c	*p*-ClC_6H_4	H	CH	100–101	8	21
d	Ph	Me	CH	149–150	7	21
e	*p*-MeC_6H_4	Me	CH	125–126	8	29
f	*p*-ClC_6H_4	Me	CH	153–154	3	20
g	Ph	Cl	CH	183–184	13	26
h	*p*-MeC_6H_4	Cl	CH	143–144	20	20
i	*p*-ClC_6H_4	Cl	CH	153–154	13	13
j	Ph	H	N	116–117	11	11
k	*p*-MeC_6H_4	H	N	120–121	10	10
l	*p*-ClC_6H_4	H	N	95–96	10	10

[a] Only m.p. for **6a** has been reported. Lit m.p. 95–96°C [19].

Table 2
Isolated yields of 1,2,3-trisubstituted pyrroles **10**

Product 10	Ar	R^2	R^3	m.p. °C	Yield	
					hv	Heat
a	Ph	Me	Ph	95–96.5	50	54
b	*p*-MeC_6H_4	Me	Ph	95–96	51	65
c	*p*-ClC_6H_4	Me	Ph	112–113	48	52
d	Ph	Bn	Ph	116–117	40	50
e	*p*-MeC_6H_4	Bn	Ph	132–122	55	58
f	*p*-ClC_6H_4	Bn	Ph	147–148	50	56
h	*p*-MeC_6H_4	Bn	Me	Viscous oil	30	40

[a] Only m.p. for **10a** has been reported. Lit m.p. 117–118°C [19].

Table 3
NMR Spectra of 2,3-disubstituted indolizines 6 and 1,2,3-trisubstituted pyrroles

Product	^{1}H NMR (δ, $CDCl_3$)[a]
6a	6.42 (1H, t, $J = 7$, 6-H_{ind}), 6.6–6.8 (2H, m, 1-H_{ind}, 7-H_{ind}), 7.1–7.5 (11H, m, $2C_6H_5$, 8-H_{ind}), 7.93 (1H, d, $J = 7$, 5-H_{ind})
6b	2.42 (3H, s, Me), 6.40 (1H, t, $J = 7$, 6-H_{ind}), 6.6–6.8 (2H, m, 1-H_{ind}, 7-H_{ind}), 7.1–7.5 (10H, m, C_6H_5, C_6H_4, 8-H_{ind}), 7.92 (1H, d, $J = 7$, 5-H_{ind})
6c	6.44 (1H, t, $J = 7$, 6-H_{ind}), 6.6–6.8 (2H, m, 1-H_{ind}, 7-H_{ind}), 7.2–7.6 (10H, m, $2C_6H_5$, C_6H_4, 8-H_{ind}), 7.93 (1H, d, $J = 7$, 5-H_{ind})
6d	2.31 (3H, s, Me), 6.40 (1H, t, $J = 7$, 6-H_{ind}), 6.6–6.8 (2H, m, 1-H_{ind}, 7-H_{ind}), 7.0–7.5 (10H, m, C_6H_5, C_6H_4, 8-H_{ind}), 7.93 (1H, d, $J = 7$, 5-H_{ind})
6e	2.31 (3H, s, Me), 2.41 (3H, s, Me), 6.40 (1H, t, $J = 7$, 6-H_{ind}), 6.6–6.8 (2H, m, 1-H_{ind}, 7-H_{ind}), 7.0–7.3 (8H, m, $2C_6H_5$), 7.38 (1H, d, $J = 9$, 8-H_{ind}), 7.92 (1H, d, $J = 7$, 5-H_{ind})
6f	2.33 (3H, s, Me), 6.43 (1H, t, $J = 7$, 6-H_{ind}), 6.6–6.8 (2H, m, 1-H_{ind}, 7-H_{ind}), 7.0–7.5 (9H, m, $2C_6H_5$, 8-H_{ind}), 7.91 (1H, d, $J = 7$, 5-H_{ind})
6g	6.42 (1H, t, $J = 7$, 6-H_{ind}), 6.6–6.8 (2H, m, 1-H_{ind}, 7-H_{ind}), 7.1–7.5 (10H, m, $2C_6H_5$, C_6H_4, 8-H_{ind}), 7.93 (1H, d, $J = 7$, 5-H_{ind})
6h	2.42 (3H, s, Me), 6.40 (1H, t, $J = 7$, 6-H_{ind}), 6.6–6.8 (2H, m, 1-H_{ind}, 7-H_{ind}), 7.1–7.3 (8H, m, $2C_6H_4$), 7.38 (1H, d, $J = 9$, 8-H_{ind}), 7.90 (1H, d, $J = 7$, 5-H_{ind})
6i	6.46 (1H, t, $J = 7$, 6-H_{ind}), 6.6–6.8 (2H, m, 1-H_{ind}, 7-H_{ind}), 7.1–7.5 (9H, m, $2C_6H_5$, 8-H_{ind}), 7.91 (1H, d, $J = 7$, 5-H_{ind})
6j	6.41 (1H, t, $J = 7$, 6-H_{ind}), 6.6–6.7 (1H, m, 7-H_{ind}), 7.0–7.6 (10H, m, C_6H_5, 3-H_{py}, 4-H_{py}, 5-H_{py}, 8-H_{ind}), 7.82 (1H, d, $J = 7$, 5-H_{ind}), 8.60 (1H, d, $J = 7$, 6-H_{py})
6k	2.43 (3H, s, Me), 6.39 (1H, t, $J = 7$, 6-H_{ind}), 6.6–6.7 (1H, m, 7-H_{ind}), 7.0–7.5 (9H, m, C_6H_4, 3-H_{py}, 4-H_{py}, 5-H_{py}, 1-H_{ind}, 8-H_{ind}), 7.80 (1H, d, $J = 7$, 5-H_{ind}), 8.62 (1H, d, $J = 7$, 6-H_{ind})
6l	6.40 (1H, t, $J = 7$, 6-H_{ind}), 6.6–6.7 (1H, m, 7-H_{ind}), 7.0–7.5 (9H, m, C_6H_4, 3-H_{py}, 4-H_{py}, 5-H_{py}, 1-H_{ind}, 8-H_{ind}), 7.82 (1H, d, $J = 7$, 5-H_{ind}), 8.61 (1H, d, $J = 7$, 6-H_{py})
10a	3.53 (3H, s, Me), 6.46 (1H, d, $J = 3$, 4-H), 6.76 (1H, d, $J = 3$, 5-H), 7.1–7.5 (10H, m, $2C_6H_5$)[b]
10b	2.33 (3H, s, Me), 3.47 (3H, s, Me), 6.38 (1H, d, $J = 3$, 4-H), 6.72 (1H, d, $J = 3$, 5-H), 7.1–7.4 (9H, m, C_6H_5, C_6H_4)
10c	3.48 (3H, s, Me), 6.43 (1H, d, $J = 3$, 4-H), 6.76 (1H, d, $J = 3$, 5-H), 7.1–7.5 (9H, m, C_6H_5, C_6H_4)[c]
10d	5.00 (2H, s, CH_2), 6.50 (1H, d, $J = 3$, 4-H), 6.80 (1H, d, $J = 3$, 5-H), 7.1–7.4 (15H, m, $3C_6H_5$)[d]
10e	2.34 (3H, s, Me), 5.00 (2H, s, CH_2), 6.52 (1H, d, $J = 3$, 4-H), 6.78 (1H, d, $J = 3$, 5-H), 7.1–7.4 (14H, m, $2C_6H_5$, C_6H_4)
10f	2.37 (3H, s, Me), 5.00 (2H, s, CH_2), 6.52 (1H, d, $J = 3$, 4-H), 6.82 (1H, d, $J = 3$, 5-H), 7.1–7.4 (14H, m, $2C_6H_5$, C_6H_4)
10g	2.07 (3H, s, Me), 2.37 (3H, s, Me), 5.00 (2H, s, C_H2), 6.17 (1H, d, $J = 3$, 4-H), 6.67 (1H, d, $J = 3$, 5-H), 7.1–7.4 (9H, m, C_6H_5, C_6H_4)

[a] Spectra of 6a–l and 10d–g were obtained on a Varian GEM INI (300 MHz) spectrometer and spectra of 10a–c on Varian T-60 (60 MHz) spectrometer.
[b] [18]: ^{1}H NMR (200 MHz, CD_3CN): δ 3.26 (3H, s), 7.32–7.72 (12H, m).
[c] *m/z* 267 $[M]^+$.
[d] [19]: ^{1}H NMR (270 MHz, $CDCl_3$): δ 4.88 (2H, s), 6.43 (1H, d, $J = 3$Hz), 6.68 (IH, d, $J = 3$ Hz), 6.8–7.3 (15H, m).
[20,21]: ^{1}H NMR ($CDCl_3$): δ 4.95 (2H, s), 6.48 (1H, d, $J = 3$ Hz), 6.66 (1H, d, $J = 3$ Hz), 7.10–7.37 (15H, m).

multiplier and Tektronix 7912 transient recorder) has a response time of approximately 4 ns.

3. Results and discussion

3.1. LFP of the reaction of p-chlorophenylchlorocarbene with substituted vinylpyridines

LFP ($\lambda = 355$ nm) of solution of chlorodiazirine **1c** in isooctane/methylene chloride, 9 : 1, produces a transient absorption at 310 nm due to the formation of the carbene **2c**. In the presence of substituted vinylpyridines **3a–c** (where R^1 = H, Me, Cl and X = CH) new transients attributed to vinylpyridinium ylides grow in at a rate equal to the rate of decay of the carbene, as measured at 310 nm. The absorption spectra are broad and the main band peaks around 540 nm, resembling the spectrum reported for vinylpyridinium ylide [8]. The plots of the observed pseudo-first-order rate constants for growth of the absorption at 540 nm versus substrate concentrations are linear and yield the rate constants for the reactions of chlorocarbene 2c with 3a, 3b and 3c at 25°C: $k_{yl} = 3.6 \pm 0.2 \times 10^8\ M^{-1}\ s^{-1}$, $4.0 \pm 0.2 \times 10^8\ M^{-1}\ s^{-1}$, $2.6 \pm 0.2 \times 10^8$ respectively. The ylides **4c**, **4f** and **4i** decay with a lifetime equal to 3.8, 3.6 and 4.0 μs respectively at 25°C independent of the concentration of the substituted vinylpyridines **3a–c**. Since the decay of the ylides matches the growth of indolizines **6c**, **6f**, **6i** ($\lambda = 330$ nm), the HCl elimination must be more rapid than the cyclization step. We studied the temperature dependence, from 5 to 55°C, of the cyclization step. The data gave three Arrhenius lines. Least squares analysis yielded the following parameters for the 1,5-cyclization of the ylides:

ylide (**4c**) $E_a = 8.0 \pm 0.2$ kcal mol^{-1}, $A = 2.0 \pm 0.2 \times 10^{11}\ s^{-1}$

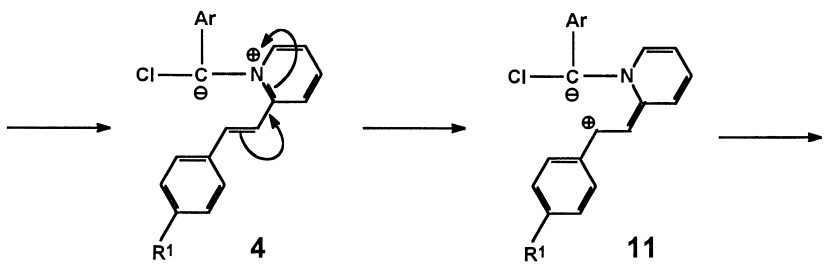
ylide (**4f**) $E_a = 8.6 \pm 0.2$ kcal mol^{-1}, $A = 5.3 \pm 0.3 \times 10^{11}\ s^{-1}$

ylide (**4i**) $E_a = 8.7 \pm 0.2$ kcal mol^{-1}, $A = 6.5 \pm 0.3 \times 10^{11}\ s^{-1}$

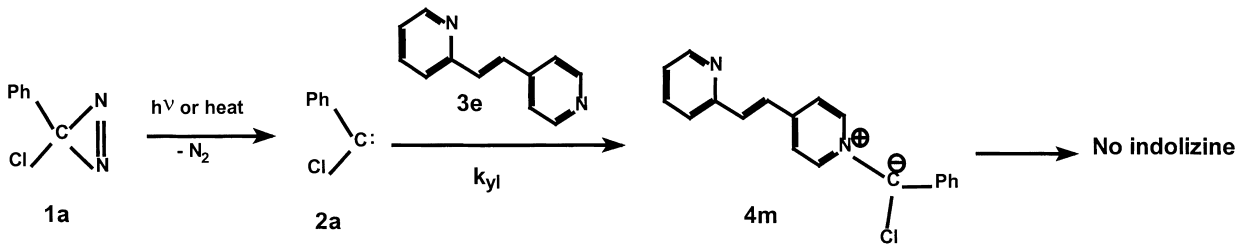
Our earlier LFP studies [8] produced the following parameters for the reaction of *p*-Cl-C_6H_4-C-Cl **2c** with 2-vinylpyridine: $k_{yl} = 2 \times 10^8\ M^{-1}\ s^{-1}$, $\tau_{(25°C)} = 33$ μs, E_a(cyclization) = 12.1 kcal mol^{-1} and $A = 2.5 \times 10^{13}\ s^{-1}$. Evidently, the substituent in β-position of the ethylenic group of vinylpyridine has no effect on the rates of ylide formation, because all the rate constants are of the order $10^8\ M^{-1}\ s^{-1}$. An approximately ten-fold reduction in the lifetimes of the ylides appears owing to the presence of the phenyl substituent on the vinyl group. The activation energies for 1,5-cyclization have been reduced by 3–4 kcal mol^{-1} in each case, even though the chloro or methyl substituent on the phenyl ring exerts no electronic effect. LFP of phenylchlorodiazirine **1a** in isooctane with 2-phenyl-1-(2-pyridyl)ethylene **3a** gave similar results: $k_{yl} = 2.3 \times 10^8\ M^{-1}\ s^{-1}$, $\tau_{(25°C)} = 2.4$ μs, E(cyclization) = 9.0 ± 0.2 kcal mol^{-1} and $A = 1.4 \pm 0.1 \times 10^{12}\ s^{-1}$. As in the case of vinylpyridine, the initially formed ylide **4** with a positive charge on nitrogen atom transforms to ylide **11**, where the positive charge is additionally stabilized due to the conjugation with a phenyl ring (Scheme 2). This might explain the reduction of the activation energy for 1,5-cyclization of the formed ylide compared to the one obtained with vinylpyridine. The effect of conjugation with the phenyl ring could be preferentially larger compared to the substituent effect on the phenyl ring. Hence the latter effect might not be easily detected.

LFP of the reaction of phenylchlorocarbene **2a** with 1,2-bis(2-pyridyl)ethylene **3d** and 1-(2-pyridyl)-2-(4-pyridyl)-ethylene **3e** is of particular interest (Scheme 3). Section 2 reports the isolation of indolizine **6j** in the case of 1,2-bis(2-pyridyl)ethylene **3d**. We detected no indolizine when we used 1-(2-pyridyl)-2-(4-pyridyl)ethylene **3e** as substrate. LFP of phenylchlorodiazirine **1a** in the presence of **3d** leads to the formation of substituted vinylpyridinium ylide with $k_{yl} = 3.7 \times 10^8\ M^{-1}\ s^{-1}$, $\tau = 7.7$ μs at 25°C. It yields the following parameters for the 1,5-cyclization of the ylide **4j**: $E_a = 9.4 \pm 0.1$ kcal mol^{-1} and $A = 1.0 \pm 0.1 \times 10^{12}\ s^{-1}$. These kinetic parameters match those for ylides **4c**, **4f**, and **4i**. The effect of the 2-pyridyl substitution resembles that of a phenyl ring substituent for the 1,5-cyclization process.

Contrarywise, LFP of phenylchlorodiazirine **1a** in the presence of 1-(2-pyridyl)-2-(4-pyridyl) ethylene **3e** offered a different set of parameters. We observed the vinylpyridinium ylide **4m** at 540 nm and $k_{yl} = 1.3 \pm 0.1 \times 10^9\ M^{-1}\ s^{-1}$, the formation of which is several times faster than that of the corresponding vinylpyridinium ylide **4j**. The



Scheme 2.



Scheme 3.

lifetime of ylide **4m**, (440 μs at 25°C) is approximately two orders of magnitude longer than the lifetime of other ylides **4c**, **4f** and **4i**. The LFP results clearly demonstrate that the carbene favors the attack on the nitrogen atom, which is in *p*-position to the ethylenic group rather than the nitrogen atom in *o*-position. The latter creates an ylide with the geometry not suitable for further 1,5-cyclization.

3.2. LFP of the reaction of phenylchlorocarbene with 1-azabuta-1,3-dienes

LFP of arylchlorodiazirine **1a** at 355 nm in isooctane produces an absorption band at 310 nm due to the formation of carbene **2a**. In the presence of 1-azabuta-1,3-diene **7a**, a new transient, attributed to the azomethine ylide **8a**, grows at a rate equal to that of the decay of the carbene measured at 310 nm. The absorption spectrum is broad and the main band peaks at approximately 550 nm (Fig. 1). This result is consistent with the spectrum of azomethine ylides generated by the LFP of substituted aziridines [5]. The plot of the observed pseudo-first-order rate constants for the growth of the absorption at 550 nm versus concentration of **7a** is linear (Fig. 2) and the rate constant for the reaction of the carbene **2a** with **7a** at 25°C is $k_{yl} = 1.0 \pm 0.1 \times 10^9\ M^{-1}\ s^{-1}$. This value resembles that measured for the reaction of arylchlorocarbene with pyridine [6,7].

The ylide **8a** decays with a lifetime equal to 160 μs at 25°C, independent of the concentration of **7a**. Hence, the

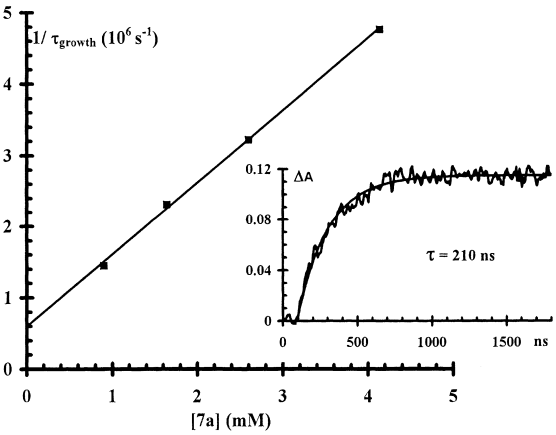


Fig. 2. Plot of $1/\tau_{growth}$ vs. [**7a**] obtained by monitoring growth of ylide **8a** at 550 nm in isooctane. Inset demonstrates growth observed with 4.2 mM of **7a**.

rate constant for the 1,5-dipolar cyclization of **8a** to **9a** is $6.25 \times 10^3\ s^{-1}$. HCl Elimination from **9a** to yield pyrrole **1Oa** must be much faster than the cyclization step, as demonstrated in similar experiments involving HCl elimination [6–9]. The temperature dependence of the ylide **8a** cyclization is shown in Fig. 3. Least squares analysis yielded the following Arrhenius parameters: $E_a = 12.5 \pm 0.2$ kcal mol^{-1} and $A = 7.7 \pm 0.2\ 10^{12}\ s^{-1}$. Similarly, LFP of chlorodiazirine 1a at 355 nm in isooctane with 1-azabuta-1,3-diene **7b** yielded ylide, **8d**, ($\lambda = 550$ nm). The

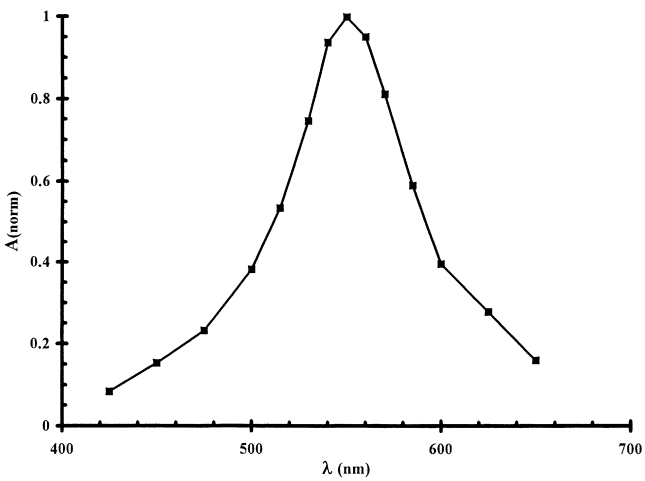


Fig. 1. Absorption spectrum for the ylide **8a** in isooctane at 25°C with 4.2 mM of **7a**.

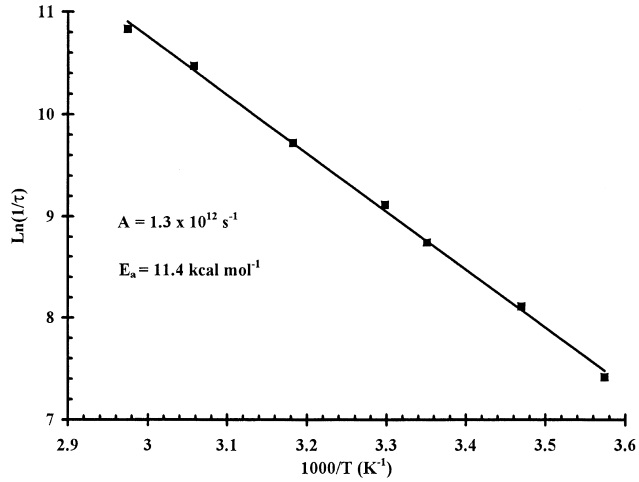


Fig. 3. Arrhenius plot obtained by measuring the rate of decay of ylide **8a** in isooctane at 550 nm.

rate constant for the reaction of **2a** with **7b** yielded $k_{yl} = 0.36 \pm 0.02 \times 10^9\ M^{-1}\ s^{-1}$. Studies at seven individual temperatures over the 7 – 63°C range provided the following Arrhenius parameters: $E_a = 11.4 \pm 0.3$ kcal mol^{-1} and $A = 1.3 \pm 0.4 \times 10^{12}\ s^{-1}$. Apparently, 1,5-cyclization for azomethine ylides requires a substantial amount of activation energy and proceeds with a normal to a tight transition state for the unimolecular process. All these data conform with the mechanism depicted in Scheme 1.

4. Conclusions

The cyclization of the vinylpyridinium ylides of arylchlorocarbenes followed by a rapid elimination of HCl leading to indolizines is not restricted to vinylpyridine. Cyclization also occurs for arylsubstituted vinylpyridines to 2,3-disubstituted indolizines. A ten-fold rate increase occurs when the vinylpyridine contains a phenyl ring as a substituent. There is no further effect on the cyclization rate when the phenyl ring has a methyl or chlorine substituent at *p*-position. The reaction of phenylchlorocarbene with 1-azabuta-1,3-dienes produces azomethine ylides, followed by intramolecular 1,5-dipolar cyclization, to yield pyrroles reminiscent of vinylpyridinium ylide.

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