Chemistry of Heterocyclic Compounds, Vol. 37, No. 10, 2001

THE LIFETIME AND REACTIVITY OF SINGLET TETRACHLOROPYRIDYL-4-NITRENE

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The principal direction in the photolytic decomposition of 4-azidotetrachloropyridine in methylene chloride solution involves the intermediate formation of singlet tetrachloropyridyl-4-nitrene, the lifetime of which amounts to 50 nsec. The nitrene reacts readily with the pyridine ($k_{pyr} = 2.67 \cdot 10^7$ mole^{-1}·sec^{-1}) with the formation of the corresponding pyridinium ylide, which has a characteristic absorption band in the UV spectrum with a maximum at 406 nm.

Keywords: azidopyridines, pyridylnitrenes, pyridinium ylides, laser-flash photolysis.

Earlier we showed that the only product from the photolysis of 4-azidotetrachloropyridine (**1c**) in inert matrices at low temperatures is triplet tetrachloropyridyl-4-nitrene (**2c**) [1]. At the same time the decomposition of the azide in solutions at room temperature can take place according to a different scheme. Under these conditions the main products from the photolysis of polysubstituted aryl azides are as a rule the corresponding singlet arylnitrenes **3**, which then undergo rapid ring expansion with the formation of azaheptatetraenes **4** [2-6]. In the presence of traps for singlet nitrenes, such as pyridine, the final products from the photolysis of aryl azides are the pyridinium ylides **5** and **6** (Scheme 1) [3]. In addition, as a result of partial internal conversion of the singlet nitrenes to triplet nitrenes, the products from transformation of the triplet nitrenes, mostly arylamines and azobenzenes, are also formed in the reactions [2]. In spite of the complexity of the chemical transformations of the singlet nitrenes in solutions at room temperature it is possible to obtain information on the lifetime and reactivity of the intermediates by measuring the kinetics of formation of the ylides **5**, which have characteristic absorption bands in the UV spectra [2-6].

In the present work we studied the kinetics of the photochemical decomposition of 4-azidotetrachloropyridine in methylene chloride solution in the presence of pyridine. From the obtained kinetic parameters we determined the lifetime and the reactivity of singlet tetrachloropyridyl-4-nitrene (**3c**) toward pyridine.

Photolysis of the azide **1c** was conducted at 23°C in methylene chloride solution with additions of various amounts of pyridine, using a laser pulse with a wavelength of 355 nm as light source. The action of light led to the appearance of a new absorption band with a maximum at 406 nm, typical of pyridinium ylides of the **5** type, in the UV spectrum (Fig. 1) [2-6]. The absence of any appreciable increase of the absorption in the region of 510 nm indicated that the rate of the reaction of the nitrene **3c** with pyridine significantly exceeded the

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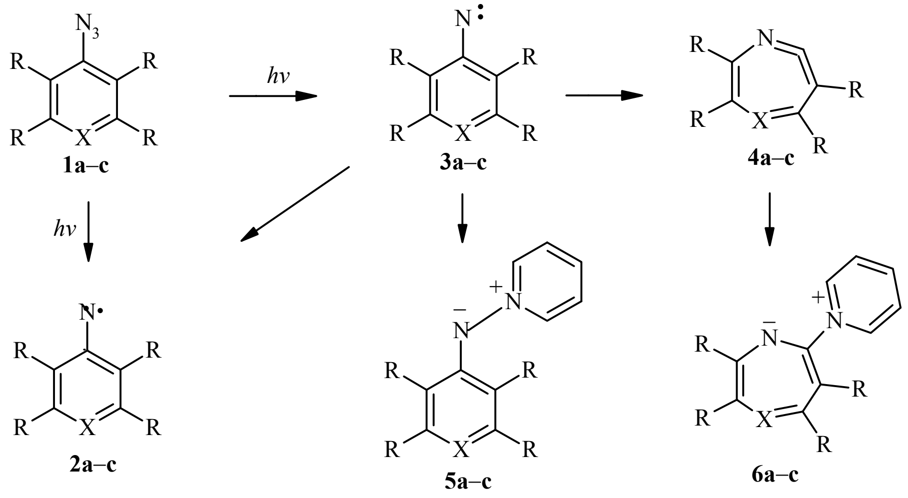
overall rate of ring enlargement and formation of ylides of the **6** type. The latter, according to published data [2-6], absorb light in the region of 500-530 nm. The appearance of an absorption band with a maximum at 406 nm was also observed during the photolysis of the azide **1c** under stationary conditions (Fig. 1).

Scheme 1



1-6 **a** R = F, X = C–F, **b** R = F, X = C–CONHCH$_3$, **c** R = Cl, X = N

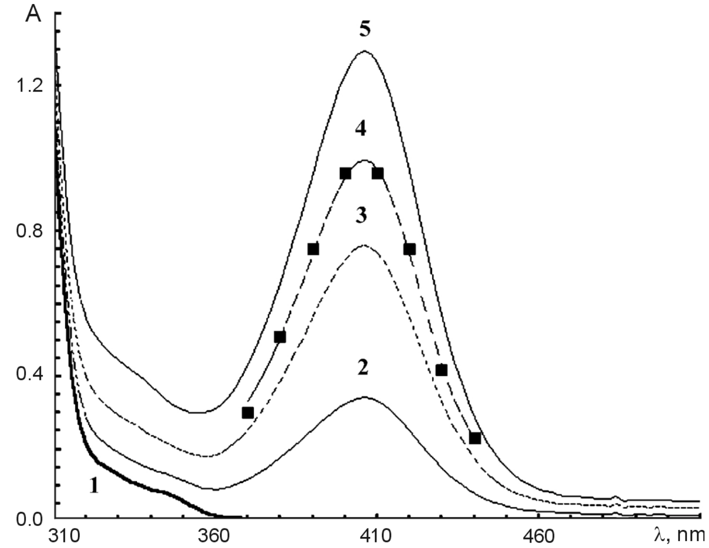


Fig. 1. The increase of the absorption of the ylide **5c** during the photolysis of the azide **1c** in methylene chloride solution in the presence of pyridine: 1) The UV spectrum of the azide **1c** before irradiation; 2) the UV spectrum of the products from photolysis of the azide **1c** after 20 sec continuous exposure to light (λ = 290-340 nm); 3) the UV spectrum of the products from photolysis of the azide **1c** after 50 sec continuous exposure to light (λ = 290-340 nm); 4) the UV spectrum of the products from photolysis of the azide **1c** after a single laser pulse (λ = 355 nm); 5) the UV spectrum of the products from photolysis of the azide **1c** after 100 sec continuous exposure to light (λ = 290-340 nm).

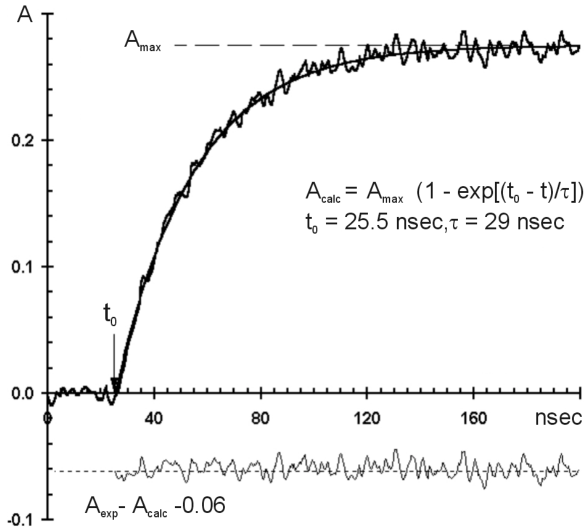


Fig. 2. A typical kinetic curve for the increase in the absorption of the ylide **5c** during pulsed photolysis of the azide **1c** in methylene chloride solution in the presence of pyridine.

The lifetimes of the nitrene **3c** in solutions containing various amounts of added pyridine were determined from the kinetics of the increase in the absorption of the ylide **5c** at 406 nm (Fig. 2, Table 1). The dependence of the lifetime τ of the nitrene on the concentration of pyridine is described by the equation:

$$1/\tau = k_{\mathrm{ICS}} + k_{\mathrm{exp}} + k_{\mathrm{pyr}}\,[\mathrm{Pyr}],$$

where k_{ICS}, k_{exp}, and k_{pyr} are the constants of internal singlet–triplet conversion (ISTC), ring enlargement, and the reaction of singlet nitrene with pyridine [3, 6] respectively.

A graphical representation of this relation is given in Fig. 3, where the slope of the line corresponds to the rate constant of the reaction of singlet nitrene **3c** with pyridine $k_{\mathrm{pyr}} = 2.67\cdot10^{7}$ $\mathrm{mole^{-1}\cdot sec^{-1}}$ and the intersection of the line with the ordinate axis gives the sum of the rate constants of ring enlargement and ISTC $k_{\mathrm{exp}} + k_{\mathrm{ISC}} = 2.03\cdot10^{7}$ $\mathrm{sec^{-1}}$. According to these values the life time τ of the nitrene **3c** in methylene chloride solution at 23°C is 50 nsec.

As far as we know the nitrene **3c** is the first example of singlet heterocyclic nitrenes for which the lifetime and the rate constant of the reaction with pyridine have been measured. In this connection it seemed of interest to compare the kinetic characteristics of this nitrene and of the nitrenes **3a**,**b**, which are widely used as photocrosslinking reagents in molecular biology and biochemistry [2]. It is seen from Table 2 that the nitrene **3c** reacts approximately twice as slowly as the nitrene **3a** with pyridine but has a significantly longer lifetime. The

TABLE 1. The Lifetime of the Nitrene **3c** in Methylene Chloride Solutions at 23°C with Various Contents of Added Pyridine

Concentration of pyridine, M	0.25	0.50	0.75	0.75	1.40	1.40
Lifetime, nsec	39	29	25	24	17	18

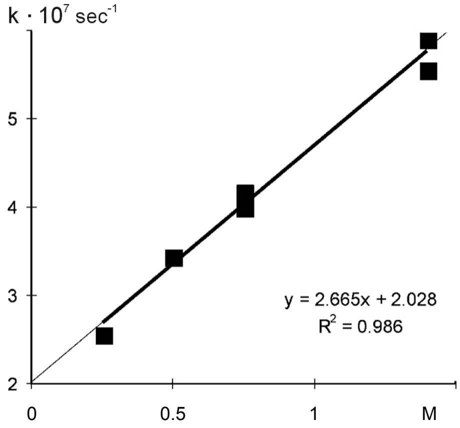


Fig. 3. The dependence of $1/\tau$ for the nitrene **3c** on the concentration of pyridine (r = 0.986).

TABLE 2. The Lifetime τ and Rate Constant k_{pyr} for the Reaction of Nitrenes **3a-c** and Singlet Phenylnitrene with Pyridine

Nitrene	**3a** [3]	**3b** [4]	**3c**	Ph–N [5]
τ (nsec)	32	200	50	0.1-1
$k_{pyr}\cdot 10^7$ M$^{-1}\cdot$sec^{-1}	5.8	3.1	2.7	—

nitrene **3b**, which contains a strong electron-withdrawing group at the *para* position to the nitrene center, is distinguished by a longer lifetime but is almost equivalent to the nitrene **3c** in reactivity in relation to pyridine. At the same time singlet phenylnitrene, which has not found widespread application in biology on account of its high instability, has a lifetime of less than 1 nsec. These comparisons show that the nitrene **3c** that we studied can also be used successfully as a photocrosslinking reagent, while the photochemical reactions of the azide **1c** in solutions at room temperature may be of interest for the synthesis of new compounds which can be obtained by the reaction of the nitrene **3c** with nucleophiles and unsaturated compounds.

EXPERIMENTAL

Laser pulse photolysis was conducted with a Quantel Nd-YAG laser (200 psec, 355 nm, 20 mJ). The light source for the analytical beam was an Osram XBO 75 W xenon lamp with a Hamamatsu R446 photomultiplier as detector. The experimental data were processed on a Tektronix 7912AD digital converter in conjunction with a personal computer. The delay between the delivery of the pulse and the recording of the spectrum amounted to 5 nsec. The working concentration of the solutions of the azide in the mixture of methylene chloride and pyridine was 0.02 M. Stationary photolysis was conducted with an NRK-125 high-pressure mercury lamp using a set of filters with a transmission range of 290-340 nm. The UV spectra were recorded on a Hewlett Packard 8452A spectrophotometer.

The 4-azidotetrachloropyridine was obtained by the familiar procedure [7].

One of the authors (S. V. Chapyshev) expresses his gratitude to the University of Bordeaux I for a grant provided for the investigation at this university.

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