

[3 + 2] Cycloadditions and Protonation by Alcohols of Photochemically Generated Nitrile Ylides from 2*H*-Azirines. Formation and Reactivities of Azaallenium Cations

Evelyn Albrecht,¹ Jochen Mattay,^{*,2} and Steen Steenken^{*,3}

Contribution from the Institut für Organische Chemie der Universität Münster, Corrensstrasse 40, D-48149 Münster, Germany, Institut für Organische Chemie der Universität Kiel, Olshausenstrasse 40, D-24098 Kiel, Germany, and Max-Planck-Institut für Strahlenchemie, D-45413 Mülheim, Germany

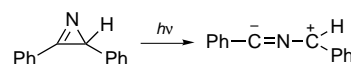
Received May 20, 1997[⊗]

Abstract: On photolysis of 2*H*-phenylazirines in acetonitrile or alcohol solution with 248 nm laser light, phenylnitrile ylides are formed by heterolytic cleavage of the C–C bond of the azirines. The absorption spectra of the ylides are characterized by two strong bands, at ca. 240 and 280 nm, and a weak band, at 380 nm. Electron-deficient olefins react with the nitrile ylides by 1,3-dipolar cycloaddition to yield 5-membered N-heterocycles (rate constants between 4×10^5 and $7 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$, the Hammett- ρ value for the *para*-substituent on the phenyl ring is -0.9). In alcohols as solvents, the nitrile ylides are protonated to yield azaallenium cations, whose spectroscopic properties and reactivities with nucleophiles are described. The protonation rates of the ylides in alcohols increase with the acidity of the alcohol. On the basis of the large kinetic isotope effect for protonation of ylide by alcohol ($k_{\text{H}}/k_{\text{D}} = 5.5$), the transition state for the ylide protonation is concluded to be linear.

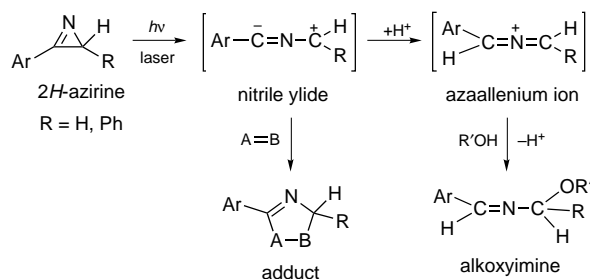
Introduction

2*H*-Azirines are photochemically highly active substances. Upon irradiation into their $n-\pi^*$ absorption bands the strained 3-membered azirine ring opens selectively at the C–C bond in a heterolytic fashion resulting in the formation of a nitrile ylide (NY)^{4,5} (Scheme 1). The nitrile ylide can be trapped by dipolarophiles (A=B) or alcohols. Due to the pronounced reactivity of nitrile ylides with dipolarophiles, azirines are frequently used in [3 + 2] cycloaddition reactions.⁶ A recent example is the facile synthesis of exohedrally functionalized fullerenes by five-membered heterocycles.⁷ In the presence of alcohols nitrile ylides form alkoxyimines,^{6,8} and a question is^{8,9} whether this reaction proceeds via the intermediate production of azaallenium cations (Scheme 2). To shed light on this and related questions, we have performed a systematic study of a

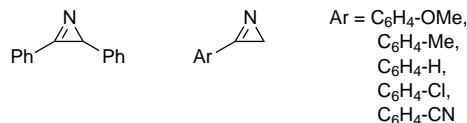
Scheme 1



Scheme 2



group of 4-aryl-substituted 2*H*-azirines as identified below



and we report the results in the following.

Results and Discussion

1. Formation of Nitrile Ylides. It has long been known that nitrile ylides can be generated by photolysis of 2*H*-azirines (AZ).^{8,10} We have now studied this reaction in more detail. For example, on flash photolysis of 0.02 to 0.1 mM solutions

[⊗] Abstract published in *Advance ACS Abstracts*, November 15, 1997.

(1) Universität Münster. Present address: SeaquistPerfect Dispensing GmbH, Hildebrandstrasse 20, D-44319 Dortmund.

(2) Universität Kiel (present address) and Universität Münster.

(3) Max-Planck-Institut für Strahlenchemie.

(4) Orahovats, A.; Heimgartner, H.; Schmid, H.; Heinzelmann, W. *Helv. Chim. Acta* **1975**, *58*, 2662–2677.

(5) Padwa, A.; Dharan, M.; Smolanoff, J.; Wetmore, S. I. *J. Am. Chem. Soc.* **1973**, *95*, 1954–1961.

(6) (a) Heimgartner, H. *Angew. Chem.* **1991**, *103*, 271–297; *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 238. (b) Gilgen, P.; Heimgartner, H.; Schmid, H.; Hansen, H.-J. *Heterocycles* **1977**, *6*, 143–212 and references therein. (c) Padwa, A. *Synthetic Organic Photochemistry*; Horspool, W. M., Ed.; Plenum Press, New York, 1984; pp 313–373. (d) Albrecht, E.; Averdung, J.; Bischof, E. W.; Heidbreder, A.; Kirschberg, T.; Müller, F.; Mattay, J. *J. Photochem. Photobiol. A: Chem.* **1994**, *82*, 219–232. (e) Müller, F.; Mattay, J. *Chem. Rev.* **1993**, *93*, 99–117. (f) Müller, F.; Mattay, J. *Chem. Ber.* **1993**, *126*, 543–549. (g) Nair, V. *The Chemistry of Heterocyclic Compounds, Small Ring Heterocycles*; Hassner, A., Ed.; Wiley Interscience: New York, 1983; Vol. 1, pp 215–332.

(7) (a) Averdung, J.; Albrecht, E.; Lauterwein, J.; Luftmann, H.; Mattay, J.; Mohn, H.; Müller, W. H.; ter Meer, H.-U. *Chem. Ber.* **1994**, *127*, 787–789. (b) Averdung, J.; Abraham, W.; Albrecht, E.; Claus, K.-U.; Jakobi, D.; Luftmann, H.; Mattay, J. *Recent Advances in the Chemistry and Physics of Fullerenes and Related Materials*; Kadish, K. M., Ruoff, R. S., Eds.; The Electrochemical Society: Pennington, NJ, 1995; Vol. 2, pp 1164–1178. (c) Averdung, J.; Mattay, J. *Tetrahedron* **1996**, *52*, 5407–5420.

(8) (a) Padwa, A.; Rasmussen, J. K.; Tremper, A. *J. Am. Chem. Soc.* **1976**, *98*, 2605–2614. (b) Padwa, A.; Smolanoff, J.; Tremper, A. *J. Am. Chem. Soc.* **1975**, *97*, 4682–4691. (c) Hansen, H.; Heimgartner, H. Nitrile Ylides. In *1,3-Dipolar Cycloaddition Chemistry*; Padwa, A., Ed.; John Wiley & Sons: New York, 1984; Bd. 1, Kap. 2, p 208. (d) Naito, I.; Ishida, A.; Takamuko, S.; Isomura, K.; Taniguchi, H. *J. Chem. Soc., Perkin Trans. 2*, **1992**, 1985–1988.

(9) Hansen, H.; Heimgartner, H. In *1,3-Dipolar Cycloaddition Chemistry*; Padwa, A., Ed.; Wiley: New York, 1984; Vol. 1, pp 177–290.

Table 1. Absorption Maxima of the Nitrile Ylides Generated by Laser Flash Photolysis of 2*H*-Azirines in Acetonitrile at Room Temperature^a

λ_{\max} , nm	Ph-C=N-C ⁺ H ₂ -Ph	X =				
		CN	Cl	H	Me	OMe
		238, 282 (385) [306]	240, 283 (385)	230, 280 (380)	236, 284 (380)	260, 288 (380) [300]

^a Numbers in parentheses are for weak absorption. Numbers in square brackets are for a shoulder.

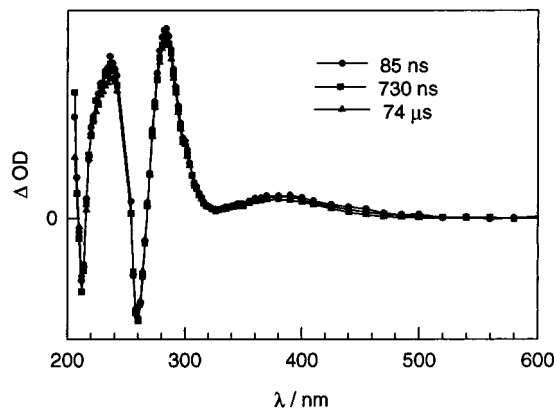
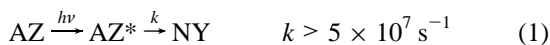


Figure 1. Spectra of transients recorded on photolysis of deoxygenated 70 μ M 3-(4-methylphenyl)-2*H*-azirine in acetonitrile, measured at several times after the laser flash as indicated.

in acetonitrile of the 2*H*-azirines mentioned above with the 248 nm light of an excimer laser, optical absorptions were observed with λ_{\max} values at ca. 205, 240, 280, and 380 nm. These signals are assigned to nitrile ylides on the basis of their similarity to those observed in matrices at 77 K.¹¹ Since the formation of the signals was complete after the 20 ns laser pulse, the rate constant k ($AZ^* \rightarrow NY$) must be $>5 \times 10^7 \text{ s}^{-1}$.



An example is shown in Figure 1 for the case of 3-(4-methylphenyl)-2*H*-azirine, dissolved in acetonitrile, and photolyzed with a 20 ns pulse of 248 nm light. There are positive peaks at ca. 205, 236, 284, and 380 nm and negative absorptions at 210 and 260 nm. The latter result from depletion of the parent, which absorbs at these wavelengths. The species produced is quite long lived: there is essentially no decay within 74 μ s. O₂ does not decrease the lifetime of the transient, an observation that is in agreement with the nitrile ylide nature of the species.

Similar experiments were performed with the other 2*H*-azirines, for which similar observations were made. The spectroscopic data of the transients observed are collected in Table 1.

To obtain further information on the details of the photochemical reaction leading to the formation of the ylides (eq 1), the yields of the ylides were measured as a function of the laser power by attenuating the laser light by placing neutral density filters between the laser and the cell. In all cases the yield turned out to be proportional to the laser power (in the range 0–10 mJ),¹² which indicates that the photochemical conversion of the

(10) (a) Huisgen, R. In *1,3-Dipolar Cycloaddition Chemistry*; Padwa, A., Ed.; Wiley: New York, 1984; Vol. 1, pp 1–176. (b) Padwa, A.; Rosenthal, R. J.; Dent, W.; Filho, P.; Turro, N. J.; Hrovat, D. A.; Gould, I. R. *J. Org. Chem.* **1984**, *49*, 3174–3180. (c) Naito, I.; Ishida, A.; Yamamoto, K.; Takamura, S.; Isomura, K.; Taniguchi, H. *Chem. Lett.* **1989**, 1615–1618. (d) Naito, I.; Morihara, H.; Ishida, A.; Takamura, S.; Isomura, K.; Taniguchi, H. *Bull. Chem. Soc. Jpn.* **1991**, *64*, 2757–2761. (e) Albrecht, E. *Dissertation*; Westfälische Wilhelms-Universität Münster, 1995.

(11) Sieber, W.; Gilgen, P.; Chaloupka, S.; Hansen, H.-J.; Schmid, H. *Helv. Chim. Acta* **1973**, *56*, 687–696.

(12) At higher laser power saturation phenomena are observed.

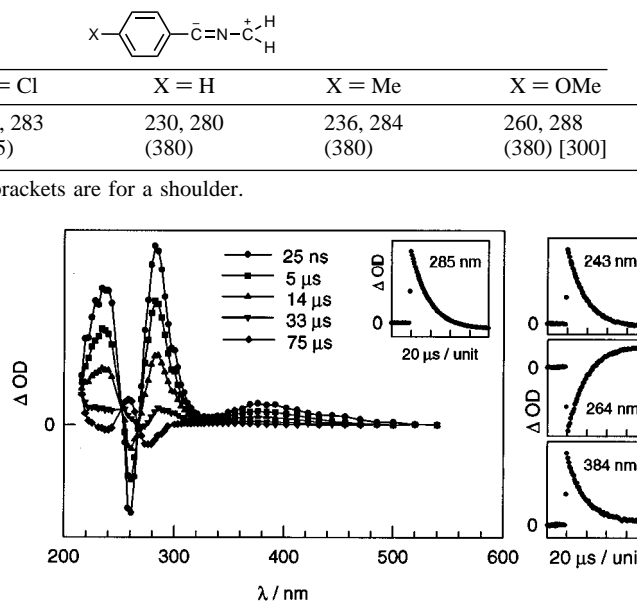
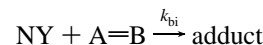


Figure 2. Absorption spectra of transients from the photolysis of 0.07 mM 3-(4-methylphenyl)-2*H*-azirine in deoxygenated acetonitrile containing 30.4 mM acrylonitrile, recorded at several times after the laser flash as indicated. The kinetic traces show that all bands belong to only one species (the nitrile ylide).

2*H*-azirine (eq 1) is monophotonic. In the absence of suitable scavengers, nitrile ylides have lifetimes of more than 1 ms in aprotic solvents. Under these conditions, they eventually form dimeric products.^{4,5}



However, in the presence of dipolarophiles, the lifetime of the nitrile ylides is drastically shortened due to their trapping via a [3 + 2] cycloaddition reaction, as known from product analysis studies.¹³



This is shown for the case of 3-(4-methylphenyl)nitrile ylide in the presence of acrylonitrile (Figure 2).

In the presence of excess dipolarophile, the decay of the nitrile ylides is by first-order kinetics. From the slopes of the linear dependencies of k_{obs} for the decay of nitrile ylide on [dipolarophile] the bimolecular rate constants for these reactions were determined. The results obtained for the reaction of different nitrile ylides with different dipolarophiles are presented in Table 2.

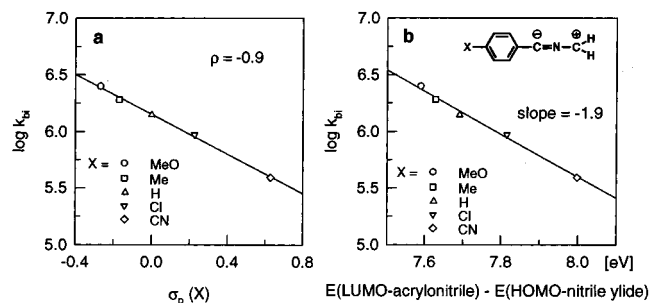
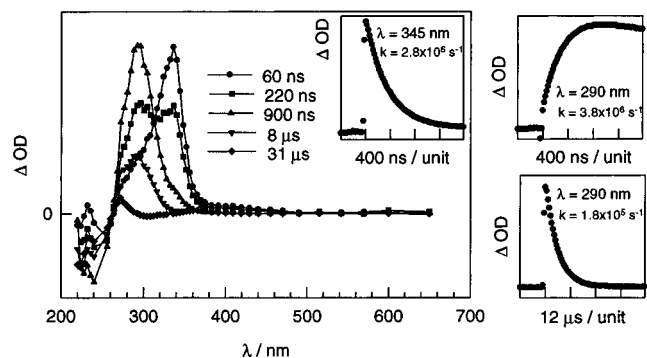
It is evident that the reaction rate constants increase with decreasing electron density of the olefinic compound and with increasing electron density of the nitrile ylide.^{5,9b} In Figure 3a is shown a Hammett plot of the data from Table 2 for the reaction of 4-X-C₆H₄-C⁽⁻⁾=N-CH₂⁽⁺⁾ with acrylonitrile, where the Hammett ρ value turns out to be -0.9. From the decrease of reactivity with decreasing electron density of the aromatic it may be concluded that the reactivity loss in this direction is due to stabilization of the nitrile ylides. This conclusion is supported by AM1 calculations.¹⁴ On this basis, a negative inductive effect of the substituent at the phenyl group

(13) (a) Padwa, A.; Smolanoff, J. *J. Am. Chem. Soc.* **1971**, *93*, 548–550. (b) Giezendanner, H.; Märky, M.; Jackson, B.; Hansen, H.-J.; Schmid, H. *Helv. Chim. Acta* **1972**, *55*, 745–748.

(14) The AM1 calculations were performed with the MOPAC program (version 6.00) (Quantum Chemistry Program Exchange (QCPE), Department of Chemistry, Indiana University, Bloomington, Indiana, 47405).

Table 2. Bimolecular Rate Constants k_{bi} for the Addition of Acrylonitrile, Dimethyl Acetylenedicarboxylate, and Tetracyanoethylene to Nitrile Ylides in Acetonitrile at $21 \pm 2^\circ\text{C}$

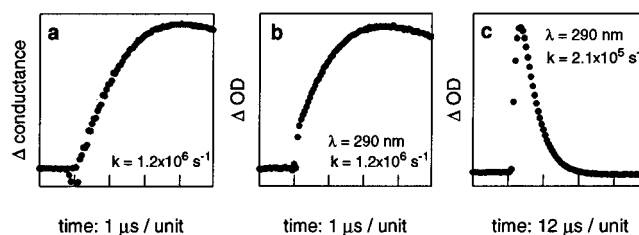
	$k_{bi} [\text{M}^{-1} \text{s}^{-1}]$					
	$\text{Ph}-\bar{\text{C}}=\text{N}-\overset{+}{\text{C}}(\text{H})-\text{Ph}$	X = CN	X = Cl	X = H	X = Me	X = OMe
$\text{H}_2\text{C}=\text{CHCN}$	8.9×10^5	3.9×10^5	9.4×10^5	1.4×10^6	1.9×10^6	2.5×10^6
$\text{MeO}_2\text{CC}\equiv\text{CCO}_2\text{Me}$	1.2×10^7		1×10^7	1.7×10^7		
$(\text{CN})_2\text{C}=\text{C}(\text{CN})_2$	4×10^9		5×10^9	6×10^9	7×10^9	
$\sigma_p(\text{X})$		0.628	0.226	0.00	-0.170	-0.268

**Figure 3.** Dependence of the logarithm of the reaction rate constants of the [3 + 2] cycloaddition of 4-substituted nitrile ylides [4-X-C₆H₄-C(=N-CH₂⁺)] with acrylonitrile on the Hammett constants (X) (a), and on the calculated energy differences of the frontier orbitals (b).**Figure 4.** Absorption spectra of transients observed on photolysis of 0.06 mM 2,3-diphenyl-2H-azirine in a deoxygenated mixture of 2-propanol/water 4:6 (v/v), recorded at several times after the laser flash as indicated. Insets: Decay kinetics at 345 nm (nitrile ylide) and formation and decay at 290 nm (new species).

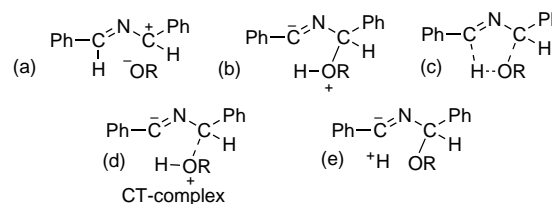
increases the energy difference between the frontier orbitals, $E_{\text{HOMO}}(\text{nitrile ylide})$ and $E_{\text{LUMO}}(\text{acrylonitrile})$. It is interesting that the relation between $\log k_{bi}$ and the energy difference is a linear one (Figure 3b), as with the Hammett relation.¹⁵

2. Azaallenium Cations. In aprotic solvents and in the absence of scavengers, the nitrile ylides generated by a laser flash slowly disappear by formation of dimers, as mentioned above. However, in protic solvents, the nitrile ylides decay with an increased rate and with the simultaneous development of new absorptions. An example for this is given in Figure 4, which contains the time-resolved absorption spectra of 1,3-diphenylnitrile ylide in a mixture of water and 2-propanol.

On the basis of the existence of an isosbestic point and on the equivalence of the nitrile ylide's decay rate with the formation rate of the new species (Figure 4, insets), the new transient is the direct successor of the nitrile ylide from its reaction with the protic solvent. In principle,⁹ the new intermediate can be explained in terms of (a) a cationic species (a protonated nitrile ylide), (b) a zwitterionic addition product,

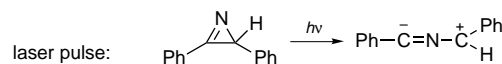
**Figure 5.** Digitizer traces (conductance (a) and optical density at 290 nm (new species) (b and c)) on photolysis of 0.06 mM 2,3-diphenyl-2H-azirine in a mixture of 2-propanol/water, 4:6 (v/v), argon, at pH 10.9 and $T = 21 \pm 2^\circ\text{C}$.

generated by nucleophilic attack of the solvent to the nitrile ylide, or (c) a species which is formed in a concerted addition reaction. Also, the formation of a charge transfer complex (d) or an anionic species (e) is conceivable.



To distinguish between these possibilities, time-resolved experiments with *conductance* detection were performed. It was found that on pulsing a solution of an azirine in, e.g., 2-propanol/water 4:6 (v/v), in the presence of base (OH^-), there was a conductance *increase* (Figure 5a), whereas in acidic solution there was—with the same rate—a conductance *decrease* (not shown). The rate of the conductance increase (Figure 5a) was the same as the rate of the optical density increase at 290 nm, where the new species absorbs (Figure 5b).

The light-induced conductance changes are interpreted as follows: The first step is the generation (within 20 ns) of the zwitterionic nitrile ylide, with *no* change of the conductance (see Figure 5a).



The next step is the reaction of the ylide with ROH (R = H, alkyl) by proton transfer to the ylide, which results in the production of an azaallenium ion and RO^- (Scheme 3, step A). Due to the high mobility of OH^- in solutions containing H_2O , there is a pronounced increase in the conductance as a result of the formation of this ion.¹⁶ In acidic solution, the OH^- produced in Scheme 3, step A, is neutralized by the excess H^+ present, i.e. after reaction 3A is complete and the OH^- neutralized, the

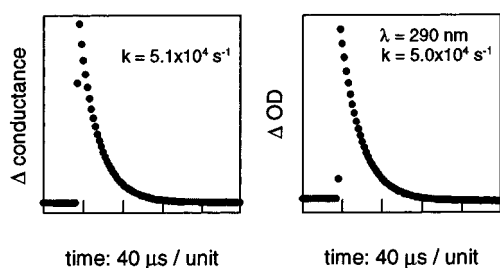
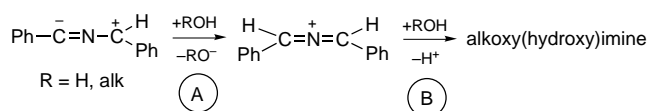
(16) The main part of the increase of the conductance is due to the formation of additional hydroxide rather than to the less mobile large organic cation. This excludes a reaction leading to an anionic intermediate (e), since in this case the formation of H^+ would neutralize the basic solution resulting in a decrease of conductivity.

(15) For a review on orbital energy control of cycloaddition reactivity see: Sustmann, R. *Pure Appl. Chem.* **1974**, *40*, 569–593.

Table 3. Observed Reaction Rates k_{obs}/s^{-1} for the Decay of *p*-X-Aryl Substituted Nitrile Ylides (d-NY), for the Formation of *p*-X-Arylaazallenium Cations (f-CA), and for the Decay of the Cations (d-CA) in Different Protic Solvents at 21 ± 2 °C

substituent X	solvent	$k_{\text{obs}}(\text{d-NY})/s^{-1}$	$k_{\text{obs}}(\text{f-CA})/s^{-1}$	$k_{\text{obs}}(\text{d-CA})/s^{-1}$
OMe	H ₂ O ^a	$>5 \times 10^7$	$>5 \times 10^7$	5.2×10^5
OMe	MeOH	3.7×10^7	5.6×10^7	7.5×10^6
	MeOD	6.5×10^6	9.8×10^6	9.4×10^5
OMe	EtOH	6.5×10^5	1.1×10^6	1.7×10^5
OMe	2-PrOH	1.8×10^4	2.9×10^4	1.5×10^3
Me	H ₂ O ^a	$>5 \times 10^7$	$>5 \times 10^7$	1.1×10^6
Me	MeOH	8.8×10^6	1.7×10^7	1.2×10^6
Me	EtOH	2.2×10^5	3.1×10^5	2.7×10^4
Me	2-PrOH	7.9×10^3	1.1×10^4	1.0×10^3
H	H ₂ O ^a	$\cong 5 \times 10^7$	$\cong 5 \times 10^7$	1.6×10^6
H	MeOH	4.9×10^6	9.6×10^6	4.3×10^5
H	EtOH	1.0×10^5	1.5×10^5	8.8×10^3
H	2-PrOH	4.4×10^3	9.4×10^3	7×10^2
Cl	H ₂ O ^a	$\cong 2 \times 10^7$	$\cong 2 \times 10^7$	3.0×10^6
Cl	MeOH	2.2×10^6	2.3×10^6	1.2×10^5
	MeOD	3.5×10^5	5.3×10^5	2.4×10^4
Cl	EtOH	3.0×10^4	4.9×10^4	4.0×10^3
Cl	2-PrOH	9.2×10^2	2.1×10^3	2.4×10^2

^aThis solvent is water/acetonitrile 9:1 (v/v).

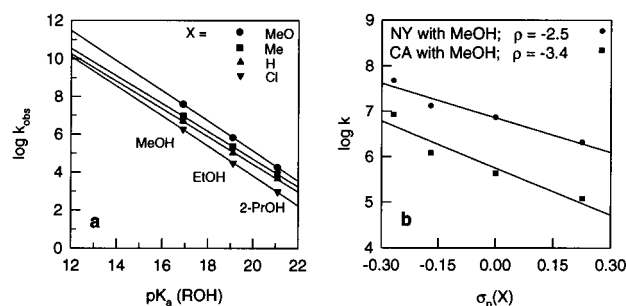
**Figure 6.** Decay of conductance and of optical density at 290 nm (cationic species) on photolysis of 0.065 mM 2,3-diphenyl-2*H*-azirine in a mixture of water/acetonitrile 9:1 (v/v), argon, at pH 9.8 and $T = 21 \pm 2$ °C.**Scheme 3**

H^+ concentration is *less* than it was before the pulse (before generation of the ylide), i.e., there is a conductance *decrease*. To summarize, the conductance results unambiguously show the formation of a positively charged organic species (a cation).

As is visible from Figure 5c, at longer times the azaallenium cation produced ($\lambda_{\text{max}} = 290$ nm) decays (with exponential kinetics). With the same rate, the conductance signal decays to zero, i.e., exactly to the same level as that before the pulse. This is shown for the case of 2,3-diphenyl-2*H*-azirine in water/acetonitrile (9:1) at pH 9.8, Figure 6. The conductance behavior is explained as follows: As a result of the reaction of the cation with water, protons are released, which are neutralized rapidly in the basic solution, leading to a decrease of the conductance ($k = 5.1 \times 10^4$ s⁻¹). This corresponds with the decay of the cation (absorbing at 290 nm, $k = 5.0 \times 10^4$ s⁻¹) by which a product is formed which does *not* absorb at 290 nm.

For a more thorough examination of the protonation step A, photolyses were performed with different azirines in different alcohols, including *O*-deuterated ones. In all cases the decay rates of the nitrile ylides were found to correspond to the formation rates of the cationic primary reaction products (the azaallenium cations).¹⁷ The reaction rates of the ylides with and in the alcohols are presented in Table 3, which also contains

(17) The fact that the agreement in the rates is not perfect (see Table 5) is due to the *formation* rates of the cations being distorted by the (large) rates of *decay* of the cations, $k_{\text{obs}}(\text{d-CA})$.

**Figure 7.** (a) Dependence of the rate of protonation on the $\text{p}K_{\text{a}}$ of the alcohol ROH. (b) Hammett plot of the rate of the reaction $4\text{-X-NY} + \text{MeOH}$ [average of the decay rate of the $4\text{-X-aryl-substituted NY (d-NY)}$ and of k_{obs} , the reaction of the cation (CA) with MeOH as a function of the Hammett constants $\rho(\text{X})$].**Table 4.** Extrapolated Decay Rates k/s^{-1} of the Nitrile Ylides in Water ($\text{p}K_{\text{a}} = 15.75$) and in Trifluoroethanol ($\text{p}K_{\text{a}} = 12.5$)

solvent	$k(\text{d-NY})/s^{-1}$			
	X = MeO	X = Me	X = H	X = Cl
H ₂ O	3.1×10^8	7.8×10^7	3.2×10^7	1.4×10^7
TFE	1.2×10^{11}	1.5×10^{10}	7.7×10^9	5.3×10^9

data on the decay rates of the resulting azaallenium cations in the alcohols.

From Table 3 it is evident that the protonation rates of the nitrile ylides depend on the acidity of the alcohol and on the substituent at the nitrile ylide. Concerning the effect of the alcohol, the decay rates of the nitrile ylides correlate with the $\text{p}K_{\text{a}}$ of the protic solvents: There is a linear dependence of $\log k(\text{decay of NY} = \text{buildup of azaallenium cation})$ on the acidity of the alcohol (see Figure 7a).¹⁸ This diagram allows the estimation of decay rates of the nitrile ylides in water ($\text{p}K_{\text{a}} = 15.75$)¹⁹ and in trifluoroethanol ($\text{p}K_{\text{a}} = 12.5$)²⁰ (Table 4), where the corresponding lifetimes could not be measured because they were within the pulse length of the laser flash (20 ns), e.g., for X = MeO, the calculated lifetimes of the NY are 3 ns in H₂O and 8 ps in CF₃CH₂OH.

(18) A dependence of the decay rate of the nitrile ylide from 3-(biphenyl-4-yl)-2*H*-azirine on the acidity of the reaction medium has previously been found by Ishida et al. (ref 8d).

(19) Kosower, E. M. *An Introduction to Physical Organic Chemistry*; John Wiley & Sons: New York, 1986.

(20) Mukherjee, L. M.; Grunwald, E. *J. Phys. Chem.* **1958**, *62*, 1311–1314.

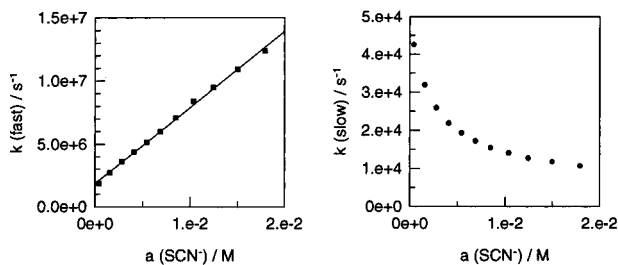
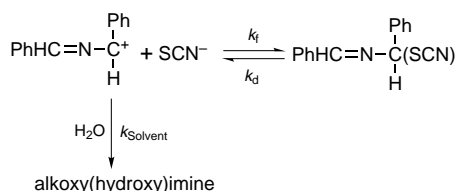


Figure 9. Observed reaction rates for the fast decay component (left) and for the slow decay component (right) as a function of the activity²⁸ of thiocyanate, $a(\text{SCN}^-)$.

Scheme 4



formation of the addition product, k_f , and of the rate of the decomposition of this product, k_d .²⁹

$$k_{\text{obs(fast)}} = k_f[\text{SCN}^-] + k_d$$

The slow reaction represents the irreversible reaction of the cation in the equilibrating mixture with the solvent water. In the equilibrium an increase of the concentration of the anion results in a decrease in the concentration of the cation. Thus, by favoring the formation reaction, with increasing thiocyanate concentration the slow reaction of the cation with the solvent is delayed. Conditions as in Scheme 4 have previously been analyzed. On the basis of that²⁹ interpretation, the equilibrium constant of the fast reaction can be evaluated. A plot of k_{obs} for the fast reaction versus the concentration of thiocyanate is linear (Figure 9), providing the rate constants for formation and decomposition and also the equilibrium constant as their ratio $K = k_f/k_d = 324 \text{ M}^{-1}$.

A second method to evaluate the equilibrium constant involves the use of the equation²⁹

$$K = (\text{OD}_o - \text{OD}_{\text{int}})/(\text{OD}_{\text{int}} \times [\text{Nu}])$$

whereby OD_o and OD_{int} correspond to the magnitude of the absorption directly after the pulse and that of the intermediary plateau, respectively. The value obtained for K is 243 M^{-1} (as taken from Figure 10). This value agrees quite well with the equilibrium constant based upon the kinetic method ($K = 324 \text{ M}^{-1}$ (taken from Figure 9)).

It is reasonable to assume that the combination reaction is reversible also in the case of the halides Cl^- , Br^- , and I^- , this being the reason for the absence of a visible effect of halide on the lifetime of the cation (see above). This means that in this case the equilibrium is such that the ionic reactants are favored ($k_d > 10^6 \text{ s}^{-1}$).

Summary and Conclusions

It has been demonstrated that the nitrile ylides generated in the 248 nm photolysis of 2*H*-phenylazirines react with electron-

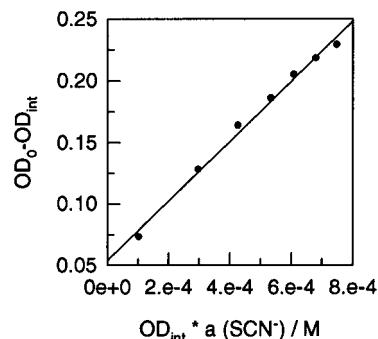


Figure 10. Determination of the equilibrium constant of the combination reaction of 1,3-diphenylazaallenium ion with thiocyanate based on ref 29.

deficient olefins with rate constants between 4×10^5 and $7 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$, depending on the olefin and on the substituent on the phenyl group, whereby the Hammett ρ value is -0.9 . The nitrile ylides are also scavenged by and in alcohols (rate constants from 10^3 to 10^7 s^{-1} , increasing with increasing acidity of the alcohol and with the electron density of the nitrile ylide as varied by a substituent (for the case of the reaction of NY with MeOH, Hammett $\rho = -2.5$)). In this reaction, which is characterized by a linear transition state $\text{O} \cdots \text{H} \cdots \text{C}^-$ for the ylide protonation as concluded from kinetic isotope effect studies, azaallenium cations are formed, as shown by time-resolved conductance measurements. The cations react with nucleophiles with rate constants between $3 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ for F^- and $1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ for the much more nucleophilic N_3^- . In the case of SCN^- , the reaction with the cations is reversible. The same is *probably* true for Cl^- , Br^- , and I^- .

Experimental Section

The syntheses of the azirines were performed in a manner analogous to the method of Hassner.³⁰ Solutions were prepared by using organic solvents of spectroscopic grade purity and water from a Millipore Milli-Q system.

The laser flash photolysis measurements were conducted with use of a computer-controlled apparatus. A Lambda Physik excimer laser provided pulses of 248 nm light (KrF^*) with a duration of 20 ns and a power ranging from 0 to 100 mJ/pulse. The relaxation of the nonequilibrium situation produced by the light pulse was followed with time-resolved optical or conductance detection (time resolution 1–2 ns).

Solutions were 50–100 μM in azirine and had OD/cm^{-1} ca. 1.0 at 248 nm. The optical and conductance signals from the photolysis were digitized by Tektronix 7612 and 7912 transient recorders interfaced with a DEC 11/73 computer, which was also used for on-line (pre)-analysis of the experimental data and for their storage and documentation.

Acknowledgment. E.A. is indebted to M. Toubartz (Mülheim) for her helpful assistance. Financial support for this work was provided by a doctoral fellowship of the “Graduiertenförderung des Landes NRW” and especially by the “Deutsche Forschungsgemeinschaft” and the “Fonds der Chemischen Industrie”.

JA971648N

(29) McClelland, R. A.; Banait, N.; Steenken, S. *J. Am. Chem. Soc.* **1986**, *108*, 7023–7027.

(30) (a) Fowler, F. W.; Hassner, A.; Levy, L. A. *J. Am. Chem. Soc.* **1967**, *89*, 2077–2082. (b) Hassner, A.; Fowler, F. W. *J. Am. Chem. Soc.* **1968**, *90*, 2869–2875.