Laser Flash Photolysis of 3-(Biphenyl-4-yl)-2*H*-azirine. Dynamic Protonation of a Nitrile Ylide

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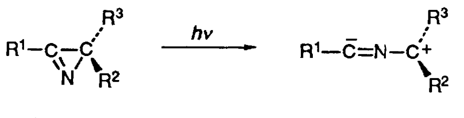
Laser flash photolysis of 3-(biphenyl-4-yl)-2*H*-azirine has been carried out in various alcohols. In each case the formation of a new band was detected, resulting from the decay of nitrile ylide (NY). The formation rate, which agreed completely with the decay rate, decreased with increasing pK_s of the alcohol. The new band was assigned to an azaallyl cation, formed by protonation of the terminal carbon atom of NY. The new band also decayed according to pseudo-first-order kinetics and its rate decreased with increasing pK_s.

Nitrile ylide (NY) is one of the most useful intermediates for the synthesis of heterocyclic compounds. This species is a 1,3-dipole and is easily produced by photoirradiation of 2*H*-azirine, as shown in reaction (1).[1,2] The structure of this species has attracted our interest because of its specific reactivity. The 1,3-dipolar addition, the most important reaction of NY, is not suited to studying the NY structure, since it proceeds concertedly and, moreover, with site- and regioselectivity.[3,4] The reaction of NY with alcohol gives adducts.[5,6] Although various kinds of mechanism may be operative, it seems clear that the reaction must proceed stepwise.



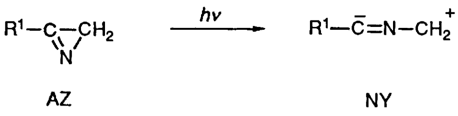
2*H*-Azirine Nitrile ylide, NY (1)

Recently, NY was measured directly in the triplet state of 2*H*-azirine during laser flash photolysis of 3-(biphenyl-4-yl)-2*H*-azirine (AZ; R^1 = biphenyl-4-yl, $R^2 = R^3$ = H).[7] NY is formed through the excited singlet state of AZ (λ_{max} *ca.* 410 nm; decay rate $8 \times 10\ s^{-1}$ in cyclohexane). To study NY, laser flash photolysis of AZ was carried out in various types of alcohol.

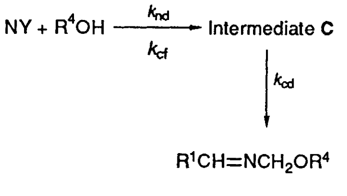
Results and Discussion

Laser flash photolysis (λ 308 nm) of AZ was carried out in ethanol in the presence of oxygen so as to measure the reaction of NY with alcohol. Fig. 1 shows the time-resolved absorption spectra monitored (*a*) and the typical decay traces (*b*). An initial transient species with λ_{max} at 410 nm, assigned to NY, decays according to pseudo-first-order kinetics with the simultaneous formation of a new band with λ_{max} at 340 nm. An isosbestic point was obtained at λ = 370 nm from 0.1 to *ca* 15 μs after the flash. The decay rate of NY and the formation rate of the new band were determined by using the decay traces monitored at λ = 460 nm (NY) and 330 nm (new band), as shown in Fig. 2. Since the decay rate of NY ($k_{nd} = 1.6 \times 10^5\ s^{-1}$: $8 \times 10\ s^{-1}$ in the absence of alcohol) is in complete agreement with the formation rate of the new band ($k_{cf} = 1.6 \times 10^5\ s^{-1}$), it can be stated that a new reaction intermediate (**C**) is formed quantitatively during the reaction of NY with alcohol. The new band also decays according to pseudo-first-order kinetics, as shown in Fig. 2(*c*) ($k_{cd} = 1.2 \times 10^4\ s^{-1}$).

Photoirradiation (λ = 313 nm) of AZ (R^1 = biphenyl-4-yl; $R^2 = R^3$ = H) in ethanol [reactions (2) and (3)] afforded an *E*/*Z* mixture of *N*-(biphenyl-4-ylmethylene)-1-ethoxymethylamine **D**.



AZ NY (2)



(3)

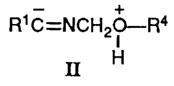
D

R^1 = biphenyl-4-yl, R^4 = Et

Two possible structures can be proposed for the intermediate **C**: either a cation formed by the protonation of NY (**I**), or a zwitterion-type intermediate formed by nucleophilic addition of NY to alcohol (**II**).

$R^1CH{=}NCH_2^+$

I



$$R^1\bar{C}{=}NCH_2\overset{+}{\underset{H}{O}}{-}R^4$$

II

R^1 = biphenyl-4-yl, R^4 = Et

If **C** is the intermediate **II**, NY should yield an intermediate of the same type (**III**) in tetrahydrofuran (THF), which is a more basic solvent. NY is, however, as stable in THF as in cyclohexane and λ_{max}(410 nm) does not shift. Therefore, the zwitterion-type intermediate **III** is not formed in THF.

If **C** is the intermediate **I**, it will be produced more rapidly in trifluoroethanol (TFE), which is an acidic and non-nucleophilic solvent, and will be scavenged by some anions. It was observed that **C** was produced most rapidly in TFE ($k_{nd} = 8.0 \times 10^6\ s^{-1}$). The laser flash photolysis of AZ in ethanol was carried out

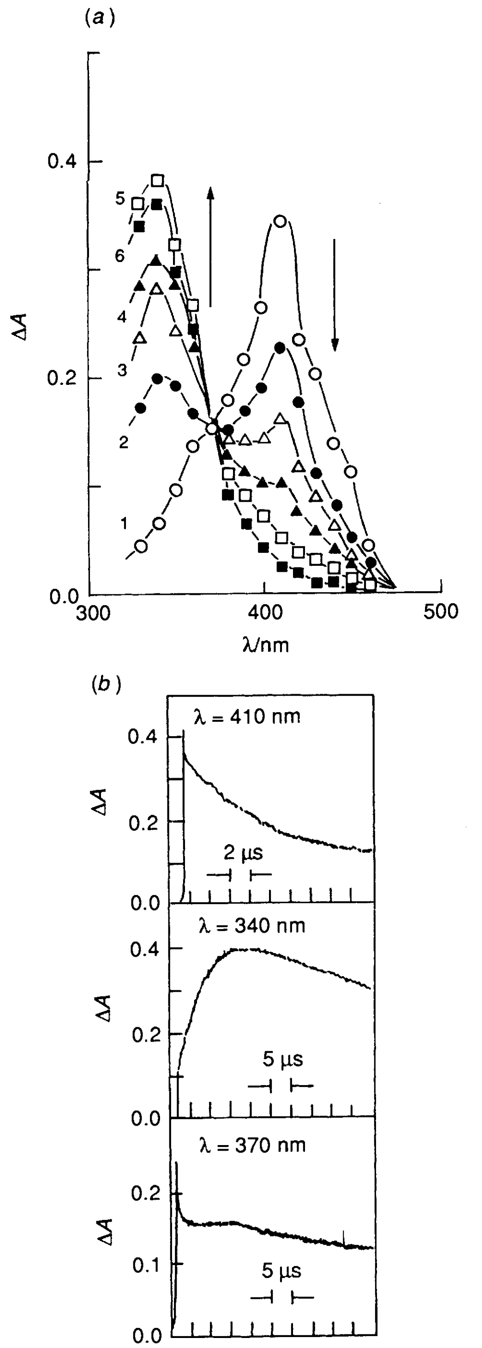
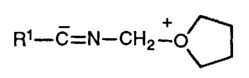


Fig. 1 (*a*) Time-resolved absorption spectra and (*b*) digitizer traces measured in the laser flash photolysis of AZ in ethanol. [AZ] = 1.0 × 10^{-3} mol dm^{-3}, monitored at 0 (1), 0.8 (2), 1.2 (3), 4 (4), 10 (5), and 30 μs (6) after the flash.



III; R^1 = biphenyl-4-yl

in the presence of KBr with 18-crown-6. The decay of **C** was accelerated depending on the amount of KBr present as shown in Fig. 3. Therefore, the decay must proceed through the reaction between the cation and the free anion. The reaction rate constant of **C** with Br anion was determined to be 7.7 × 10^5 dm^3 mol^{-1} s^{-1} from the slope of the linear plots in Fig. 3. The intermediate **C**, can then be assigned to the azaallyl cation **I** formed by the protonation of NY.

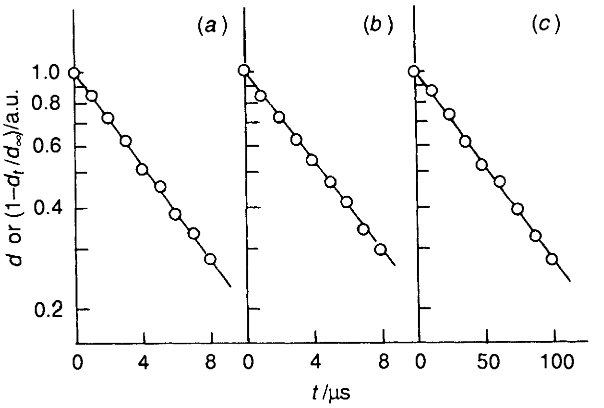


Fig. 2 First-order plots of the decay of NY (*a*), the formation of the new band (*b*), and the decay of the new band (*c*) monitored at λ = 460 nm (*a*), 330 nm (*b*), and 340 nm (*c*)

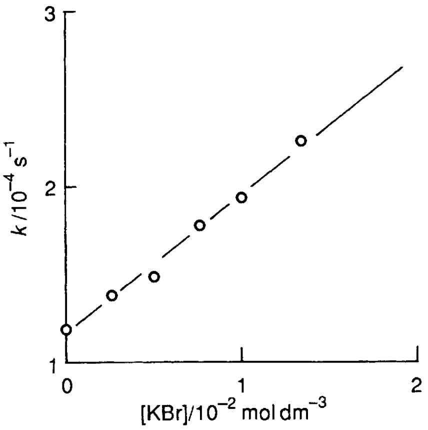


Fig. 3 Plots of the decay rate of the new band *vs.* [KBr]. The laser flash photolysis of AZ was carried out in ethanol in the presence of KBr and 18-crown-6 ([KBr]:[18-crown-6] = 2:3; [AZ] = 1.0 × 10^{-3} mol dm^{-3}).

Laser flash photolysis of AZ was carried out in various types of alcohol. In each case, except for *tert*-butyl alcohol, **C** forms and decays according to pseudo-first-order kinetics. Although the continuous irradiation of AZ in $\mathrm{Bu^tOH}$ gave a trace amount of the adduct, the decay rate of NY was not accelerated in $\mathrm{Bu^tOH}$. Even in the presence of water (1.6 mol dm^{-3} in THF), **C** was detected, as shown by the time-resolved absorption spectra in Fig. 4. The reaction rates (k_{nd}, k_{cf} and k_{cd}) are listed in Table 1. The rates are much larger in primary alcohols than in secondary alcohols. For the primary alcohols, the rates increase in the following order: Hexan-1-ol ~ Pentan-1-ol < Butan-1-ol < Pentan-1-ol < Ethanol < 2-Phenylethanol < Phenylmethanol < Methanol < TFE.

The logarithmic rates (log k_{nd} and log k_{cf}) were plotted *vs.* the negative logarithmic autoprotolysis constant (pK_s)* of alcohol, which is a function of acidity in neat alcohol, as shown in Fig. 5. The plots show a good linear relationship (slope = −0.7), which also supports the hypothesis that **C** is the cation formed by the protonation of NY. Moreover, pK_s can be estimated roughly by means of the linear relation in Fig. 5, as listed in Table 1.

Since **C** decays according to pseudo-first-order kinetics, even in TFE, the decay must proceed through the nucleophilic addition of **C** to the oxygen atom in alcohol. The decay rate of **C** (k_{cd}) also decreases with increasing pK_s. A good linear re-

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* The pK_s values for butan-1-ol and pentan-1-ol were reported to be 20.89 and 20.81, respectively.[9] However, it is very difficult to accept these values, because they are too large by comparison with the values for ethanol (19.1 [8]) and propan-1-ol (19.4 [8]), and are nearly equal to that for propan-2-ol (21.08 [8]).

Table 1 Rates determined in the reaction between NY and alcohol

Alcohol	pK_s	$k_{nd}{}^a/s^{-1}$	$k_{cf}{}^b/s^{-1}$	$k_{cd}{}^c/s^{-1}$
Methanol	16.91[d]	3.8×10^6	6.9×10^6	3.4×10^5
Ethanol	19.1[d]	1.6×10^5	1.6×10^5	1.2×10^4
Propan-1-ol	19.4[d]	8.2×10^4	1.1×10^4	1.6×10^4
Butan-1-ol	20.89[d]	7.7×10^4	8.0×10^4	5.6×10^3
Pentan-1-ol	20.81[d]	6.4×10^4	8.6×10^4	3.2×10^3
Hexan-1-ol	(19.4)[e]	7.4×10^4	8.2×10^4	2.9×10^3
TFE	(16.8)[e]	8.0×10^6	7.4×10^6	8.5×10^4
Phenylmethanol	(17.2)[e]	2.9×10^6	5.5×10^6	3.2×10^5
2-Phenylethanol	(18.4)[e]	4.0×10^5	5.4×10^5	2.6×10^4
Propan-2-ol	21.08[d]	4.0×10^3	7.5×10^3	1.5×10^3
Butan-2-ol	(21.2)[e]	2.0×10^3	4.6×10^3	4.1×10^2
tert-Butyl alcohol	26.8[d]	—	—	—
H_2O (1.4 mol dm^{-3}) in THF	—	1.4×10^5	9.4×10^4	1.2×10^2

[a] Decay rate of NY. [b] Formation rate of C. [c] Decay rate of C. [d] Ref. 8. [e] Estimated values calculated from the linear plots in Fig. 4.

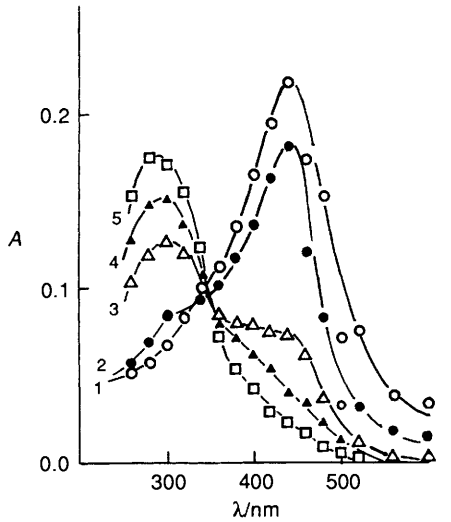


Fig. 4 Time-resolved absorption spectra measured in the laser flash photolysis of AZ in THF in the presence of H_2O. ([AZ] = 1.0×10^{-3} mol dm^{-3}, [H_2O] = 1.6 mol dm^{-3}).

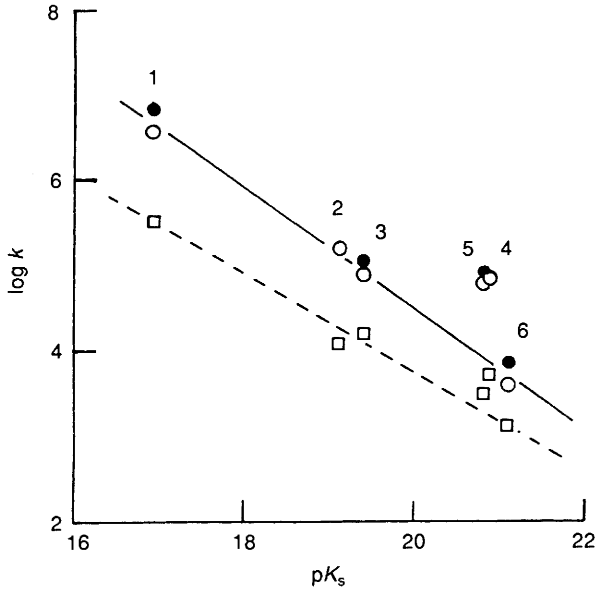
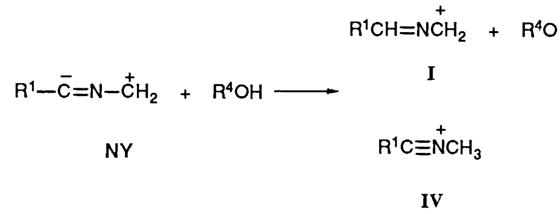
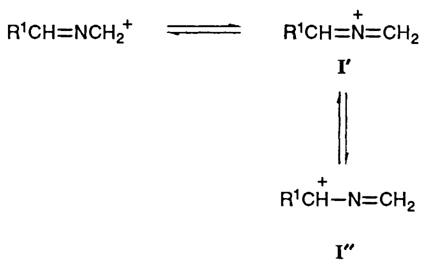


Fig. 5 Plots of the logarithmic decay rate of NY. Plots of log k_{nd}, log k_{cf}, and log k_{cd} *vs.* pK_s of the alcohol. ○: log k_{nd}, ●: log k_{cf}, □: log k_{cd}. 1, methanol; 2, ethanol; 3, propan-1-ol; 4, butan-1-ol; 5, pentan-1-ol; 6, propan-2-ol.

lationship is also obtained in the plots of log k_{cd} *vs.* pK_s (slope = −0.6). The rate, k_{cd}, must depend on the nucleophilicity of the oxygen atom in alcohol. The ratio of the rates (k_{nd}/k_{cd}) is roughly constant in the range 5–20 except for TFE (90). It seems certain that pK_s is closely related to basicity and to the nucleophilicity of the alcohol.

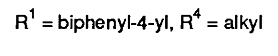
The reaction mechanism can be formulated as follows. If the reaction proceeds through the addition of NY to a dissociated proton, the reaction rate in methanol (k_{nd} = 3.8×10^6 s^{-1}) is too large for pK_s (= 16.91[8]). Therefore, the most likely conclusion is that NY abstracts a proton from alcohol, as shown in reaction (4). There are two carbon atoms which can be protonated: a terminal carbon atom, which would yield an alkynyl-type cation **IV**, and an internal carbon atom, which would yield the azaallyl cation, **I**. The latter seems to be more stable, since the cationic charge of the azaallyl cation is delocalized over the three dominant atoms, as shown in reaction (5).


(4)


(5)

R^1 = biphenyl-4-yl, R^4 = alkyl

The azaallyl cation would be expected to react with the alkoxy anion. It decays, however, according to pseudo-first-order kinetics, even in TFE, which is well known to be a non-nucleophilic solvent. The azaallyl cation then attacks the oxygen atom in the alcohol and gives **D**, as shown in reaction (6). Because of the linearity of the plots of log k_{cd} *vs.* pK_s, the nucleophilicity of the alcohol must be closely related to the pK_s.


$$\underset{\mathbf{I}}{R^1CH{=}N\overset{+}{C}H_2} + R^4OH \longrightarrow \underset{\mathbf{V}}{R^1CH{=}NCH_2OR^4} + H^+ \quad (6)$$

R^1 = biphenyl-4-yl, R^4 = alkyl

Experimental

Materials.—AZ was synthesized from 4-ethenylbiphenyl *via* 4-(1-azidoethenyl)biphenyl as reported by Hortmann *et al.*[10] The yield and physical properties are described earlier.[7]

Spectroscopic grade methanol, ethanol, propan-2-ol and THF were used without further purification. Other alcohols were dried on calcium hydride and distilled twice. Potassium bromide for IR spectroscopy was used without purification. 18-Crown-6 was used after distillation under reduced pressure.

Laser Flash Photolysis.—The laser flash photolysis of AZ in alcohol (1.0×10^{-3} mol dm^{-3}) was carried out in the presence of oxygen using a Lambda Physik EMG type excimer laser 501 with Xe and Cl_2 gases ($\lambda = 308$ nm, 15 ns pulse, *ca.* 0.1 J).

Continuous Irradiation.—Continuous irradiation of AZ (0.1301 g) was carried out in ethanol (0.5 dm^3) using a 300 W high pressure Hg lamp and a pyrex filter (thickness 2 mm) at room temperature for 3 h. After the irradiation, the products, a pale yellow oil, were distilled from which 0.1401 mg of *N*-(biphenyl-4-ylmethylene)-1-ethoxymethylamine **D** (*E*/*Z* = *ca.* 3, determined by NMR spectroscopy) was obtained (isolated yield 86.9%). Physical data for **D**: oil, b.p. 393–398 °C/2.7 Pa; $m/z = 293$; (C, 80.4%; H, 7.0%; N, 5.7%; Calc. for $C_{16}H_{17}NO$: C, 80.30%, 7.16%; N, 5.85%) δ_H($CDCl_3$, TMS) *E*-isomer: 1.29 (t, CH_3), 3.66 (q, CH_2CH_3), 5.11 (d, NCH_2O), 7–8 (m, biphenyl-4-yl), 8.45 (m, –CH=); *Z*-isomer: 1.34 (t, CH_3), 4.24 (q, CH_2CH_3), 5.11 (d, NCH_2O), 7–8 (m, biphenyl-4-yl), 8.63 (m, –CH=). ν_{max}/cm^{-1} 1672 (C≡N), 1648 (C≡N), 1450 (CH_3), 1386 (CH_3), 1102 (CH), 1008 (CH).

The continuous photoirradiation of AZ (0.1056 g) was carried out in *tert*-butyl alcohol at 313 °C. After irradiation, the products were studied by means of GC–MS. A trace amount of a compound (m/z = 267, 210, 194 and 180) was detected, presumably an adduct of NY and alcohol.

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