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Photolysis of open-chain 1,2-diazidoalkenes: generation of 2-azido-2*H*-azirines, formyl cyanide, and formyl isocyanide☆

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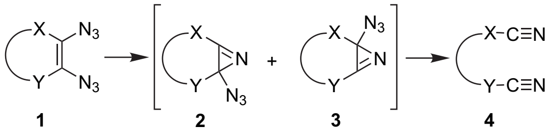
ABSTRACT

Solutions of several open-chain 1,2-diazidoethenes were photolyzed to yield 2-azido-2*H*-azirines, which were identified by NMR spectroscopy at low temperature. On prolonged irradiation or warm-up of the NMR solutions, these heterocycles lost a second molecule of nitrogen to be cleaved into two fragments of cyano compounds. In the case of (*Z*)-2,3-diazidocinnamaldehyde, the formation of formyl cyanide was detected by IR spectroscopy when the photolysis was performed in argon matrix. The latter substance was rearranged to formyl isocyanide on irradiation. This new species was characterized by comparison of its experimental and calculated (B3LYP/6-311+G**) IR spectrum.

1. Introduction

It is well known that cyclic 1,2-diazidoethenes of type **1** or 1,2-diazidobenzenes undergo thermal[2–9] and photochemical[2,3,10] degradations to form the corresponding dicyano derivatives **4** (Scheme 1). In order to rationalize this cleavage process, several intermediates were postulated.[5–8] By photolysis of 1,2-diazidobenzene in an inert matrix at low temperature, *ortho*-phenylene-bisnitrene was generated.[10] However, beyond the case of 1,2-diazidobenzenes, 2-azido-2*H*-azirines **2** and **3** are the most plausible intermediates for the transformation of **1** to yield **4**.[11] Nevertheless, direct proof of such intermediates had not yet been obtained. Most probably, **2** and **3** could not be observed spectroscopically due to their anti-Bredt structures.[12,13] It emerges that open-chain 1,2-diazidoethenes **5** may lead to spectroscopically observable 2-azido-2*H*-azirines (Table 1). Fortunately, the syntheses of the first representatives of compounds **5** were published recently.[14] In this paper, we report that the photolyses of such substances indeed furnish proof of intermediate 2-azido-2*H*-azirines **6** and **7** in the transformation of **5** into cyano compounds **8** and **9**.



Scheme 1.

2. Results and discussion

2.1. Photolysis of 1,2-diazidoethenes in solution

When solutions of the diazides (*E*)/(*Z*)-**5a**, (*E*)/(*Z*)-**5b**, or (*E*)/(*Z*)-**5c** in deuterated chloroform were irradiated at low temperature, ^{1}H NMR monitoring indicated the formation of the corresponding intermediates **6** and **7** with maximum total yields of 54–67% (Table 1). These heterocyclic compounds were easily assigned by comparing

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☆ See Ref. 1.

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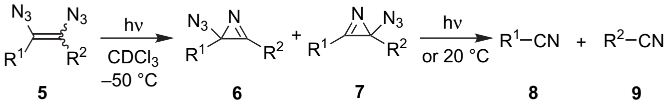
Table 1
Photolysis of open-chain 1,2-diazidoethenes **5**[a]



Starting material	R^1	R^2	Maximum yield of **6** (%)	Maximum yield of **7** (%)	Yield of **8** (%)	Yield of **9** (%)
(*E*)/(*Z*)-**5a**	$CH_2S(O)Ph$	H	28[b]	39[b]	>80	>80
(*E*)/(*Z*)-**5b**[c]	CH_2SO_2Ph	H	26	34	>99	>99
(*E*)/(*Z*)-**5c**	CH_2SO_2Ph	Me	28	26	>99	>99
(*Z*)-**5d**	Ph	CHO	0	43	37	0
(*Z*)-**5e**	4-Cl-C_6H_4	CHO	0	33	30	0

[a] Irradiation was conducted by using a high-pressure mercury lamp and monitored by NMR spectroscopy at −40 to −50 °C. All yields (%) were based on precursors **5** and calculated by utilizing an internal ^1H NMR standard.

[b] Mixture of two diastereomers.

[c] Using the single isomers of (*E*)-**5b** and (*Z*)-**5b** or performing the photolysis of (*E*)/(*Z*)-**5b** in CD_2Cl_2 at −80 °C gave nearly the same results.

their ^1H and ^{13}C NMR data with those of known 2*H*-azirines.[15] For example, the isomers **6c** and **7c** are unequivocally distinguishable because the ^1H NMR signals of alkyl groups in the 3-position of 2*H*-azirines are shifted downfield whereas the corresponding signals of alkyl groups in the 2-position resonate at relative high field.

On prolonged irradiation or warm-up of the NMR solutions to 20 °C, good to excellent yields of the nitriles **8a**, **8b** (=**8c**), **9a** (=**9b**), and **9c** were obtained.[16] Thermal cleavage of **6c** to give **8c** and **9c** was significantly slower than the analogous reaction of isomeric **7c**. This can be explained by the known[17] fact that 2*H*-azirines are stabilized by donor substituents in 3-position and destabilized by electron-withdrawing substituents in the same position. In the latter case, the electron deficiency at C-3 is increased, and thus the small-ring heterocycle should be more reactive and rich in energy when compared to the other 2*H*-azirines. While methyl is obviously a donor, the sulfonylmethyl group has to be classified most probably as a weak acceptor. This is in agreement with B3LYP/6-311+G** computations, which indicated that **6b** is lower in energy by 3.2 kcal/mol in comparison to **7b**. Experimental results supported these calculations because the NMR signals of **6c** but not those of **7c** were detected when a solution of (*E*)/(*Z*)-**5c** was stored at 20 °C.

In the case of the diazides (*Z*)-**5d** and (*Z*)-**5e**, the aldehyde group acts as a strong acceptor. Thus, B3LYP/6-311+G** computations show that **6d** is 13.9 kcal/mol higher in energy than **7d**. Therefore, after irradiation at low temperature, only **7d** and **7e** but not highly unstable **6d** or **6e** were identified by NMR spectroscopy. The distinction between **6d**,**e** and **7d**,**e** succeeded unequivocally with the help of the ^1H and ^{13}C NMR data of the formed heterocycles. The aromatic nitriles **8d** and **8e** were the only final products verified by the same method because formyl cyanide (**9d**=**9e**) cannot be characterized by NMR.[18] Therefore, the photolysis of (*Z*)-**5d** was investigated using matrix isolation techniques.

2.2. Photolysis of (*Z*)-2,3-diazidocinnamaldehyde in argon matrix

When (*Z*)-**5d** was irradiated in argon matrix at 366 nm, the precursor was consumed after 1 min and a 2-azido-2*H*-azirine was formed (Scheme 2). However, the new IR absorptions at 2134, 1727, 1456, 1296, 1260, 830, 764, and 680 cm^{-1} did not allow to distinguish between **6d** and **7d** or a mixture of both in the desired unambiguous manner (Fig. 1).

Further photolysis at 313 nm transformed the intermediate heterocycles **6d** and/or **7d** completely into benzonitrile (**8d**) and known[19] formyl cyanide (**9d**) within 10 min (Fig. 1). The latter species was identified by its IR absorptions at 2907, 2225, 1708, 1383, and 905 cm^{-1} (Table 2, negative bands in the difference spectrum shown in the center of Fig. 2).[20] This result demands that during low temperature irradiation of **5d** in solution besides

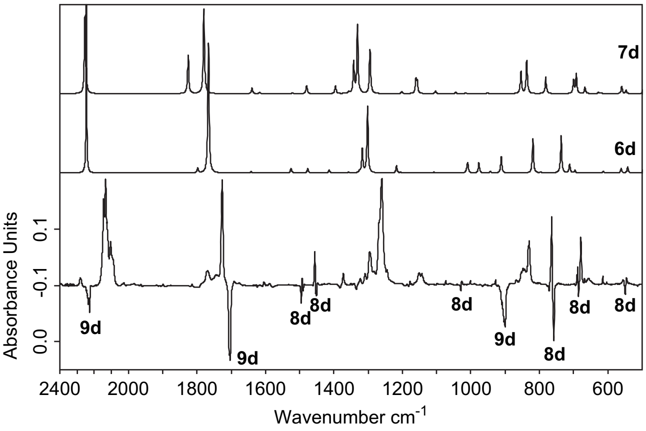


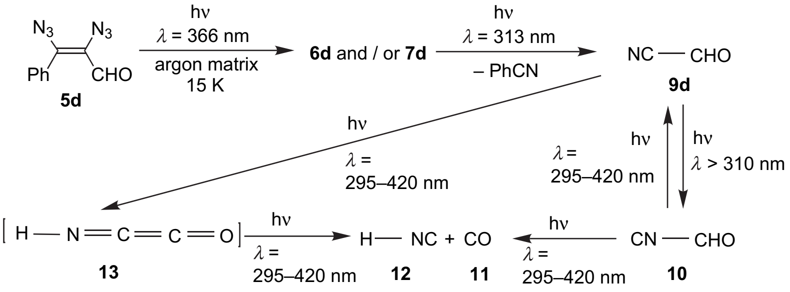
Figure 1. Top: calculated (B3LYP/6-311+G**) IR spectrum of azirine **7d**. Middle: calculated IR spectrum of azirine **6d**. Bottom: difference-FTIR spectrum from the photocleavage of azirines **6d** and/or **7d** (obtained by subtraction of the spectra after and before irradiation with 313 nm for 10 min, positive signals resulting mainly from the azirines).

Table 2
Computed (B3LYP/6-311+G**, harmonic approximation) and experimental (argon matrix, 10 K) IR absorptions of formyl cyanide **9d**

Sym.	Mode	Computation[a]	Experiment[b]
a′	CH str.	2986.4 (37.5)	2906.9 (vw)
a′	CN str.	2332.0 (30.6)	2225.2 (w)
a′	CO str.	1782.1 (170.6)	1708.4 (s)
a′	OCH def.	1406.3 (8.0)	1382.7 (vw)
a″	CH wag.	1002.3 (0.1)	—
a′	CC str.	919.6 (104.2)	904.9 (s)
a′	OCC def.	625.3 (1.0)	—
a″	NCC def.	301.1 (1.4)	—
a′	NCC def.	227.2 (14.3)	—

[a] Band positions in cm^{-1}, intensities ($km\ mol^{-1}$) in parentheses.

[b] Band positions in cm^{-1}, intensities (vw: very weak, w: weak, s: strong, vs: very strong) in parentheses.



Scheme 2.

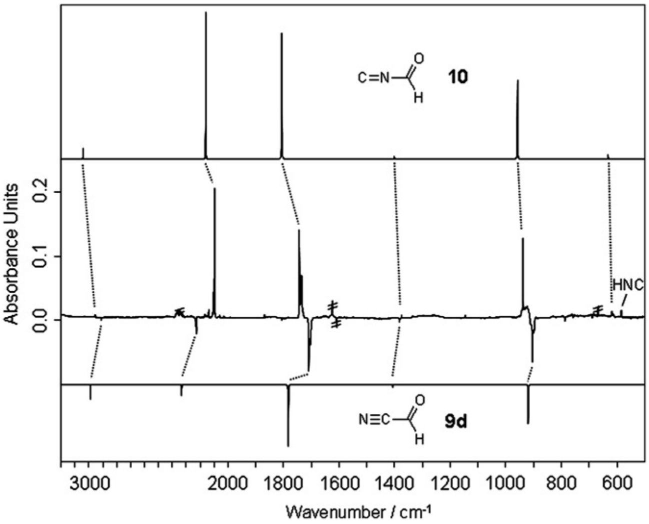


Figure 2. Top: computed (B3LYP/6-311+G**) IR spectrum of formyl isocyanide (**10**). Middle: difference-FTIR spectrum from the photoisomerization of formyl cyanide (**9d**) into formyl isocyanide (**10**) (obtained by subtraction of the spectra before and after irradiation with λ>310 nm for 19 h; crossed-out signals belong to matrix-isolated traces of atmospheric CO_2 and H_2O). Bottom: computed IR spectrum of formyl cyanide (**9d**).

benzonitrile (**8d**) also formyl cyanide (**9d**) must have been formed but escaped detection by secondary reactions.

Prolonged irradiation with λ>310 nm led to a mixture of **9d** and a new substance, which turned out to be unknown[21] formyl isocyanide (**10**). This assignment was based on IR absorptions at 2952, 2093, 1742, 1375, 938, and 619 cm^{-1} (Fig. 2, Table 3), which correlate very convincingly with those from B3LYP/6-311+G** computation. Relative energies of relevant minima and transition states on the C_2HNO energy hypersurface can be taken from the literature.[21]

The intensity of the signals of **9d** and **10** decreased and new absorptions at 3503, 2030, and 585 cm^{-1} resulting exclusively from hydrogen isocyanide (**12**)[22] and a band for carbon monoxide (**11**) appeared when photolysis was continued with λ=295–420 nm. Because no hydrogen cyanide (**9a**) was generated in this final step, formation of intermediate formyl and cyano radicals is unlikely. A possible option for the splitting of **10** into **11** and **12** may be a back reaction **10**→**9d**, followed by a 1,3-hydrogen shift **9d**→**13**, and decay of short-lived cumulene **13**[21] to yield **11** and **12**.

Table 3
Computed (B3LYP/6-311+G**, harmonic approximation) and experimental (argon matrix, 10 K) IR absorptions of formyl isocyanide **10**

Sym.	Mode	Computation[a]	Experiment[b]
a′	CH str.	3040.2 (29.7)	2951.9 (vw)
a′	NC str.	2156.9 (400.7)	2093.1 (vs)
a′	CO str.	1805.7 (321.1)	1742.4 (s)
a′	OCH def.	1400.6 (8.4)	1374.9 (vw)
a″	CH wag.	1020.1 (0.2)	—
a′	CN str.	958.6 (199.2)	937.9 (s)
a′	OCN def.	632.3 (11.5)	618.8 (w)
a″	NCN def.	202.2 (0.5)	—
a′	NCN def.	175.3 (4.3)	—

[a] Band positions in cm^{-1}, intensities (km mol^{-1}) in parentheses.

[b] Band positions in cm^{-1}, intensities (vw: very weak, w: weak, s: strong, vs: very strong) in parentheses.

3. Conclusion

In summary, we have demonstrated for the first time that 2-azido-2*H*-azirines are intermediates in the photochemical or thermal transformation of vicinal vinyl diazides to yield cyano compounds. In the case of formyl cyanide being one of the final products of this fragmentation, prolonged irradiation led to unknown formyl isocyanide, which was identified unequivocally by its IR spectrum measured in argon matrix.

4. Experimental

4.1. General

4.1.1. NMR studies and photolyses in solution

Caution should be exercised during handling of neat azides **5**, which may be explosive. ^{1}H NMR spectra were recorded at 300 MHz and ^{13}C NMR spectra at 75 MHz. Chemical shifts (δ) are reported in parts per million (ppm) downfield from TMS. Coupling constants (*J*) are given in hertz (Hz) and spin multiplicities are indicated by the following symbols: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet). The photolyses of the solutions of the azides **5** were performed with a 150-W Hg high-pressure lamp (polychromatic) TQ 150 from Heraeus GmbH. Quartz or glass equipment was used for cooling the lamp with the help of an ethanol cryostat (Lauda GmbH). Solutions of the substrates (60–80 mg/mL) in normal NMR sample tubes were cooled in the same way to −50 °C or to −80 °C while being irradiated. In order to get good yields of the 2*H*-azirines by preventing unwanted photochemical reactions, solutions in $CDCl_3$ or CD_2Cl_2, which perhaps function as UV filter, were utilized. In some cases, these solutions were flushed with argon in an ultrasonic bath prior to irradiation to exclude oxygen. Dioxane, silicone grease, or TMS was used as an internal standard to determine the yields based on ^{1}H NMR data. Monitoring the photolyses by ^{1}H NMR spectroscopy means that spectra were recorded at low temperature, e.g., −40 to −50 °C, after a definite time of irradiation. In most cases, the starting material **5** was consumed after an irradiation time of 10–20 min.

4.1.2. Photolyses in matrix

The cryostat used for the matrix isolation studies was an APD Cryogenics HC-2 closed-cycle refrigerator system fitted with KBr windows for IR measurements. IR spectra were recorded with a Bruker IFS 55 FTIR spectrometer (4500–300 cm^{-1}, resolution 0.7 cm^{-1}) and UV/vis spectra with an Agilent HP 8453 Diode-Array spectrometer. Matrix isolation of diazide **5d** was achieved by slowly subliming the substance from a glass tube at ca. 30 °C onto the 10 K cold matrix window and condensing a high excess of argon at the same time. For irradiations either a mercury low-pressure spiral lamp (Gräntzel) with an interference filter (254 nm) or a mercury high-pressure lamp (HBO 200, Osram) with a monochromator (Bausch & Lomb) was used.

4.2. 2-Azido-2-phenylsulfinylmethyl-2*H*-azirine (6a) (mixture of diastereomers)

^{1}H NMR ($CDCl_3$, −40 °C): δ=2.57 (d, ^2J=ca. 13.5 Hz, 1H, CH_2), 2.97 (d, ^2J=ca. 13.8 Hz, 1H, CH_2), 3.41 (d, ^2J=ca. 13.5 Hz, 2H, CH_2), 7.50–7.73 (m, 2×5H), 10.45 (s, 1H, H-3), 10.60 (s, 1H, H-3). ^{1}H NMR ($CDCl_3$, 19 °C): δ=2.62 (d, ^2J=13.5 Hz, 1H, CH_2), 2.99 (d, ^2J=13.8 Hz, 1H, CH_2), 3.43 (d, ^2J=13.5 Hz, 1H, CH_2), 3.45 (d, ^2J=13.8 Hz, 1H, CH_2), 7.50–7.73 (m, 2×5H), 10.38 (s, 1H, H-3), 10.50 (s, 1H, H-3). ^{13}C NMR ($CDCl_3$, −40 °C): δ=45.95 (s, C-2), 46.52 (s, C-2), 61.01 (t, CH_2), 63.78 (t, CH_2), 123.40 (d, 2C), 123.64 (d, 2C), 129.43 (d, 2C), 129.50 (d, 2C), 132.08 (d, C–*p*-Ph), 132.14 (d, C–*p*-Ph), 140.89 (s, C–*i*-Ph), 141.67 (s, C–*i*-Ph), 170.67 (d, C-3), 171.44 (d, C-3).

4.3. 2-Azido-3-phenylsulfinylmethyl-2*H*-azirine (7a) (mixture of diastereomers)

^{1}H NMR ($CDCl_3$, −40 °C): δ=3.61 (s, 1H, H-2), 3.75 (s, 1H, H-2), 4.23 (d, ^2J=14.7 Hz, 2H), 4.44 (d, ^2J=14.7 Hz, 2H), 7.50–7.73 (m, 2×5H). ^{1}H NMR (CDCl$_3$, 19 °C): δ=3.59 (s, 1H, H-2), 3.67 (s, 1H, H-2), 4.24 (d, ^{2}J=14.7 Hz, 1H, C*H*$_2$), 4.25 (d, ^{2}J=14.7 Hz, 1H, C*H*$_2$), 4.38 (d, ^{2}J=14.7 Hz, 1H, C*H*$_2$), 4.39 (d, ^{2}J=14.7 Hz, 1H, C*H*$_2$), 7.50–7.73 (m, 2×5H). ^{13}C NMR (CDCl$_3$, −40 °C): δ=46.24 (d, C-2), 46.56 (d, C-2), 52.45 (t, *C*H$_2$), 53.56 (t, *C*H$_2$), 123.67 (d, 2C), 123.74 (d, 2C), 129.43 (d, 2C), 129.50 (d, 2C), 131.61 (d, C–*p*-Ph), 131.70 (d, C–*p*-Ph), 140.38 (s, C–*i*-Ph), 140.68 (s, C–*i*-Ph), 168.87 (s, C-3), 169.07 (s, C-3).

4.4. 2-Azido-2-phenylsulfonylmethyl-2*H*-azirine (6b)

^{1}H NMR (CD$_2$Cl$_2$, −50 °C): δ=3.07 (d, ^{2}J=14.8 Hz, 1H, *H*$_2$C), 3.94 (d, ^{2}J=14.8 Hz, 1H, *H*$_2$C), 7.72 (m, 3H), 8.00 (m, 2H, H–*o*-Ph), 10.41 (s, 1H, H-3). ^{13}C NMR (CD$_2$Cl$_2$, −50 °C): δ=44.93 (s, C-2), 61.30 (t, H$_2$*C*), 127.64 (d, 2C), 129.24 (d, 2C), 134.38 (d, C–*p*-Ph), 137.25 (s, C–*i*-Ph), 168.56 (d, C-3).

4.5. 2-Azido-3-phenylsulfonylmethyl-2*H*-azirine (7b)

^{1}H NMR (CD$_2$Cl$_2$, −50 °C): δ=3.84 (s, 1H, H-2), 4.70 (s, 2H, *H*$_2$C), 7.72 (m, 3H), 8.00 (m, 2H, H–*o*-Ph). ^{13}C NMR (CD$_2$Cl$_2$, −50 °C): δ=46.23 (d, C-2), 53.36 (t, H$_2$*C*), 128.04 (d, 2C), 129.30 (d, 2C), 134.82 (d, C–*p*-Ph), 136.42 (s, C–*i*-Ph), 167.70 (s, C-3).

4.6. 2-Azido-3-methyl-2-phenylsulfonylmethyl-2*H*-azirine (6c)

^{1}H NMR (CDCl$_3$, −40 °C): δ=2.65 (s, 3H, Me), 2.92 (d, ^{2}J=14.7 Hz, 1H, *H*$_2$C), 3.97 (d, ^{2}J=14.7 Hz, 1H, *H*$_2$C), 7.60–7.80 (m, 3H), 7.91–8.03 (m, 2H, H–*o*-Ph). ^{13}C NMR (CDCl$_3$, −40 °C): δ=13.88 (q, Me), 47.88 (s, C-2), 62.65 (t, H$_2$*C*), 127.89 (d, 2C), 129.47 (d, 2C), 135.57 (d, C–*p*-Ph), 137.89 (s, C–*i*-Ph), 173.36 (s, C-3).

4.7. 2-Azido-2-methyl-3-phenylsulfonylmethyl-2*H*-azirine (7c)

^{1}H NMR (CDCl$_3$, −40 °C): δ=1.58 (s, 3H, Me), 4.69 (s, 2H, *H*$_2$C), 7.60–7.80 (m, 3H), 7.91–8.03 (m, 2H, H–*o*-Ph). ^{13}C NMR (CDCl$_3$, −40 °C): δ=20.20 (q, Me), 45.67 (s, C-2), 53.12 (t, H$_2$*C*), 128.17 (d, 2C), 129.56 (d, 2C), 135.06 (d, C–*p*-Ph), 136.63 (s, C–*i*-Ph), 173.50 (s, C-3).

4.8. 2-Azido-2-formyl-3-phenyl-2*H*-azirine (7d)

^{1}H NMR (CDCl$_3$, −50 °C): δ=7.60–7.70 (m, 2H), 7.73–7.82 (m, 1H), 7.89–7.97 (m, 2H), 8.88 (s, 1H, C*H*=O). ^{13}C NMR (CDCl$_3$, −50 °C): δ=59.19 (s, C-2), 120.14 (s, C-1′), 129.70 (d), 130.76 (d), 135.48 (d, C-4′), 161.89 (s, C-3), 193.88 (d, *C*H=O). The ^{13}C NMR data and especially the δ values of C-1′ and C-4′ indicate clearly that the phenyl group of **7d** is bound to C-3 of the 2*H*-azirine ring, see for comparison Ref. 23.

4.9. 2-Azido-3-(4-chlorophenyl)-2-formyl-2*H*-azirine (7e)

^{1}H NMR (CDCl$_3$, −50 °C): δ=7.63 (AA′BB′, 2H), 7.88 (AA′BB′, 2H), 8.88 (s, 1H, C*H*=O). ^{13}C NMR (CDCl$_3$, −50 °C): δ=59.25 (s, C-2), 118.71 (s, C-1′), 130.21 (d), 131.87 (d), 141.86 (s, C-4′), 161.21 (s, C-3), 193.65 (d, *C*H=O).

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References and notes

1. Part 23 of the series ‘Reactions of unsaturated azides’. For part 22, see Banert, K.; Wutke, J.; Rüffer, T.; Lang, H. *Synthesis*, in press.
2. Banert, K. *Angew. Chem.* **1987**, *99*, 932–934; *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 879–885.
3. Banert, K. *Chem. Ber.* **1989**, *122*, 123–128.
4. Pearce, D. S.; Lee, M.-S.; Moore, H. W. *J. Org. Chem.* **1974**, *39*, 1362–1368.
5. Pearce, D. S.; Locke, M. J.; Moore, H. W. *J. Am. Chem. Soc.* **1975**, *97*, 6181–6186.
6. VanAllan, J. A.; Priest, W. J.; Marshall, A. S.; Reynolds, G. A. *J. Org. Chem.* **1968**, *33*, 1100–1102.
7. Hall, J. H. *J. Am. Chem. Soc.* **1965**, *87*, 1147–1148.
8. Hall, J. H.; Patterson, E. *J. Am. Chem. Soc.* **1967**, *89*, 5856–5861.
9. Smolinsky, G.; Pryde, C. A. *J. Org. Chem.* **1968**, *33*, 2411–2416.
10. Nicolaides, A.; Nakayama, T.; Yamazaki, K.; Tomioka, H.; Koseki, S.; Stracener, L. L.; McMahon, R. J. *J. Am. Chem. Soc.* **1999**, *121*, 10563–10572.
11. Monocyclic 2-azido-2*H*-azirines were produced by another method, see: Gallagher, T. C.; Storr, R. C. *Tetrahedron Lett.* **1981**, *22*, 2905–2908.
12. For the ring strain in 2*H*-azirines, see: Würthwein, E.-U.; Hergenröther, T.; Quast, H. *Eur. J. Org. Chem.* **2002**, 1750–1755.
13. For other 2,3-bridged 2*H*-azirines, see: Banert, K.; Meier, B. *Angew. Chem., Int. Ed.* **2006**, *45*, 4015–4019; *Angew. Chem.* **2006**, *118*, 4120–4123.
14. Fotsing, J. R.; Hagedorn, M.; Banert, K. *Tetrahedron* **2005**, *61*, 8904–8909.
15. Review: Nair, V. *The Chemistry of Heterocyclic Compounds, Small-Ring Heterocycles*; Hassner, A., Ed.; Wiley: New York, NY, 1983; Vol. 42, Part 1, pp 215–332.
16. All nitriles **8** and **9** are commercially available or known in literature in the case of **9a**: Kanemasa, S.; Matsuda, H.; Kamimura, A.; Kakinami, T. *Tetrahedron* **2000**, *56*, 1057–1064.
17. Review: Gilchrist, T. L. *Aldrichimica Acta* **2001**, *34*, 51–55.
18. For unsuccessful attempts even at very low temperature, see: Vallée, Y.; Ripoll, J.-L.; Lacombe, S.; Pfister-Guillouzo, G. *J. Chem. Res., Miniprint* **1990**, 401–412.
19. (a) Judge, R. H.; Moule, D. C.; Biernacki, A.; Benkel, M.; Ross, J. M.; Rustenburg, J. *J. Mol. Spectrosc.* **1986**, *116*, 364–370; (b) Clouthier, D. J.; Moule, D. C. *J. Am. Chem. Soc.* **1987**, *109*, 6259–6261; (c) Bogey, M.; Destombes, J. L.; Vallée, Y.; Ripoll, J. L. *Chem. Phys. Lett.* **1988**, *146*, 227–229; (d) Karolczak, J.; Clouthier, D. J.; Judge, R. H.; Moule, D. C. *J. Mol. Spectrosc.* **1991**, *147*, 61–70; (e) Clouthier, D. J.; Karolczak, J.; Rae, J.; Chan, W.-T.; Goddard, J. D.; Judge, R. H. *J. Chem. Phys.* **1992**, *97*, 1638–1648; (f) Lewis-Bevan, W.; Gaston, R. D.; Tyrrell, J.; Stork, W. D.; Salmon, G. L. *J. Am. Chem. Soc.* **1992**, *114*, 1933–1938; (g) Bogey, M.; Demuynck, C.; Destombes, J. L.; Vallée, Y.; Ripoll, J. L. *J. Mol. Spectrosc.* **1995**, *172*, 344–351; (h) Born, M.; Ingemann, S.; Nibbering, N. M. M. *J. Phys. Chem.* **1996**, *100*, 17662–17669; (i) Tyndall, G. S.; Orlando, J. J.; Wallington, T. J.; Hurley, M. D. *J. Phys. Chem. A* **2001**, *105*, 5380–5384; (j) Ding, W.-J.; Fang, W.-H.; Liu, R.-Z. *Chem. Phys. Lett.* **2003**, *369*, 570–578.
20. Vallée, Y.; Ripoll, J.-L.; Lacombe, S.; Pfister-Guillouzo, G. *J. Chem. Res., Synop.* **1990**, 40–41.
21. Formyl isocyanide (**10**) was discussed in theoretical studies as an intermediate of the dissociation of **9d** and in other processes: (a) Chang, N.-y.; Yu, C.-h. *Chem. Phys. Lett.* **1995**, *242*, 232–237; (b) Sengupta, D.; Peeters, J.; Tho Nguyen, M. *Chem. Phys. Lett.* **1998**, *283*, 91–96.
22. Milligan, D. E.; Jacox, M. E. *J. Chem. Phys.* **1963**, *39*, 712–715.
23. Isomura, K.; Taniguchi, H.; Mishima, M.; Fujio, M.; Tsuno, Y. *Org. Magn. Reson.* **1977**, *9*, 559–562.