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Carbenes in Constrained Systems. 2. First Carbene Reactions within Zeolites—Solid State Photolysis of Adamantane-2-spiro-3′-diazirine[§]

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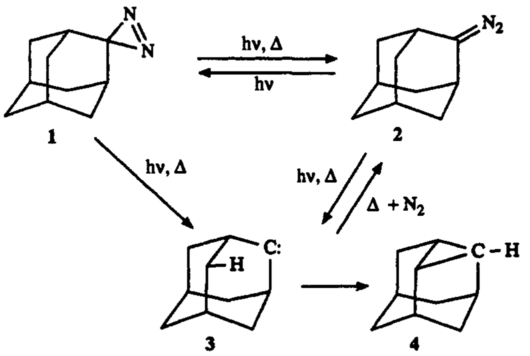
Abstract: Inclusion complexes of adamantane-2-spiro-3′-diazirine (**1**) in different X- and Y-type zeolites (faujasite) have been prepared. These complexes were analyzed by FT-IR and ^{13}C CP-MAS NMR spectroscopy. The guest–host complexes were irradiated with UV light in the solid state and the reaction products separated from the host and analyzed. Product ratios obtained in zeolites are totally different from those obtained by irradiation of **1** in solution or as a pure compound. In zeolites the main products isolated are 2,4-dehydroadamantane (**4**) and 2-adamantanol (**6**). In addition, adamantanone (**5**) and adamantane are formed. While 2-adamantanol (**6**) is thought to be a product from an acid-catalyzed reaction, the strained 2,4-dehydroadamantane (**4**) derives from an intramolecular 1,3 C–H insertion of adamantanylidene (**3**). In stark contrast to reactions in solution, in zeolites the formation of adamantanone azine (**7**) resulting from an *inter*molecular reaction is only of minor significance.

Introduction

The chemistry of carbenes or the corresponding carbenoids in different media has been studied extensively over the past decades.[1] However, nearly nothing is known about the reactive behavior of carbenes inside a guest molecule.[2] Komiyama and Hirai proposed a reaction of dichlorocarbene within α- and β-cyclodextrin-containing phenolate.[2a,b] On treatment of a ternary complex of phenol, cyclodextrin, and chloroform with aqueous sodium hydroxide solution, *o*- and *p*-hydroxybenzaldehyde were formed (ratio, 18:82 up to 0:100). In contrast, when no cyclodextrin was present a 59:41 ratio was observed. The preferential or exclusive formation of *p*-hydroxybenzaldehyde was explained by attack of dichlorocarbene at the para position of phenolate at the smaller rim of the cyclodextrins. For spatial reasons, this site is favored over attack at the ortho position.[2a,b] Abelt and Pleier[2c] used a diazirine precursor which was photolyzed or thermolyzed in the presence of β-cyclodextrin. It was, however, not established whether a true inclusion complex had been formed. In addition, the products from this reaction can also be explained without evoking carbenes as intermediates.

In general, upon photolysis, diazirines can isomerize to linear diazo compounds and both of them can split off nitrogen to generate the corresponding carbenes.[3] For diazirine **1** the rearrangement to the linear diazo compound **2** was proposed.[4b,d] An equilibrium between **1** and **2** is assumed; however, this could not be proved yet experimentally (Scheme 1). Recently, we reported[5] on the photolysis of adamantane-2-spiro-3′-diazirine (**1**)[4] within the β-cyclodextrin cavity.[5] In this case, the formation of 2,4-dehydroadamantane (**4**) which is the result of an intramolecular 1,3 C–H insertion of adamantanylidene (**3**) increased from ≤1% (for photolysis of **1** in hydrocarbon solution,[5,6] as a pure compound or as a physical mixture with β-cyclodextrin[5]) to ca. 30% within β-cyclodextrin.[5] The reactivity of adamantylidene (**3**) had been altered dramatically by its inclusion into β-cyclodextrin. However, adamantanone azine (**7**), which is formed in an intermolecular reaction, still dominates the photolysis reaction of **1** (ca. 60% total). It was anticipated that with zeolites[7] as host molecules the motion of the guest molecule should be even more restricted than with cyclodextrins and therefore intramolecular reactions should be strongly favored over intermolecular pathways.

Scheme 1



[§] Carbene Rearrangements. 43 (Carbene Rearrangements in Constrained Systems. 2. Part 1[5]). Part 42: Miebach, T.; Wüster, H.; Brinker, U. H. *J. Org. Chem.* **1993**, *58*, 6520.

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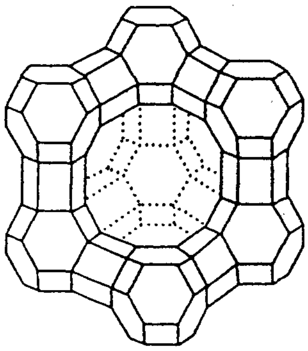

Figure 1. Structure of zeolites X and Y (faujasite).

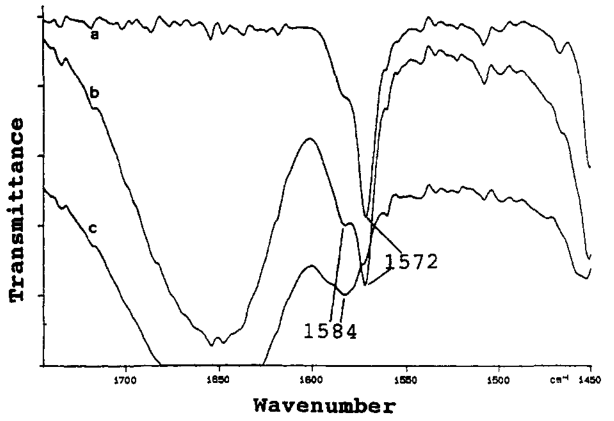

Figure 2. FT-IR spectra (KBr) of (a) diazirine **1**, (b) the physical mixture of **1** and the **1**/NaX complex, and (c) **1** @ zeolite (NaX).

Zeolites are microporous solids with open networks consisting of channels and cages which serve as molecular sieves[7c] or catalysts.[7d] When compared with the case of cyclodextrins, the extensive three-dimensional framework of zeolites and their ability to restrict diffusion should make it more difficult for the entrapped diazirine **1**@zeolite, the diazocompound **2**@zeolite, and/or the carbene **3**@zeolite to undergo intermolecular reactions (e.g. formation of an azine). Zeolites also show Brønsted and/or Lewis acidity which could lead to different reaction pathways of the entrapped carbene precursor compounds.

In this paper, we report our findings from the photolysis of adamantane-2-spiro-3′-diazirine (**1**) in X- and Y-type zeolites. Both zeolites have the same crystalline form (faujasite) but differ in the Si/Al ratio (Figure 1). They comprise supercages with a diameter of about 13 Å, and each supercage is connected tetrahedrally to four other supercages via windows with a diameter of about 7 Å. The cations can be easily exchanged in order to alter the space inside the cages or channels as well as the acidity. Reactions with zeolites as acidic[8] or electron-transfer catalysts[9] have been extensively studied. In addition, the photochemistry of ketones and their Norrish-type reactions involving diradicals as reactive species have already been described in the literature.[10] In 1982 it was claimed that, in methanol reactions over HZSM-5 zeolites, "carbene-like C_1 intermediates" were involved.[11a] This, however, was refuted later.[11b] Therefore, a carbene intermediacy within a zeolite has yet to be established.

Results

The inclusion complexes which were prepared contained about 8–13% of **1** by mass. FT-IR spectroscopy and solid-state ^{13}C CP/MAS NMR spectroscopy of the NaX complex revealed that an inclusion complex had been formed as opposed to mere surface adsorption. The FT-IR spectrum clearly shows a shift of the N=N stretching vibration from 1572 cm^{-2} for pure **1** (in KBr) to 1584 cm^{-1} for **1**@zeolite (in KBr), as illustrated in Figure 2. A mixture of diazirine **1** and the diazirine **1**@zeolite (NaX) complex shows clearly *both* bands.

Figure 3 consists of solid-state ^{13}C CP/MAS NMR spectra[12] of the complex (155 mg of **1** in 1.2 g of NaX zeolite) before photolysis and of the physical mixture of diazirine **1** and NaX zeolite. Approximately 125 000 scans were required to produce a reasonable signal to noise ratio. A broad almost featureless spectrum was obtained for the complex. Maximum carbon-13 intensity was obtained using a contact time of 0.5 ms. Variation of the proton decoupling field strength from 50 to 95 kHz did not alter the appearance of the spectrum, eliminating the possibility of partial proton dipolar decoupling. Introduction of a 60-μs dipolar dephasing delay between the end of cross-polarization and the beginning of decoupling and acquisition[13] did not eliminate all of the ^{13}C signals, an indication that there is relatively weak dipolar coupling between carbons and protons.

When the zeolite and diazirine **1** were physically mixed, a significantly different spectrum resulted, as shown in Figure 3. After 125 000 scans, only three relatively narrow signals resulted (each having chemical shifts in the same range as those observed for **1**); no broad components were observed. Maximum carbon-13 intensity was observed after 6 ms of contact time, a 12-fold increase over that of the complex. T_{cp} was calculated from cross-polarization-transfer kinetic data taken over contact times ranging from 100 μs to 12 ms, as shown by Veeman *et al.*[14] and Zumbulyadis and O'Reilly.[15] Protons contributing to cross-polarization are approximately two times closer to the diazirine guest molecule than those in the physical mixture. Adamantane and its derivatives such as **1** are known to spin freely along their symmetry axis and hence exhibit "plastic crystallinity".[16] The molecular motions of free **1** should be greater than those of **1** as a guest molecule constrained in a zeolite cavity. Specific molecular motions and correlation times have not been measured. Changes in cross-polarization times can also reflect on significant changes in the solid-state dynamics. The guest molecule as a neat solid has such significant molecular motion that cross-polarization is very inefficient, and maximum cross-polarization enhancement was obtained only after 6 ms. Upon entrapment within a zeolite cavity, as in a complex, these motions become constrained, making cross-polarization more efficient and reducing the contact time (0.5 ms) needed to obtain a maximum enhancement. Therefore, the physical mixture and complex **1**@zeolite (NaX) differ substantially—evidence for the formation of a true inclusion complex. Though we have provided evidence only for the formation of **1** entrapped in NaX, we assume that all other

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[10] (a) Turro, N. J. *Pure Appl. Chem.* **1986**, *58*, 1219. (b) Ramamurthy, V.; Corbin, D. R.; Eaton, D. F. *J. Org. Chem.* **1990**, *55*, 5269.

[11] (a) Chang, C. D.; Chu, C. *J. Catal.* **1982**, *74*, 203. (b) van Hooff, J. H. C. *J. Catal.* **1983**, *79*, 242.

[12] Powdered samples (200–300 mg) were contained in a 7-mm sapphire rotor with Kel-F endcaps. A Doty Scientific two-channel magic-angle spinning probe was used; the spinning speed was 3.1 kHz. The proton and carbon 90° pulse was 5 μs (50 kHz) for preparation and cross polarization (CP); during dipolar decoupling (DD) the proton power was increased to 90 kHz. Fifty thousand scans were normally averaged using a relaxation delay of 1.2 s.

[13] Opella, S. J.; Frey, H. M. *J. Am. Chem. Soc.* **1979**, *101*, 5854.

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[16] Sherwood, J. N., Ed. *The Plastically Crystalline State*; Wiley: New York, 1979.

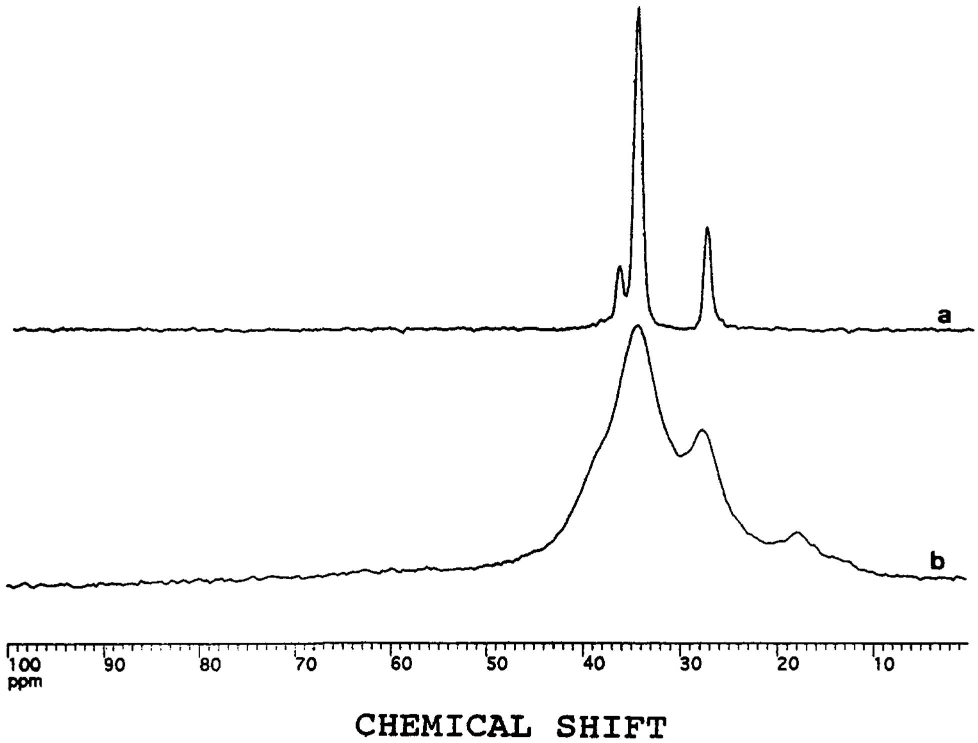
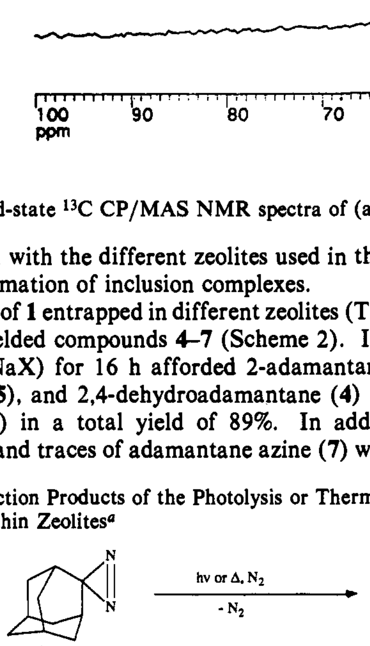


Figure 3. Solid-state ^{13}C CP/MAS NMR spectra of (a) diazirine **1** and (b) the diazirine **1** @ zeolite (NaX).

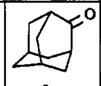
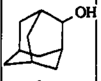
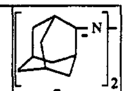
reactions of **1** with the different zeolites used in this study also led to the formation of inclusion complexes.

Photolyses of **1** entrapped in different zeolites (Table 1) in the solid state yielded compounds **4**–**7** (Scheme 2). Irradiation of **1**@zeolite (NaX) for 16 h afforded 2-adamantanol (**6**), adamantanone (**5**), and 2,4-dehydroadamantane (**4**) (see entry 9; ratio 80:11:7) in a total yield of 89%. In addition, 2% of adamantane and traces of adamantane azine (**7**) were detected.

Table 1. Reaction Products of the Photolysis or Thermolysis of Diazirine **1** within Zeolites[a]



1

ENTRY	ZEOLITE	 **4**	 **5**	 **6**		 **7**
1	HY hν	——	43 %	49 %	traces	7 %
2	LiY hν	——	9 %	91 %	traces	——
3	NaY hν	2 %	14 %	80 %	3 %	——
4	KY hν	4 %	32 %	64 %	——	——
5	MgY hν	traces	21 %	79 %	traces	——
6	CaY hν	——	35 %	54 %	traces	11 %
7	BaY hν	traces	9 %	91 %	traces	traces
8	LiX hν	7 %	12 %	81 %	——	——
9	NaX hν	7 %	11 %	80 %	2 %	traces
10	KX hν	7 %	30 %	51 %	traces	12 %
11	MgX hν	——	11 %	89 %	traces	——
12	CaX hν	——	14 %	86 %	——	——
13	BaX hν	——	17 %	83 %	traces	——
14	NaY Δ	——	60 %	——	40 %	——

[a] Activation of zeolite at 500 °C for 6 h.

In the solid-state ^{13}C CP/MAS spectrum of the reaction mixture, sharp features appeared, an indication that chemical shift dispersion has been reduced. A 60-μs dipolar dephasing delay removed all sharp features of the spectra, an indication that these signals represent carbons with large dipolar couplings to protons and which are perhaps more rigidly held in the complex.

On photolysis and thermolysis diazirines rearrange to linear diazo compounds (see Scheme 1). In contrast to diazirines, diazo compounds are relatively sensitive toward acidic conditions. The rearrangement of adamantane-2-spiro-3'-diazirine (**1**) to diazoadamantane (**2**) could be monitored by FT-IR spectroscopy in *n*-heptane solution and as well as in a KBr pellet (Figure 4). The transformation of the cyclic diazirine to the linear diazo compound **1** → **2** seems to be fast. After only a few seconds of photolysis (Hanovia, 450 W) at room temperature, a strong band indicative of the CN_2 vibration of the diazo compound **2** (2032.8 cm^{-1} in KBr or 2041.6 cm^{-1} in *n*-heptane) could already be seen.[17b] After ca. 90 min (in KBr) or 45 min (in *n*-heptane) the reaction was complete. The signals due to diazirine **1** and diazo compound **2** had vanished, concomitant with the emergence of a new band at 1647 cm^{-1} for the C=N stretching vibration of azine **7**.

Upon photolysis of diazirine **1**@zeolite (NaX) in KBr, however, no diazo compound **2**@zeolite (NaX) could be detected. This might be due to the instability of **2** under acidic conditions, like those prevailing in NaX zeolite.

Platz and Bally *et al.* have shown that adamantanylidene (**3**) is a ground-state singlet carbene.[17] Even in the presence of triplet sensitizers as measured by low-temperature EPR spectroscopy, generation of the triplet state fails.[17a] The question of whether adamantanylidene entrapped in zeolites is also a singlet cannot be answered at this time. For the formation of azine **7**, at least three mechanisms have to be discussed.[18] Two of them require the intermediacy of a carbene. It was anticipated that by

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(17) (a) Morgan, S.; Jackson, J. E.; Platz, M. S. *J. Am. Chem. Soc.* **1991,** *113,* 2782. (b) On May 5, 1994, we learned from Professor Platz, The Ohio State University, that he in collaboration with Professor Bally, Fribourg, Switzerland, had performed UV and IR matrix experiments with **1** at 10 K. Bally, T.; Matzinger, S.; Truttmann, L.; Platz, M. S.; Morgan, S. *Angew. Chem.*, submitted.

(18) Liu, M. T. H., Ed. *Chemistry of Diazirines*; CRC Press: Boca Raton, FL, 1987; Vols. I and II.

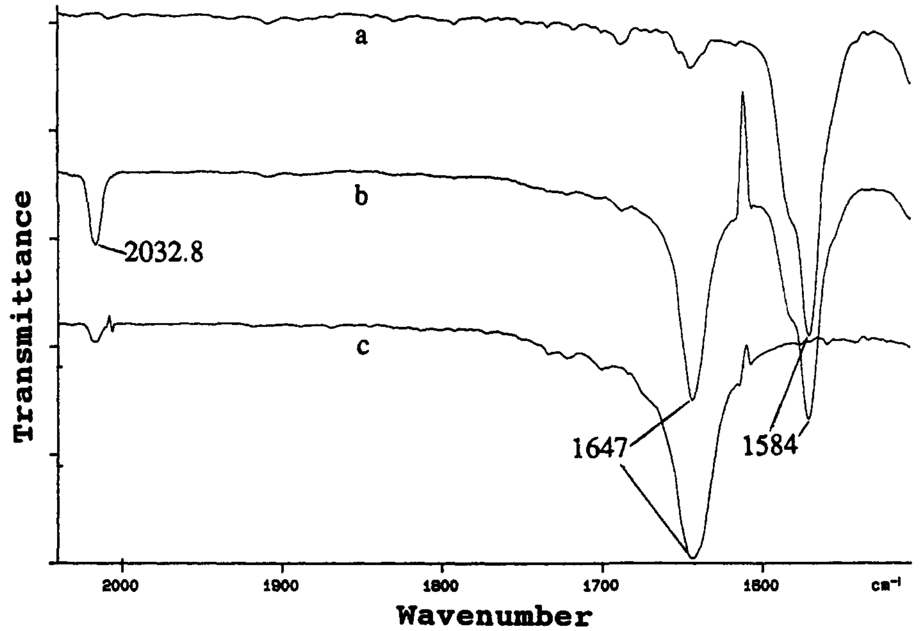
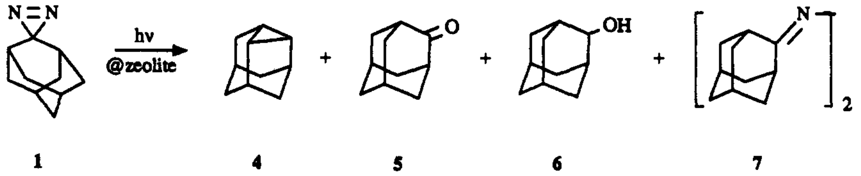


Figure 4. FT-IR spectra of adamantane-2-spiro-3'-diazirine (**1**) in KBr (a) before photolysis, (b) after a 20-min photolysis, and (c) after a 90-min photolysis.

Scheme 2



irradiation of zeolite-entrapped diazirine **1**, due to their large three-dimensional network, intermolecular reactions involving **1**, **2**, and/or **3** should only be of minor significance.

Indeed, the results shown in Table 1 suggest that intermolecular reactions of **1**, **2**, and/or **3** leading to azine **7** are now almost negligible. In most of the reactions studied, no **7** could be detected. 2,4-Dehydroadamantane (**4**), which only can derive from insertion of carbene **3** (Scheme 1), is formed in up to 7% yield after 16 h of photolysis. The results obtained from the photolyses of **1** in zeolites are in stark contrast to those in hydrocarbon solvents.[5,6] Here, adamantanone azine (**7**) is found in 75.5% besides adamantanone (**5**) (21.4%). 2,4-Dehydroadamantane (**4**), however, is not[6] or only in traces formed (0.2% in heptane[5]). A physical mixture of diazirine **1** with NaX under standard photolysis conditions gave 76% azine **7** and no 2,4-dehydroadamantane (**4**). Furthermore, irradiation of pure diazirine **1** under argon gave almost quantitatively azine **7** and no detectable 2,4-dehydroadamantane (**4**).[5]

However, when 2,4-dehydroadamantane (**4**)@zeolite (NaX) was photolyzed under the standard photolysis conditions, it was completely converted into 2-adamantanol (**6**), adamantanone (**5**), and adamantane (ratio 90:6:4). Thus, 2-adamantanol (**6**) and adamantanone (**5**) found in the reaction of **1**@zeolite (NaX) derive in part from secondary reactions of 2,4-dehydroadamantane (**4**). In addition, it could be shown that, in the photolysis of azine **7**@zeolite under the reaction conditions applied above, adamantanone (**5**) is formed in 30% yield (70% unreacted azine **7**). Thus, adamantanone (**5**) derives at least in part from hydrolysis of azine **7** by water molecules present in the zeolite. Adamantanone (**5**), 2-adamantanol (**6**), and adamantane entrapped in zeolites are stable under the photolysis conditions. In all reactions of **1** entrapped in different zeolites, the total isolated yield of **4**–**7** was 85–95%.

Furthermore, time-dependent photolysis of **1**@zeolite (NaX) revealed that 2,4-dehydroadamantane (**4**) is initially formed in yields of at least ca. 40% (see Table 2 and Figure 5). Once adamantanylidene (**3**) is generated in the cavity of the zeolite, the intramolecular 1,3 C–H insertion reaction to 2,4-dehydroadamantane (**4**), which is slow in solution, becomes dominant. Upon further photolysis, however, yields of dehydroadamantane (**4**) decrease from 40% (1 h) to 0% (24 h) and 2-adamantanol (**6**) formation increases (44–92%) during that time span. The loss of **4** and a comparable gain of 2-adamantanol (**6**) suggest that **6** derives (in part) from 2,4-dehydroadamantane (**4**). Wynberg *et al.* have shown that the cyclopropane ring in 2,4-dehydroadamantane (**4**) can easily be opened by halogen acids and a variety of electrophilic reagents.[19] The yield of adamantanone (**5**) and adamantane does not change significantly (see Table 2) and was therefore omitted in Figure 5.

Liu,[20] Moss,[21] and Platz[22] *et al.* have provided substantial evidence that rates of 1,2 H shift reactions of carbenes are increased in polar solvents. In order to find out whether polar solvents accelerate the 1,3 insertion reaction of adamantylidene (**3**) to 2,4-dehydroadamantane (**4**), photolyses of **1** were performed in dimethylformamide, tetrahydrofuran, and *tert*-butyl alcohol.[23] While in *n*-heptane 0.2%[5] of **4** was observed, in dimethylformamide, tetrahydrofuran, and *tert*-butyl alcohol 1.5%, 3%, and 4.5% (22-fold increase) were formed, respectively. Therefore, when compared with the results obtained in *n*-heptane, the polar environment appears to increase the formation of 2,4-dehydroadamantane (**4**). The higher yields of **4** in polar solvents,

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[22] Sugiyama, M. H.; Celebi, S.; Platz, M. S. *J. Am. Chem. Soc.* **1992**, *114*, 966.

[23] We thank a reviewer for the suggestion to perform the photolysis of **1** in polar solvents.

Table 2. Product Ratios and Conversions during Photolysis Depending on Time[a]

time (h)	conversion (%)	dehydro-adamantane (**4**) (%)	adamantane (**5**) (%)	adamantanol (**6**) (%)	adamantanone (**7**) (%)
1	35	40	4	44	12
2	60	36	3	54	7
4	78	30	2	62	6
6	91	26	3	66	5
8	97	22	3	69	6
10	100	20	3	72	5
12	100	14	2	80	4
14	100	11	2	82	5
16	100	8	2	84	6
18	100	6	2	86	6
20	100	3	2	88	7
22	100	1	2	91	6
24	100	0	2	92	6

[a] Activation of zeolite at 300 °C and 0.15 Torr for ca. 30 min.

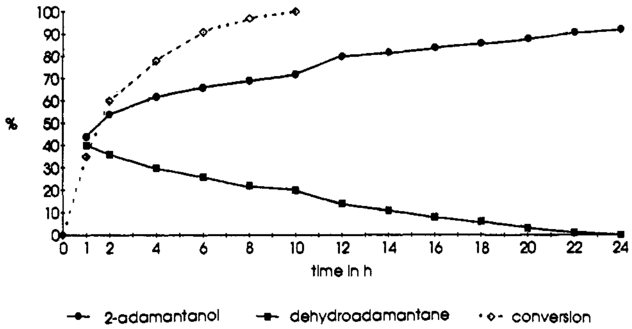

Figure 5. Time-dependent photolysis of **1** @ zeolite (NaX).

however, cannot account for the dramatic increase in the formation of **4** in zeolite by a factor of at least 800.

Adamantanylidene (**3**) has been trapped with alcohols.[17a] The mechanism of the ether formation, however, is not yet fully understood.[17,24] 2-Adamantanol (**6**) can also be formed by an ionic reaction mechanism. Protonation of the nitrogen function of either diazirine **1** or the linear diazo compound **2**, followed by loss of nitrogen, results in formation of the adamantyl cation, which picks up water present in the zeolites.

Differences in reactivity are to be seen between first group and second group cations (see Table 1). Zeolites with second group cations generally show a higher Brønsted acidity than those with first group cations because of the following reaction:[25]

$$M^{2+} + H_2O \rightarrow M(OH)^+ + H^+$$

Therefore (see entries 5–7 and 11–13 in Table 1), either no carbene intermediate was formed and the reaction led predominantly to 2-adamantanol (**6**) via the adamantyl cation or 2,4-dehydroadamantane (**4**) did not survive the more acidic conditions. A similar result was obtained for the photolysis in the acidic HY-zeolite (entry 1, Table 1).

Conclusions

Upon inclusion of adamantane-2-spiro-3′-diazirine (**1**) into several zeolites (**1**@zeolite), intermolecular reactions, such as the formation of azine **7**, are almost neglible. This is in stark contrast to the reactive behavior of diazirine **1** entrapped in β-cyclodextrin (**1**@β-cyclodextrin) where still up to 60% of azine **7** is formed.[5] Instead, in zeolites, 2-adamantanol (**6**) and adamantanone (**5**) are isolated as major products. The strained 2,4-dehydroadamantane (**4**), obtained in yields of at least 40% in NaX, derives from a 1,3 C–H insertion of carbene **3**. We have very strong evidence for having established the first carbene reactions inside a zeolite.

Experimental Section

General Methods. Mass spectra (electron impact) were recorded at 70 eV as *m*/*z*. ^{1}H and ^{13}C NMR spectra in solution were recorded on a Bruker AM-360 (90.6)-MHz] spectrometer. Solid-state ^{13}C CP/MAS spectra were taken at 25.18 MHz on a spectrometer constructed from Tecmag, ENI, and Amplifier Research components with an Oxford 2.35 T superconducting magnet. IR spectra were obtained on a Perkin Elmer FT-IR (model 1600) instrument. Analytical gas chromatography was performed on a Sichromat 1–4 using a 25 mm × 0.272 mm (i.d.) OV 101 glass capillary column.

Adamantane-2-spiro-3′-diazirine (**1**) was prepared from adamantanone (**5**) according to Isaev *et al.*[4a] on the basis of the general method of Schmitz and Ohme.[26] All reagents were obtained commercially and used without further purification. Where dry, water-free solvents were necessary, those were distilled from lithium aluminum hydride under a N_2 or Ar atmosphere. Standard laboratory glassware was used under an inert atmosphere (N_2).

Zeolites LZ-Y52 (NaY), LZ-Y62 (NH_4Y), and 13X (NaX) were obtained from Aldrich. Cation exchange was performed according to the following general procedure[27] for the preparation of LiY: To a solution of 10 g of LiCl in 100 mL of distilled water were added 10 g of NaY, and this mixture was heated under reflux for about 6 h. After the mixture was filtered and the solids were washed with water, this procedure was repeated three times in order to accomplish the most exchange. Cation exchange was not expected to be complete, especially for bigger cations.[28] The approximate amount of exchange for each cation in X- and Y-zeolites is described in the literature.[28] Finally, the zeolite was washed thoroughly with water and activated at 500 °C for 6 h or at 300 °C and 0.15 Torr for 30 min. HY was prepared by calcination of NH_4Y.[29]

Inclusion of Diazirine 1. Activated zeolite (1.2 g) was added to a solution of 200 mg (1.23 mmol) of diazirine **1** in 15 mL of cyclohexane. After the mixture was stirred for 10 h, the complex was filtered off, washed with cyclohexane, and dried in the desiccator under vacuum. The amount of **1** entrapped in the zeolite was determined by analytical gas chromatography of the cyclohexane solution by comparing the concentration of diazirine **1** before and after inclusion. Depending on the cation size usually about 100–160 mg (~8 to 13%) of diazirine could be entrapped into 1.2 g of zeolite. Attempts to include **1** in CsX failed.

Photolyses of the complexes were performed by irradiation of the solid complex in a rotating 250-mL quartz round-bottom flask with a Hanovia 450-W UV lamp. The products were extracted by stirring 200 mg of the complex with 40 mL of ether or by extraction of the complex with ethyl ether in a Soxhlet apparatus for 20 h. The latter method turned out to be the better one, especially for determining the total isolated yield, which was 85–95%. This was further confirmed by dissolving **1**@zeolite (NaX) after photolysis in concentrated HCl and extraction of the acidic layer with methylene chloride.

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The product ratios were determined by analytical GC and ^1H and ^{13}C NMR spectroscopy. If conversion of diazirine **1** was not complete, the amount of 2,4-dehydroadamantane (**4**) could not be determined by GC because of decomposition of **1** to 2,4-dehydroadamantane (**4**) in the injector. Here, ^{13}C NMR spectroscopy was used to determine the product ratios of 2,4-dehydroadamantane (**4**), adamantanone (**5**), and 2-adamantanol (**6**). Signal intensities of the product mixture obtained were compared to those of a standard solution of 2,4-dehydroadamantane (**4**), adamantanone (**5**), and 2-adamantanol (**6**). All spectra were standardized and run under the same conditions.

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