Photolysis of Alkylhalodiazirines and Direct Observation of Benzylchlorocarbene in Cryogenic Matrices

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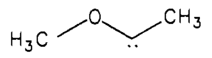
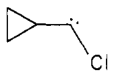
Abstract: Photolysis of 3-benzyl-3-chlorodiazirine and its deuterated homologues 3-chloro-3-(phenyldideuteriomethyl)diazirine and 3-chloro-3-((pentadeuteriophenyl)methyl)diazirine has been investigated by means of IR and UV–vis spectroscopy in argon and xenon matrices. Parent benzylchlorocarbene was produced in low yields and could be detected by UV–vis spectroscopy only, while among the photoproducts of the diazirine bis-deuterated at the benzylic positions, (phenyldideuteriomethyl)chlorocarbene was readily detected by IR spectroscopy. It still is a minor product, though, in a mixture of (*Z*)-β-chlorostyrene, (*E*)-β-chlorostyrene, a distorted styrene, and traces of diazo compound. The benzylchlorocarbenes are very photolabile and also decay thermally at temperatures as low as 10 K. The rearrangement of benzylchlorocarbene-d_2 has been monitored using IR spectroscopy. The small temperature dependence of the rate and the curved Arrhenius plot indicate that tunneling is important at low temperatures. After photolysis at 10 K of any of the benzylhalodiazirines, warming the matrix gives rise to a second thermal process which can also be followed by IR spectroscopy. This process is assigned to the relaxation of a β-halostyrene which is produced from the diazirine in a distorted conformation. Its thermal relaxation, induced by the softening of the matrix at temperatures above 20 K (Ar) or 30 K (Xe), mainly produces (*Z*)-β-chlorostyrene. The carbene rearrangement can be distinguished from the relaxation processes by kinetic analysis of the thermal reactions. For comparison, benzylbromodiazirine and methylchlorodiazirine have also been photolyzed in argon matrices. In these two cases, HX elimination is a side reaction.

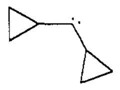
[1,2]-H shifts of alkylcarbenes to olefins are among the fastest carbene rearrangements and determine the lifetimes of these carbenes in many cases. This rearrangement has been the subject of a number of recent kinetic studies in solution[1–8] and also in rare gas matrices.[9] So far, cyclopropylchlorocarbene,[10] dicyclopropylcarbene,[11] cyclopropenylidene,[12a] and methylmethoxycarbene[12b] are the only singlet alkylcarbenes bearing α-hydrogens which could be characterized by infrared spectroscopy. No thermal rearrangement was observed under the conditions applied. Triplet 1-phenylethylidene, however, allowed direct monitoring of the thermal rearrangement to styrene.[9] This carbene is stable at 10–30 K in the dark but is converted to the olefin upon irradiation. The primary kinetic isotope effect after deuteration of the methyl group is so large that kinetic analysis was precluded due to the very small changes in carbene concentration even at temperatures as high as 80 K. An attempt to increase the rate of hydrogen migration by introduction of a *p*-methoxy group at the phenyl ring failed, since only the corresponding styrene was observed after matrix photolysis of the diazo compound. Very recently, Seburg and McMahon have expended considerable effort in detecting ethylidene (methylcarbene) in cryogenic matrices, but methylketene formed in a trapping reaction with CO was the only hint for the intermediate generation of that species.[13]



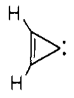
methylmethoxycarbene



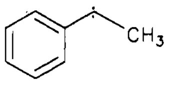
cyclopropylchlorocarbene



dicyclopropylcarbene



cyclopropenylidene



phenylethylidene

From product analysis and laser flash photolysis (LFP) kinetics in solution, it has long been known that olefin formation must proceed through more than a single (carbenic) pathway, and recently, more experimental evidence has been given for a second pathway involving hydrogen shift in an excited state of the precursor molecule.[2,14,15] Therefore, detection of an alkylcarbene under matrix isolation conditions is restricted to cases where (i) the carbene is photochemically stable under the conditions of precursor photolysis, which must include the generated thermally excited "hot" state undergoing fast vibrational relaxation instead of passing the rearrangement barrier, (ii) the production of the carbene can compete with other reaction pathways, and (iii) the carbene is thermally stable under the conditions of matrix isolation at 10 K. The latter condition is met for rearrangement barriers >1 kcal/mol as long as quantum chemical hydrogen tunneling

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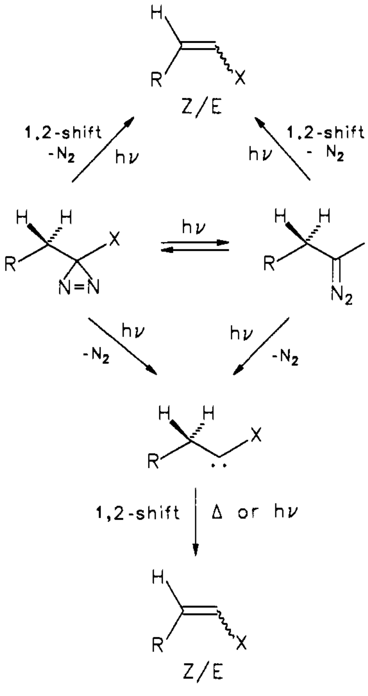
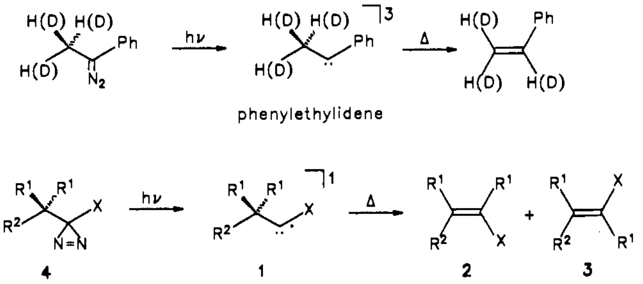
Scheme I



is not significantly involved in the reaction. Observation of a thermal rearrangement at temperatures sufficiently low for matrix-isolation spectroscopy (up to 100 K) is restricted to reactions with a barrier of significantly less than 10 kcal/mol. At 65 K, a first-order reaction with a barrier of 4 kcal/mol and a preexponential factor of 10^{11} s^{-1} proceeds at a rate of 3×10^{-3} s^{-1}. Scheme I illustrates the possible reaction pathways in alkylcarbene precursor photolysis.

The [1,2]-H shift of benzylchlorocarbene (**1a**) produces a mixture of (*Z*)- and (*E*)-β-chlorostyrenes (**2a** and **3a**) and has been extensively studied using trapping experiments,[16,17] LFP,[2,5,18-23] matrix-isolation techniques,[24] and theoretical methods.[25] In solution, rearrangement barriers of 4.5–4.8 kcal/mol and a preexponential factor, $A = 10^{11}$ s^{-1}, were determined by means of two independent methods.[18] The barrier is in the range of the values determined for triplet phenylethylidene both in the matrix[9] and in solution.[1] The activation energies for the rearrangement of benzylbromocarbene (**1d**) and methylchlorocarbene (**1e**) in solution were measured as 4.7 and 4.9 kcal/mol, respectively.[4,7,26] All these barriers appear to be sufficiently large to allow the detection of carbenes **1a-e**, provided that they can be generated at all by diazirine photolysis. They are also low enough to make a thermally induced rearrangement appear possible (Scheme II). We here report a matrix-isolation study of the $1 \rightarrow 2 + 3$ rearrangement, which, in the case of benzylchlorocarbenes **1a-c**, for the first time allows observation of the thermal [1,2]-H shift of a singlet alkylcarbene independently from the photolysis of the precursor.

Scheme II[a]



[a] **a**, R^1 = H, R^2 = Ph, X = Cl; **b**, R^1 = D, R^2 = Ph, X = Cl; **c**, R^1 = H, R^2 = Ph-d_5, X = Cl; **d**, R^1 = H, R^2 = Ph, X = Br; **e**, R^1 = H, R^2 = H, X = Cl.

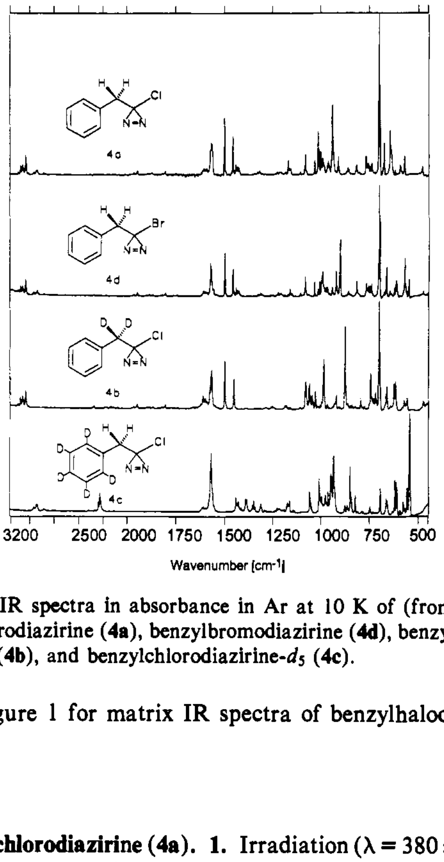


Figure 1. IR spectra in absorbance in Ar at 10 K of (from the top) benzylchlorodiazirine (**4a**), benzylbromodiazirine (**4d**), benzylchlorodiazirine-d_2 (**4b**), and benzylchlorodiazirine-d_5 (**4c**).

See Figure 1 for matrix IR spectra of benzylhalodiazirines **4a-d**.

Results

Benzylchlorodiazirine (4a). 1. Irradiation (λ = 380 ± 20 nm) of benzylchlorodiazirine (**4a**), matrix isolated in argon at 10 K, produced benzylchlorocarbene (**1a**), the hydrogen shift products (*Z*)-β-chlorostyrene **2a** and (*E*)-β-chlorostyrene **3a**, a new species, **5a**, and traces of benzylchlorodiazomethane **6a** (IR absorption at 2048 cm^{-1}). Carbene **1a** was identified by its weak and broad UV absorption (298–334 nm), which exactly matches the UV spectrum of **1a** derived from single-point LFP experiments[18] (Figure 2a), but no IR bands could be attributed to the carbene. The intense UV absorptions of β-chlorostyrenes **2a** and **3a** (λ_{max} = 250, 284, 292 nm) obscure the absorptions of **5a**, which were observed by IR spectroscopy only. The approximate ratio of products **5a**, **2a**, and **3a** after diazirine decomposition and before warm-up was 2:1:2. α-Chlorostyrene, the phenyl-shift product, was not observed, as was reported earlier.[24] Four minutes of broadband irradiation (λ > 360 nm) as well as warming the matrix to 30 K leads to the complete disappearence of **1a** and concomitant growth of the styrene absorptions (Figure 2b). The carbene band even decreased on standing in the dark at 10 K, but, due to the very small changes, meaningful decay kinetics could not be established.

6a could be selectively destroyed by irradiation at λ > 550 nm. As was monitored by IR spectroscopy, warming the matrix to 35 K leads to the complete decay of **5a** and concomitant growth of the absorptions of (*Z*)-β-chlorostyrene (**2a**) (Figure 3). The

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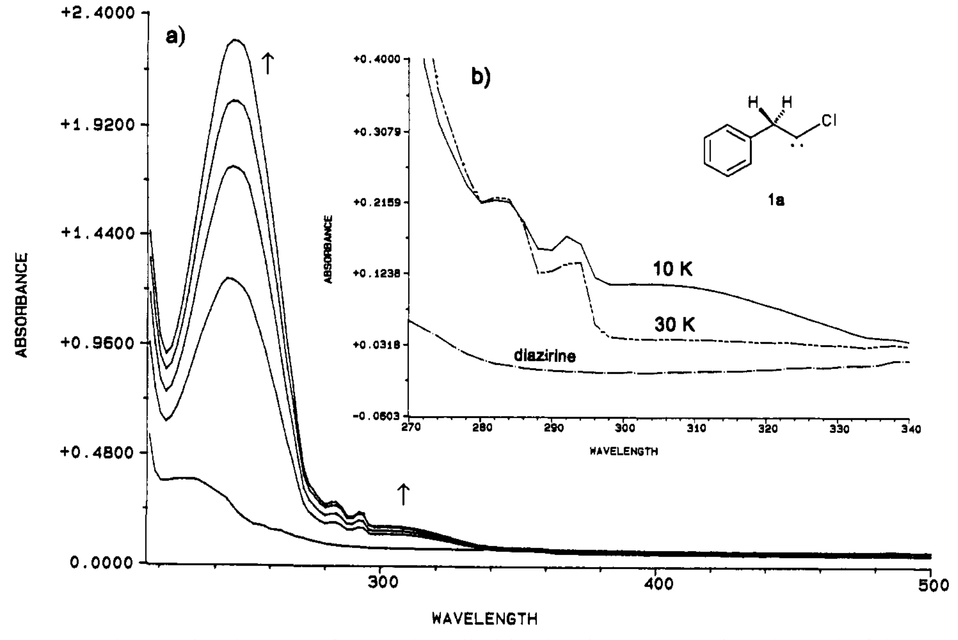

Figure 2. (a) UV–vis spectra of the stepwise photolysis of benzylchlorodiazirine (**4a**) in argon at 10 K and growth of the absorptions of **1a**, **2a**, and **3a** and (b) decay of benzylchlorocarbene (**1a**) (solid line) after warm-up to 30 K.

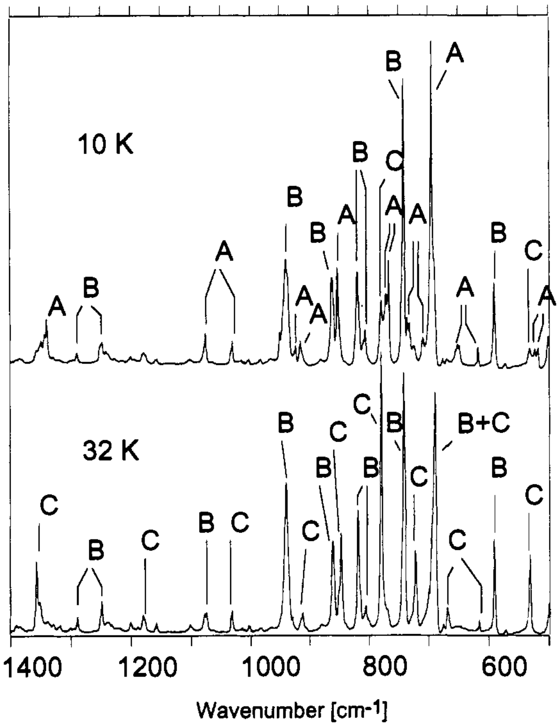

Figure 3. Changes occurring in the IR spectra (Ar) when the initial photoproduct mixture of benzylchlorodiazirine (**4a**) is warmed from 10 K (top) to 32 K (bottom). A = **5a**, B = **3a**, and C = **2a**.

overall *Z*/*E* ratio after photolysis and warm-up therefore was approximately 3/2. Interestingly, species **5a** was completely stable to photolysis conditions under which isomerization of the styrenes occurs ($\lambda > 280$ nm). We postulate that **5a** has the structure of a distorted β-chlorostyrene (see below for Discussion).

β-Chlorostyrenes **2a** and **3a** have been identified as reaction products by comparison of the IR and UV–vis spectra with those of the authentic matrix-isolated compounds. Short-wavelength irradiation ($\lambda > 295$ nm) causes **3a** to photoisomerize to **2a** (photoequilibrium concentration >90% *Z*), while at $\lambda = 380 \pm 20$ nm (and $\lambda > 360$ broad-band irradiation)—the conditions of diazirine photolysis—**2a** and **3a** are photostable. Relative concentrations of compounds **2a**, **3a**, and **5a** in the matrix were assessed by comparison with the spectra obtained after the stepwise photoisomerization **3a** → **2a** in an argon matrix.

2. Photolysis of **4a** in solid xenon produced a similar product mixture with the exception that the initial ratio of **2a**/**5a** was higher than in argon. The thermal reaction **5a** → **2a** took place in the same manner as in argon but at higher temperatures. At 50 K, the reaction was quantitative.

3. Photolysis of **4a** in the presence of HCl, CO, or CO_2 did not affect the observed chemistry. In the presence of oxygen, carbon dioxide was produced, but no species characteristic for a carbene reaction were found.

Benzylchlorodiazirine-d_2 (4b). 1. Photolysis of the deuterated diazirine **4b**, matrix isolated in argon at 10 K, gave rise to the UV absorptions of β-chlorostyrenes **2b** and **3b** and a carbene UV absorption ($\lambda_{max} = 304$ nm), which was about twice as intense as in the case of **1a**. Also, carbene **1b** was readily detected by IR spectroscopy. This indicates a kinetic deuterium effect. Carbene **1b** is photolabile, and broad-band irradiation ($\lambda > 360$ nm) quickly produced β-chlorostyrenes (Figure 4b). After the matrix was warmed to 30 K, a considerable carbene UV absorption persisted, and, even at higher temperatures up to 42 K, the absorption still remained to a small extent. However, on standing in the dark at 10 K for 40 h, the carbene decays to about 60% of the initial value following a nonexponential rate law, while the styrene absorption increased in intensity (Figure 4a).

IR spectroscopy confirmed, besides the production of carbene **1b**, the presence of styrenes **2b** and **3b** along with a small amount of diazomethane **6b** (2047 cm^{-1}) and another set of bands which reflected the behavior of the bands of compound **5a**, i.e., the absorptions were stable to short-wavelength irradiation but decayed upon warming the matrix.

The carbene IR absorptions disappeared completely within 15 min of broad band irradiation ($\lambda > 360$ nm), and they decreased significantly in intensity after a short warm-up to 30 K as well as when standing at 10 K in the dark for 2 days, which is in complete analogy to the behavior of the UV–vis absorption. As shown in the IR difference spectra (Figure 5), other absorptions increased only slightly during the carbene decay, as if the increase in intensity was distributed over more than one species (see below for Discussion). Unfortunately, the thermal changes which are not related to the carbene's decay are much less readily interpreted in terms of the decay of a discrete species than in the case of **5a**. Most styrene bands are slightly shifted before warm-up, and although (*Z*)-β-chlorostyrene (**2b**) appears to be the principal warm-up product, other bands increase in intensity as well. In contrast to compound **5a**, which shows a well-defined set of

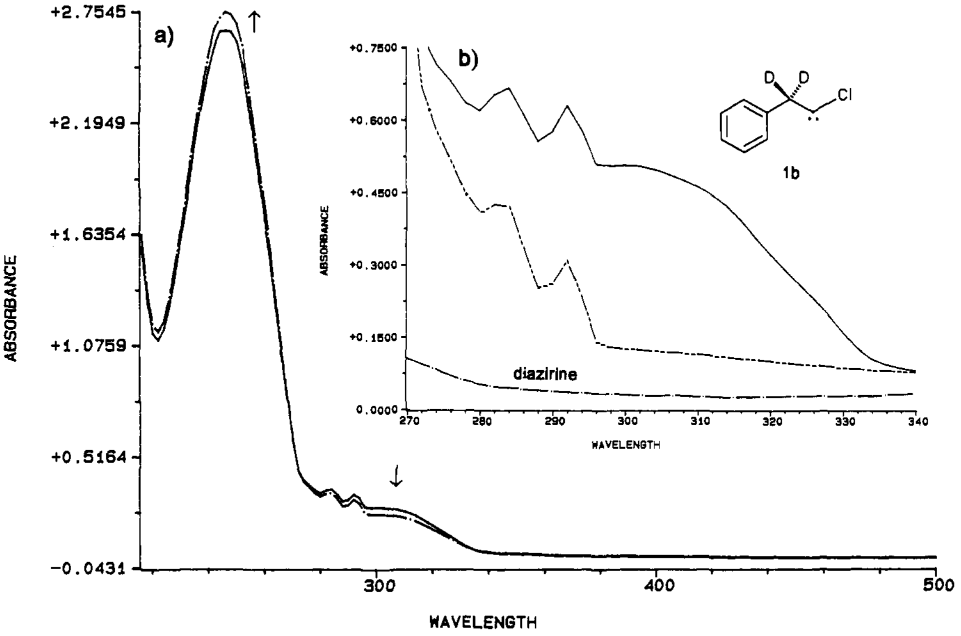

Figure 4. (a) UV–vis spectra of the photoproducts of benzylchlorodiazirine-d_2 (**4b**) (solid line) showing the thermal decay of benzylchlorocarbene-d_2 (**1b**) and the concomitant formation of dideuterio-β-chlorostyrenes in argon at 10 K after 12 h and (b) photolysis of benzylchlorocarbene-d_2 (**1b**) (solid line) after 13-min irradiation with $\lambda > 360$ nm.

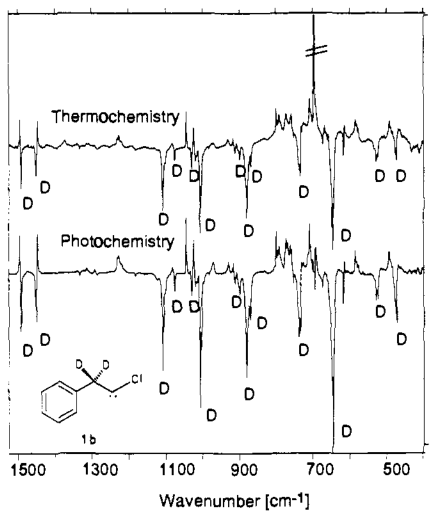

Figure 5. Difference IR spectra of the 1,2-hydrogen migration of benzylchlorocarbene-d_2 (**1b**) in argon. Bands marked D are assigned to **1b**; product bands go upward (see text and Figure 9 for discussion); top, thermal rearrangement (2 days at 10 K) and bottom, photochemical rearrangement (15-min irradiation with $\lambda > 360$ nm).

absorptions, the photostable set of bands which might be assigned to **5b** is only shifted a few wavenumbers and appears as shoulders of the styrene absorptions. The overall Z/E ratio after diazirine photolysis and warm-up again is approximately 3/2.

Identification of the deuterated styrenes was made in analogy to the parent compounds by analysis of the photochemical isomerization, and Z-conformation was assigned to the compound whose absorptions grew at 295-nm irradiation.

2. Photolysis of **4b** in solid xenon produced a product mixture whose infrared spectrum was similar to that in argon with a slightly diminished yield of carbene **1b**. No significant changes in product distribution were assessed.

3. Photolysis of **4b** in the presence of CO or CO_2 did not yield carbene-derived products. **4b** could be photolyzed in pure carbon dioxide without α-lactone formation (1850–1950 cm^{-1}).[27,28] In the presence of oxygen, an intense CO_2 absorption was produced. However, when **4b** was photolyzed in an argon matrix containing 0.45% HCl, the yield of styrenes and of carbene was markedly reduced and new bands appeared at 560 (m), 617 (m), 635 (m), 657 (m), 732 (vs), 759 (s), 898 (m), 917 (m), and 950 cm^{-1} (w). These absorptions are in agreement with the formation of a geminal dichloride. Photolysis in 1.3% HCl further reduced the yield of styrenes, and the new bands represented the main product. No subsequent thermal bimolecular reaction was found.

Benzylchlorodiazirine-d_5 (4c). Photolysis of this compound in solid argon under the same conditions as above proceeded in complete analogy to diazirine **4a**. Carbene **1c** was only detected by UV–vis spectroscopy. The structural assignment of the β-chlorostyrenes again rests on their photochemical interconversion by irradiation at $\lambda = 295$ nm. In analogy to diazirines **4a** and **4b**, thermal changes were observed when the matrix containing the photolysis products was warmed to higher temperatures. The corresponding absorptions are even less shifted from the styrene bands than in the case of **4b**, but in analogy to **4a** and **4b**, the Z/E ratio of the hydrogen shift products is again ca. 60% Z.

Benzylbromodiazirine (4d). Photolysis of **4d**, matrix-isolated in argon at $\lambda = 380 \pm 20$ nm, produced the intense UV absorption of the β-bromostyrenes **2d** and **3d**. No other UV–vis bands were observed. IR spectroscopy confirms the generation of the styrenes and traces of benzylbromodiazomethane (**6d**) (2045 cm^{-1}). In analogy to the photolysis mixtures of the chlorodiazirines, warming to 30 K results in severe changes of the spectra. The IR spectra also reveal the photochemical production of prominent additional bands which do not match the reference spectra of the two β-bromostyrenes. A sharp split band (2429 and 2437 cm^{-1}) is assigned to HBr complexed[29] to phenylacetylene. Alkynes may account for rather broad absorptions at 2258, 2203, and 2135 cm^{-1} and a peak at 3331 cm^{-1}. The IR spectrum of authentic matrix-isolated phenylacetylene matches many of the new bands, and it clearly is present in the product mixture. No traces of a carbene absorption were found. The Z/E ratio after diazirine photolysis and warming to 40 K is slightly lower than in the case of the chloro compounds **4a**–**4c**. Both isomers were produced in about equal amounts.

β-Bromostyrenes **2d** and **3d** have been identified as reaction products by comparison of the IR spectra with those of authentic

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matrix isolated compounds. (*E*)-β-Bromostyrene (**3d**) is converted to the *Z*-isomer upon irradiation at >345 nm. At 380 nm, no photoreaction was observed.

Methylchlorodiazirine (4e). Irradiation (30 min at 335 ± 10 nm or 12 h at >400 nm) resulted in the complete disappearance of the diazirine bands and concomitant growth of the absorptions of vinyl chloride. A diazo band (2100–2000 cm^{-1}) was never detected, and no significant thermal changes occurred when, after decomposition of the diazirine, the matrix was warmed to 30–35 K. As a byproduct, diazirine photolysis produced very small amounts of complexed HCl (2760 cm^{-1}). A weak but sharp absorption at 3282 cm^{-1} matches the C–H vibration of the T-shaped acetylene–HCl complex,[29]but none of the other bands reported in the literature could be detected. Carbene **1e** was not detected.

The IR absorptions of methylchlorodiazirine (**4e**), matrix-isolated in argon, match the published gas-phase data[30] very well, and vinyl chloride is easily identified.

Solid-State Kinetics. A thorough analysis of the kinetics of the thermal reactions observable by infrared spectroscopy was done to further prove the carbene identity as well as the nature of intermediate **5**.

By IR spectroscopy, we observed two different kinds of thermal reactions: (i) the deuterium shift of carbene **1b**, which can also be induced by irradiation, and (ii) a second reaction which is purely thermal. In the following paragraphs, we will speak of thermal *relaxation* to denote the thermal changes which occur after photolysis of each of the benzylhalodiazirines and which are not caused by a carbene rearrangement. Due to its well-established set of IR absorptions and the stereospecific decay to **2a**, we consider **5a** to be a defined species. In the other cases, when we speak of compound **5**, we do this to give a name to the set of shoulders which disappear on annealing of the matrix. In these latter cases, the shifts which occur during warm-up are small and analysis of the spectra is difficult.

Both reactions, i.e., the thermal decay of carbene **1b** as well as the thermal decay of the absorptions assigned to **5**, follow nonexponential rate laws,[9,31–34] a severe restriction to the assessment of meaningful kinetic data. An additional problem arises from the fact that relatively high concentrations of the reactive species are needed for IR investigations. This means that precursor photolysis typically takes hours. Therefore, in an infrared spectroscopic kinetic study, photolysis of the precursor can not take place at the same temperature at which the thermal decay will be followed, i.e., a warm-up interval must be undertaken before beginning the acquisition of the kinetic data. Photolysis typically takes place at the lowest achievable temperature, which in our case is 10 K. The time required to warm the matrix to 30 K is on the order of 45–60 s. This leads to an experimental error due to the distribution of activation barriers over a whole range of different matrix sites. In contrast to a first-order reaction in solution, the rate constant of a nonexponential process in the solid state is time-dependent; molecules located at the low barrier edge of the distribution will have decayed during the warm-up time, and the measured rate constants will be lower than expected.

The decay curves can be fitted to a function of the form

$$[\mathrm{A}]_t = [\mathrm{A}]_0 \exp[-(k_\mathrm{T}t)^\beta] \qquad (1)$$

where β is in the range of $0 < \beta < 1$. A low value of β is expected for reactions with a broad distribution of reactive sites, while for a process in homogenous solution, β is 1. The smaller the value of β, the more a "site-clearing" effect is observed, i. e., warming the matrix induces a fast decay of a small part of the reactive species and then very quickly the reaction seems to come more or less to a complete stop.

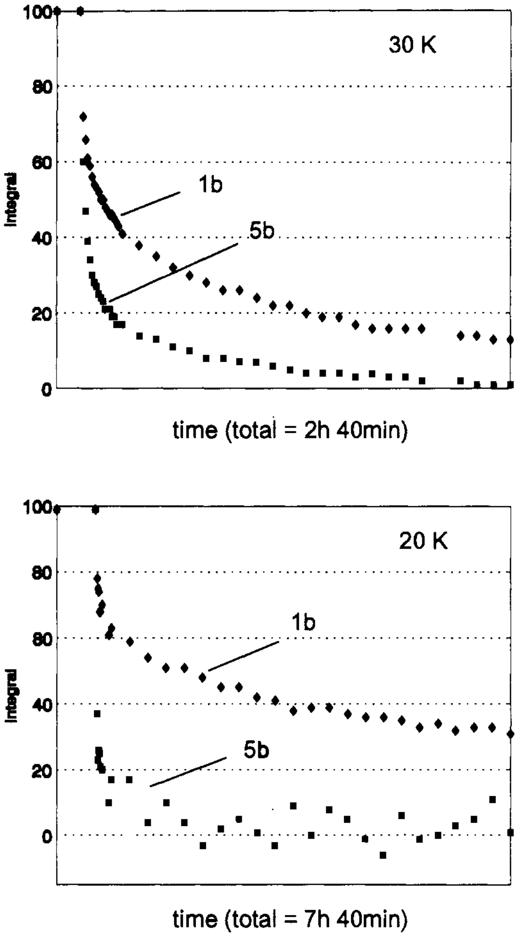

Figure 6. Decay curves of two IR absorptions at 30 K (top) and 20 K (bottom). The upper curve in both cases represents the carbene decay (**1b**, 645 cm^{-1}). The lower curve belongs to a shoulder at 753 cm^{-1} (**5b**). The 100% value represents the starting point before warm-up. Peak integrals were normalized to the *calculated* end value (= 0%) in order to be able to show the difference in the initial decay rates. Note that in the case of **5b** at 20 K, 100% corresponds to an actual change in peak intensity of less than 10%.

A possibility to distinguish the two thermal reactions comes from the observation that solid-state effects are far more effective for the relaxation compared with the decay of the carbene peaks. In kinetics experiments at higher temperatures, above 20 K, the carbene absorptions have already decreased by one-third of the overall change in intensity during the experiment, when the kinetics measurement begins. The relaxation, however, has already proceeded by more than 50% during the warm-up interval.

While the decay of the infrared absorptions assigned to carbene **1b** is easily followed at temperatures as low as 10 K, the second thermal reaction involves only a very small quantity of the molecules below a minimum temperature of about 25 K. Such a behavior is typical for conformational isomerism.[35 a] It results in very low β values of 0.3–0.4 and represents the often mentioned $t^{1/3}$ dependence of ln *k*. The carbene bands, in contrast, give values of 0.4–0.7 ($t^{1/2}$ dependence). We have been able to follow the decay of carbene **1b** and the decay of a shoulder assigned to a distorted styrene, **5b**, simultaneously, and for two temperatures, the decay curves are shown in Figure 6. Note that at 20 K, the relaxation of **5b** actually stops after the first scans.

1. Distribution Slicing Experiments. A way to illustrate the existence of a distribution of reactive sites for a matrix isolated transient species was given by Dougherty et al.[31] This analysis is restricted to the case of species which are stable at the lowest

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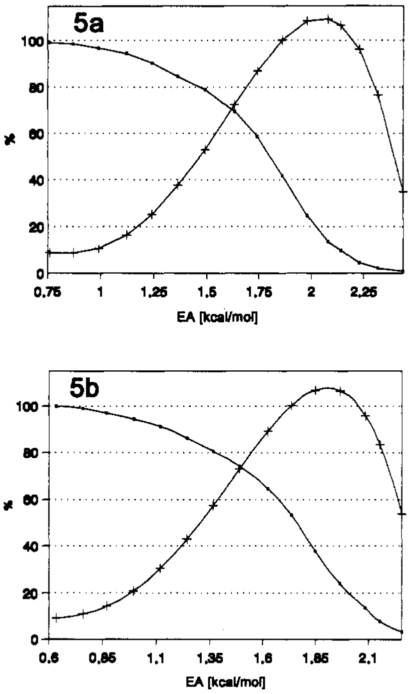

Figure 7. Distribution slicing.[31] Distributions were measured in argon for the 1340-cm^{-1} band of **5a** (top) and for a shoulder at 753 cm^{-1} in the photolysis mixture of **4b** (bottom, **5b**). Following the peak integral of the corresponding IR absorptions from 10 to over 40 K in steps of 2 K yields the remaining concentration of the thermally labile species. This concentration is plotted with the activation barrier E_A calculated by means of eqs 2 and 3. Warm-up intervals were in the range of 1–3 min. After this time, the matrix was cooled down to 10 K again to assess the remaining concentration of the labile species. Then, the matrix was warmed to the next higher temperature. The Gaussians (–×–) were calculated as the derivatives of the measured integral curves (—). log A was set to 11 in both cases. See text for discussion.

achievable temperature. The method requires setting of the preexponential constant A, which can not be extracted from the experimental data. It is not meant for the calculation of physically significant values of E_A but rather provides a measure of the impact of the rigid medium on a given reaction. Here, we use it to compare the significant solid-state effects which influence the different thermal reactions which we observed. We would expect similar reactions to show similar distribution curves. The method was developed by Dougherty et al. and has been extensively described in ref 31, and in the following paragraphs, we will only sum up the basic features.

Warming to successively higher temperatures for a given time followed by recooling and taking a spectrum yields the concentration of a thermally labile intermediate as a function of warm-up time and temperature. In our experiments, this was done by following the peak integral of the corresponding IR absorptions from 10 to over 40 K in steps of 2 K. Warm-up intervals were in the range of 1–3 min. After this time, the matrix was cooled down to 10 K again to assess the remaining concentration of the labile species. Then, the matrix was warmed to the next higher temperature.

When a rate, k, is assigned to the sites which experience 50% decay during warm-up, then for these sites, the warm-up interval corresponds to 1 half-life. This means that E_A can be calculated with eqs 2 and 3:

$$k = \ln 2/t_{1/2} \qquad (2)$$

$$E_A = -RT\ln(\ln 2/At_{1/2}) \qquad (3)$$

A was arbitrarily set to 10^{11} s^{-1}, a value which is close to the one derived for the s-cis to s-trans isomerization of but-3-en-2-one in solid CCl_4[35b] and which is also the value determined for the 1,2-hydrogen migration of benzylchlorocarbene (**1a**) in solution.[18] The procedure yields the concentration of a special site (i.e., the one which at the given temperature experiences 50% decay) as a function of its thermal activation barrier, which was calculated by means of eqs 2 and 3. The resulting curve represents the distribution of reactive sites in an integrated form. In order to obtain an analytical function for its derivative, this integrated distribution was simply fitted to a 5th-order polynomial by means of a statistics program. The derivative of the resulting function (the actual representation of the distribution of activation barriers) was calculated and plotted with E_A. For both **5a** and **5b**, Gaussian-type distributions with similar half-widths were obtained (Figure 7). Note that the actual location of the maximum depends on the setting of A.

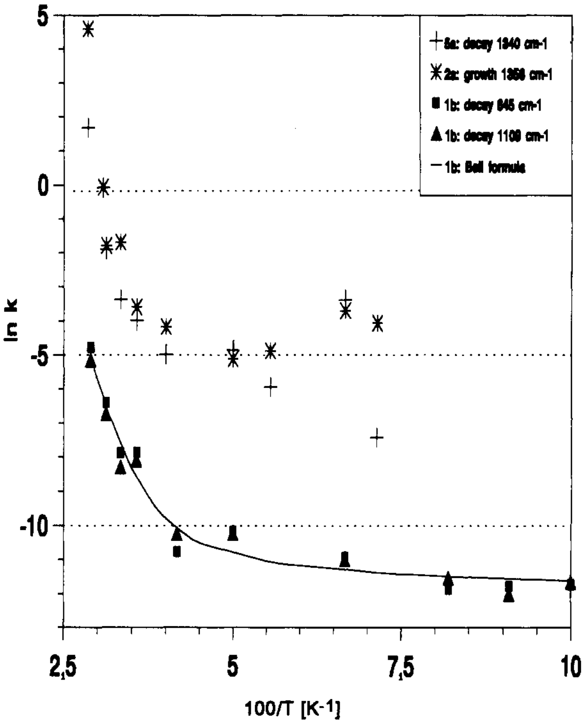

Figure 8. Arrhenius plots for the thermal rotational relaxation of **5a** (upper curve) and for the thermal 1,2-deuterium shift of benzylchlorocarbene-d_2 (**1b**) (lower curve), matrix isolated in argon.

Due to the thermolability of **1b** at 10 K, this procedure is not feasable for the carbene absorptions and strongly distorted curves are obtained. We take these results as a hint for strong similarities in the thermal decay of **5a** and **5b**, in contrast to the decay of **1b**.

2. Arrhenius Kinetics. Arrhenius plots of the decay kinetics have been obtained by following the reactions at 10 temperatures between 10 and 34.5 K (Figure 8). The decay curves (peak integral = f(t)) of the IR absorptions of carbene **1b** and compound **5a** were fitted to a model of the type

$$\text{peak integral} = \text{A1} \pm \text{A2}\exp(-(kt)^{\beta}) \qquad (4)$$

i.e., all variables including the "infinity" peak integral value A1, the proportional constant A2, the rate constant k, and the "stretched exponent" β were calculated using Marquardt-type nonlinear regression statistics.

In the case of **5a**, it was possible to follow the concomitant growth of (Z)-β-chlorostyrene (**2a**), and the derived rate constants for the decay of **5a** and the growth of **2a**, which are included in the Arrhenius plot, are in good agreement. The decay of **1b** was monitored following two IR absorptions, but, due to the small changes in intensity, a meaningful analysis of the simultaneous growth of products at low temperatures was not possible. At higher temperatures above 20 K, analysis of such data would be complicated inasmuch as the growth of products is a result of two independent reactions. However, the shapes of the absorptions of styrenes **2b** and **3b** before and after warm-up differ so much that we could not integrate their peaks in a reproducible way. Following the decay of **5b** was difficult due to the small shifts and problems with the integration of shoulders. Therefore, we did not include the data of this decay in the Arrhenius plot. It should be noted, however, that these shoulders do not decay at the same rate as those of compound **5a** but slower. The β values, however, are in the range of 0.3–0.4, in analogy with those of the decay of **5a**.

Finally, the shifts which occur during warm-up of the mixture obtained after photolysis of diazirine **4c** are too small to allow any proper integration, so no kinetic data were obtained for this compound.

The rate constants were calculated with an average statistic error of 10%. The experimental error primarily stems from the difficulty in reproducing the exact time interval needed to reach the desired temperature, which may result in a small change of the shape of the decay curve and, therefore, in a change of the calculated β value. For a given decay curve, a change of β from 0.7 to 0.4 increases the calculated rate constant by 1 order of magnitude. In a double-exponential model, as is the case for eq 4, small changes of parameters may cause large changes in the results. We consider the calculated rate constants to be reliable within 1 order of magnitude. It should be empasized, however, that the values obtained at higher temperatures are too small because of the loss of reactive sites during warm-up. The curvature of the Arrhenius plots would be even more drastic if the complete distribution of reactive sites could be observed.

(i) **Decay of Carbene 1b.** The rate of the reaction is much higher than could be expected by extrapolation of the LFP data obtained at room temperature. The observed curvature has been taken as a hint for tunneling.[36] Treatment of the carbene decay (Figure 8, lower curve) with Bell's equation[37]

$$k = QA\exp(-E_A/RT)$$

with $Q = (e^a/(b-a))\,(be^{-a} - ae^{-b})$, $a = E_A\,/\,RT$, and $b = 2\pi^2 d(2mE_A)^{1/2}/h$ yields with $m = 2$ (deuterium):

$$E_A \text{ (classical barrier)} = 1.47 \pm 0.21 \text{ kcal/mol}$$

$$A = 2.18 \times 10^6 \text{ s}^{-1}, \log A = 6.33 \pm 1.38$$

$$d \text{ (tunneling distance)} = 1.08 \pm 0.05 \text{ Å}$$

At 10 K, k was measured as 0.9×10^{-5} s^{-1}. Introduction of the mass of a proton (H-shift) into the above equation gives $k' = 1.8 \times 10^{-2}$ s^{-1} and $k_H/k_D = 2000$ at 10 K. Dissection of the plot into a classical and a nonclassical region gives

$$T = 34.5\text{–}24 \text{ K}, E_A = 0.80 \pm 0.08 \text{ kcal/mol}, \quad \log A = 2.67 \pm 0.60, r \text{ (correlation)} = 0.961$$

$$T = 34.5\text{–}28 \text{ K}, E_A = 0.92 \pm 0.16 \text{ kcal/mol}, \quad \log A = 3.53 \pm 1.17, r = 0.915$$

$$T = 10\text{–}24 \text{ K}, E_A = 56.8 \pm 8.1 \text{ cal/mol}, \quad \log A = -3.94 \pm 0.13, r = 0.911$$

As was mentioned before, the values of E_A and $\log A$ at higher temperatures reflect an experimental error. In contrast, an activation barrier of several calories per mol at very low temperatures represents a typical value for a tunneling reaction.

It was also possible to compare the decay of the IR bands and the decay of the UV–vis absorption of **1b** directly. At 10 K, a decay rate of 2.0×10^{-5} s^{-1} was measured by UV–vis spectroscopy. This difference is in the range of error.

(ii) **Decay of Compound 5a and Concomitant Growth of (*Z*)-Styrene 2a.** Growth and decay rate constants are in good correlation. Note that the reaction actually stops below 20 K, which is reflected in the large errors. The 10 points at the highest temperatures (five decay and five growth rates) gave $E_A = 1.73 \pm 0.31$ kcal/mol and $\log A = 11.5$.

Discussion

Carbene Characterization. The UV absorptions of the reactive species produced on irradiation of each of the three benzylchlorodiazirines **4a–c** clearly match the LFP solution spectrum of benzylchlorocarbene (**1a**). The LFP spectrum allowed us to directly follow the carbene decay in solution, and the value of E_A which was derived is consistent with the value established by the indirect pyridine ylide method.[38] It is difficult to imagine such a behavior for a species which is not a carbene. In argon, carbene decay takes place with concomitant growth of the styrene absorption, which again provides evidence for the identity of the reactive species.

Since only very small quantities of carbenes **1a** and **1c**, respectively, are produced, it is not surprising that they do not appear in the IR spectra but are only detected by the more sensitive UV–vis spectrometer. The broad, longest wavelength absorption which we were able to observe, at 304 nm, exhibits a large blue-shift compared to the absorptions of cyclopropylchlorocarbene (460 nm)[10] but is in good agreement with that of phenylchlorocarbene (300 nm).[39] The carbene's photochemistry on irradiation at $\lambda > 360$ nm, however, indicates that there is absorption at longer wavelengths.

All photoproducts of diazirines **4a–d** show the characteristic IR absorptions of a monosubstituted benzene ring.[40] On the one hand, this complicates the analysis of the spectra because many absorptions of different molecules differ only by a few wavenumbers. Examples are the pair of absorptions at about 1450 and 1500 cm^{-1} (ring C–C-stretching and C–H-bending) as well as the vibration (ring CH out of plane) at 700 cm^{-1}. These absorptions are very sensitive to deuteration of the ring (vibration 4 of compound **4c** appears to be shifted by more than 100 wavenumbers, Figure 1) but not to deuteration of the benzylic carbon. On the other hand, the spectral similarities of all compounds exclude the formation of a species with a completely different structure such as the products of an intramolecular addition of the carbene carbon at the phenyl ring.

Benzylchlorocarbene-d_2 (**1b**) shows the IR absorptions expected for a monosubstituted benzene ring bearing deuterium and chlorine in the side chain, although the 700-cm^{-1} band is not resolved due to the variety of molecules absorbing at the same wavenumber. Finally, our assignment of the IR absorptions of carbene **1b** is based on the analogy in behavior with those of the UV–vis absorption (photochemistry, thermochemistry, and decay kinetics). Most of the prominent carbene absorptions are split into two bands, which might indicate the presence of more than one carbene rotamer. The impact of conformation on carbene rearrangements has been described in qualitative[41,42] and ab initio[43] studies.

Figure 9 clearly shows the formation of intermediate species **5b** from carbene **1b**. A number of bands formed during carbene photolysis (Figure 9a) decay again when the matrix is warmed to higher temperatures, and the styrene absorptions grow in. Note that the changes which occur upon warming the matrix (Figure 9b) stem from both the decay of carbene rearrangement products and the decay of photolysis products which were not produced

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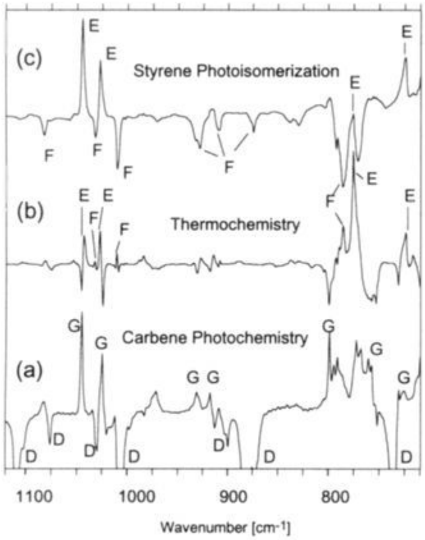
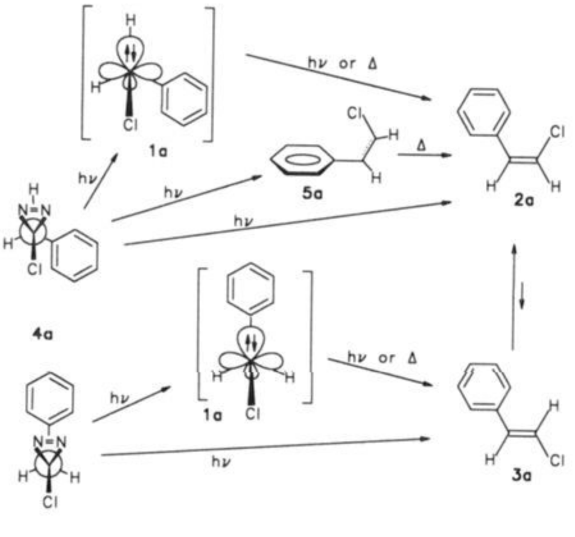


Figure 9. Difference IR spectra showing the production of distorted products from benzylchlorocarbene-d_2 (**1b**) and their subsequent thermal decay upon annealing of the matrix: (a) bands produced by the photochemical 1,2-hydrogen migration in benzylchlorocarbene-d_2 (**1b**) (carbene bands are cutoff), matrix isolated in argon at 10 K; (b) changes occurring upon subsequent warming to 32 K of the same matrix (product bands go upward); and (c) photoisomerization **3b** → **2b** by irradiation of the matrix-isolated mixture with λ > 295 nm. D = **1b**, E = **2b**, F = **3b**, and G = **5b**.

Scheme III



via the carbene but directly from the diazirine. It is obvious, however, that the hydrogen shift of **1b** produces two species with absorptions close to those of **2b** and **3b**. (*Z*)-Styrene **2b** appears to be the predominant product.

The UV–vis spectra of (*Z*)- and (*E*)-β-chlorostyrenes (**2a** and **3a**) differ slightly inasmuch as the weak, long-wavelength absorptions of the *E*-isomer at 284 and 292 nm are weaker and shifted to 282 and 290 nm in the case of the *Z*-isomer. These differences are in the range of the resolution limit in our experiments, and we can not resolve the formation of one isomer.

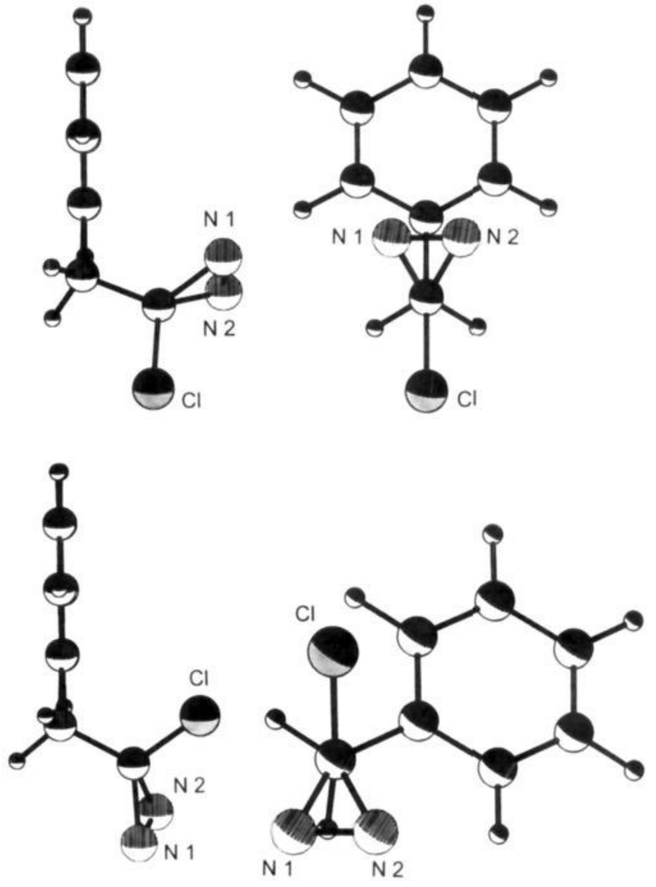


Figure 10. Conformations of **4a** predicted by semiempirical AM1 calculations. The results of semiempirical AM1 calculations indicate two rotamers for benzylchlorodiazirine **4a** which are separated by 1 kcal/mol only and may therefore coexist at room temperature. Top: two views of the anti conformer. The same conformation is displayed by 3-chloro-3-(naphthylmethyl)diazirine in the solid state.[45] Bottom: the gauche conformer is calculated as a shallow minimum, as was verified by calculation of the vibrational constants. Note that the heavy atoms which are to form the plane of the future double bond are not in a plane.

Characterization of the Distorted Styrenes. We attribute the absorptions of the thermolabile species which is produced after photolysis of benzylchlorodiazirine (**4a**) (Figure 3) to a discrete molecule, a distorted styrene, **5a**. This assignment rests on the stereospecific decay of **5a** to (*Z*)-β-chlorostyrene (**2a**) as well as on the purely thermal nature of this reaction (Scheme III). The results indicate that the photochemical formation of (*Z*)-β-chlorostyrene (**2a**) in xenon proceeds with less sterical hindrance due to the larger matrix sites and that the thermal decay of **5a** is due to the decrease of matrix rigidity at higher temperatures (at 30 K, xenon is not as soft as argon, and therefore, the relaxation takes place at a higher temperature).

Distortion may involve (i) the dihedral angle between ring and double bond π-systems (rotation around a σ-bond), (ii) a twist of the olefinic double bond, or (iii) a mixture of both effects. A closer look at the IR spectra (Figure 3) reveals that by far the largest changes in the infrared spectrum occur in the range of absorptions typical[44] for cis alkenes (the most prominent features in the reaction **5a** → **2a** are the growth of the CH out of plane vibration at 779 cm^{-1}, the CH in plane vibration at 1356 cm^{-1}, and the medium strong band at 531 cm^{-1} which is also attributable to the alkene moiety (twisting)).

Since a twisted double bond is a necessary transition state in the photoisomerization of olefins, we would be surprised to observe photostability of such a species under irradiation conditions which induce styrene isomerization. On the other hand, semiempirical AM1 calculations predict two conformations of benzylchlorodiazirine separated by 1 kcal/mol in energy only (Figure 10). The anti conformer is the global minimum and displays the same conformation as (naphthylmethyl)chlorodiazirine in the solid state.[45] In this conformer, the heavy atoms are in the proper planer conformation for the double bond to be formed. In contrast, photolysis of the gauche conformer and subsequent formation of the double bond must proceed under reorganization of the heavy atoms.

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Compound **5a** may also have a conformation which is characterized by a distortion of the optimal dihedral angle between ring and double bond. The phenyl ring, which in diazirine **4** is not expected to be coplanar with the plane formed by the two carbon atoms in the alkyl chain and the chlorine atom, has to rotate after nitrogen extrusion and H-shift to achieve optimum conjugation with the newly formed double bond. Note that **2a** is not planar due to steric restraints. Semiempirical AM1 calculations predict a dihedral angle of 40°. In the case of (*E*)-styrene **3**, the sterical hindrance for this relaxation is smaller, and most of the *E*-isomer is produced directly in its proper conformation. The distorted styrene is stable to irradiation conditions under which *E–Z*-isomerization takes place. This may be interpreted as the result of a blue-shift of the UV absorptions due to the lack of full conjugation. It would nevertheless be surprising if a rotamer, which in the gas phase is not even a local minimum, exhibited such extraordinary photostability as compound **5a** does.

Although distortion of an H-shift product is plausible due to the constraints of the rigid matrix environment and the unfavorable conformation of the precursor, we can not answer the question for the structure of **5a**. In the cases of the deuterated diazirines, the set of photostable bands which decay thermally might be caused by only slight deformations of the photolysis products and/or matrix effects. We can not provide any proof for the existence of a discrete species.

Kinetic Analysis. Decay and distribution curves clearly show a difference in mechanism and a different impact of the solid state effect on the two processes which we observed. This is reflected in the time and temperature dependences of the concentration of the reactive species. It should be noted that rotation around the σ-bond to the phenyl ring as well as reorganization of a distorted double bond of a styrene to give the compound its minimum energy conformation is not expected to proceed via an activation barrier at all. Therefore, the observed relaxation may be a *pure* matrix effect, and the entire "barrier" is provided by the rigid environment.

The carbene rearrangement is much less influenced by the matrix than the relaxation of **5a** to **2a**. This is an important result because solid state kinetic data are difficult to interpret in terms of their physical significance.

The 1,2-hydrogen shift which we observed is much faster than expected. From extrapolation of the data at room temperature, a rate of 10^{-2} s^{-1} at 80 K is expected. This indicates that tunneling is important at low temperature. The curvature of the Arrhenius plot stands for a change in mechanism, but it does not necessarily stand for a change from a classical mechanism to quantum chemical tunneling—it needs to be emphasized that the curvature appears at temperatures where the matrix softens. A distinct change in mobility of the reactive species might well account for an unproportional increase of the rate constant. Nevertheless, the small temperature dependence of the rate constant and its measurability at low temperatures are signs of a true tunneling reaction. If tunneling takes place in the frozen conformations of the carbene, then it is not surprising that we observe distorted products since they are produced in reactant conformations. Warm-up, only, i.e., softening of the matrix, allows relaxation to the minimum energy conformations.

It is difficult to analyze how the β-chlorostyrenes are formed during precursor photolysis. We can not distinguish between (i) a thermal reaction of "hot" carbene, (ii) the tunneling from the carbene ground state, and (iii) a one step reaction involving extrusion of nitrogen and concomitant rearrangement, all of which, including the possibility of more than one pathway, could account for the initial photoproduct mixture. In analogy to the classical hydrogen shift, tunneling also depends on the conformation of the carbene, i.e., on the distance between the migrating hydrogen and the carbene carbon. One can imagine that part of the carbene molecules with proper conformation undergoes fast tunneling during precursor photolysis, but this is hypothetical. On the other hand, if (iii) is a major pathway in the formation of the styrenes, then our results indicate different barriers for hydrogen and deuterium migration in an excited state of the diazirine.

During $\lambda = 380 \pm 20$ nm irradiation, diazo compound **6** grows in over the entire photolysis time and is stable even after prolonged irradiation and complete destruction of **4**. This indicates that **6** is a minor byproduct rather than an intermediate formed in a photostationary equilibrium.

The difference in thermal stability of singlet benzylchlorocarbene compared with that of triplet phenylethylidene may be interpreted as caused by the different spin states. In solution, a minimum barrier of 4.3 kcal/mol was assessed for the triplet carbene,[1] which is in the range of the value which had been measured for benzylchlorocarbene in solution (4.8 kcal /mol).[18] Tunneling at low temperatures was excluded for the triplet species since it is stable up to 30 K in argon.[9] Intersystem crossing is not necessary in the reaction of the singlet species. Therefore, spin control may play an important role in the triplet molecule, resulting in a minimum activation barrier in the order of magnitude of the singlet–triplet gap.

Summary

Benzylchlorocarbenes **1a–c** have been generated and characterized in low-temperature matrices. Due to a kinetic isotope effect and a higher concentration of the reactive species, the thermal and photochemical 1,2-deuterium shift of **1b** could be followed IR-spectroscopically. The reaction is faster than that expected from extrapolation of the room temperature data, and at very low temperatures, the barrier to the rearrangement decreases. This may be due to tunneling, but no proof can be given. A second thermal reaction was observed and distinguished from the carbene decay. It is interpreted as the thermal relaxation of a primary photoproduct, which is produced in the frozen conformation of the precursor. In the case of the parent compound, benzylchlorodiazirine (**4a**), this photoproduct shows distinct IR absorptions as well as a stereospecific decay and it is therefore assigned the conformation of styrene **5a** with a distorted π-system. As long as the matrix is rigid, this rotamer is stable even to short-wavelength irradiation, but when the matrix softens, **5a** relaxes to (*Z*)-β-chlorostyrene (**2a**).

Experimental Section

The setup for matrix experiments has been described elsewhere.[46] The samples were sublimed at −38 °C (**4a–c**), −20 °C (**4d**, **2d**, and **3d**) and −47 °C (**2a**, **3a**) at 10^{-6} mbar and codeposited with argon (99.9999%) or xenon (99.99%) to form a matrix. **4e** was mixed with argon (1:300) prior to deposition. The purity of other gases used was 99.998% (O_2) and 99.995% (CO_2). CO was used as a 4.5% mixture with nitrogen (all gases by Messer-Griesheim). Infrared spectra were recorded on a Bruker IFS 66 FT–IR spectrometer in the range of 4000–450 cm^{-1}; the standard resolution was set to 1 cm^{-1}. UV–vis spectra were recorded on a Hewlett-Packard 8452A diode array spectrophotometer. Irradiation was performed by using a 500-W high-pressure mercury arc lamp, dichroic mirrors to preselect the range of irradiation, and appropriate cutoff and interference filters.

Kinetics. A Lake Shore Cryotronics DRC 81C temperature controller wired to a DT-500 silicon diode was used to assure the most accurate temperature readout. Care was taken to reach the desired temperature as fast as possible without over shooting. For IR kinetics, peak integrals, and UV kinetics, single-wavelength absorbances as a function of time were fitted to eq 4 by means of a statistics computer program (nonlinear regression).

Sample Preparation. NMR spectra were recorded on Bruker AM 400 and Bruker AC 200 F spectrometers. Melting points are uncorrected. 3-Benzyl-3-chlorodiazirine (**4a**), 3-benzyl-3-bromodiazirine (**4d**), and 3-chloro-3-methyldiazirine (**4e**) were synthesized according to Graham's procedure.[16,47,48] (*Z*)- and (*E*)-β-chlorostyrenes (**2a** and **3a**) were synthesized by means of a Wittig reaction and then separated on a

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preparative GC column.[49] A mixture of the β-bromostyrenes was purchased from JM Alfa Products, and pure (*Z*)-β-bromostyrene (**2d**) was synthesized according to a published procedure.[50,51]

3-Benzyl-3-chlorodiazirine (4a): ^{1}H NMR (200 MHz, CDCl$_3$) δ 7.38–7.18 (m, 5 H), 3.27 (s, 2 H); ^{13}C NMR (50.6 MHz, CDCl$_3$) δ 132.8, 129.5, 128.8, 127.7, 48.4 (diazirine), 43.6; IR (Ar, 10 K) 481.6 (6.1), 573.2 (10.2), 593.9 (4.5), 640.2 (16.4), 644.1 (16.6), 646.5 (20.7), 676.8 (17.2), 702.4 (100), 739.5 (4.7), 757.8 (7.5), 768.9 (10.7), 818.6 (5.3), 912.6 (7.8), 940.1 (38.6), 941.0 (37.3), 963.2 (7.2), 991.2 (8.8), 1001.8 (12.3), 1010.9 (13.2), 1014.8 (18.5), 1032.2 (7.3), 1080.9 (10.8), 1170.0 (6.3), 1334.2 (4.8), 1442.4 (5.2), 1457.9 (21.1), 1499.8 (28.3), 1564.9 (18.1), 1569.2 (15.8), 1803.5 (1.2), 1946.7 (1.1), 2860.3 (1.2), 2925.4 (3.1), 2933.6 (2.9), 2960.6 (1.8), 3041.6 (9.2), 3073.9 (5.4), 3097.1 (4.5), 3120.2 (1.9) cm^{-1} (rel intensity).

(*Z*)-β-Chlorostyrene (2a): IR (Ar, 10 K) 531.7 (14.4), 615.6 (2.7), 668.6 (5.5), 689.4 (29.9), 722.2 (23.2), 779.1 (100), 847.5 (27.8), 913.1 (2.5), 929.0 (2.2), 1031.7 (4.4), 1078.4 (3.8), 1180.7 (3.3), 1338.3 (2.3), 1351.3 (9.8), 1356.6 (18.9), 1449.2 (17.3), 1495.0 (22.4), 1622.8 (7.9), 3035.4 (3.5), 3055.6 (2.7), 3064.3 (2.7), 3079.2 (4.5), 3101.9 (3.4) cm^{-1} (rel intensity).

(*E*)-β-Chlorostyrene (3a): IR (Ar, 10 K): 591.0 (52.5), 688.4 (58.9), 739.5 (100), 806.0 (4.1), 819.5 (71.2), 862.0 (42.1), 936.2 (48.5), 938.1 (48.7), 939.6 (52.3), 1074.6 (4.2), 1249.1 (14.9), 1289.1 (3.2), 1450.6 (17.2), 1500.3 (14.5), 1580.3 (3.1), 1612.6 (23.5), 1615.0 (31.7), 3029.1 (5.2), 3034.9 (6.2), 3066.2 (3.3), 3079.7 (6.1), 3087.9 (10.8) cm^{-1} (rel intensity).

β-Chlorostyrene (5a): IR (Ar, 10 K) 470.5 (5.1), 517.3 (5.4), 523.0 (5.1), 617.1 (5.7), 651.3 (6.6), 653.7 (5.2), 694.2 (100), 709.1 (8.6), 730.8 (13.8), 733.2 (12.8), 735.2 (14.6), 766.0 (32.2), 770.9 (22.5), 852.3 (30.1), 915.5 (7.5), 922.7 (6.6), 950.2 (10.2), 1030.2 (7.5), 1076.0 (9.9), 1340.2 (14.3), 1344.1 (9.7), 1348.9 (7.7), 1447.7 (22.6), 1494.0 (21.2), 1604.0 (8.5), 1630.5 (15.7), 3056.1 (10.8) cm^{-1} (rel intensity).

Phenyldideuterioacetonitrile. Phenylacetonitrile (5 g, 43 mmol) was stirred at room temperature in a mixture of 80 mL (4 mol) of D$_2$O, 5 g of NaCN (0.1 mol) and 20 mL of dry dioxane for 6 h. The mixture was extracted once with 100 mL of dry Et$_2$O, and the organic fraction was dried over Na$_2$SO$_4$. After removal of the ether on a rotatory evaporator, the dioxane was distilled off under reduced pressure. The remaining crude product which contained 10–20% dioxane was directly introduced into the following reaction: ^{13}C NMR (100.6 MHz, CDCl$_3$) δ 129.9, 129.1, 128.0, 127.9, 117.9, 23.1 (quintet, *J* = 21 Hz).

Phenyldideuterioacetimidic Acid Ethyl Ester Hydrochloride was prepared from phenyldideuterioacetonitrile dissolved in 1.1 equiv of EtOD saturated with HCl at 0 °C in 95% yield: mp 90–91 °C dec; ^{1}H NMR (200 MHz, DMSO-*d*$_6$) δ 7.45–7.30 (m, 5 H), 4.47 (quartet, 2 H, *J* = 7 Hz), 1.28 (t, 3 H, *J* = 7 Hz); ^{13}C NMR (50.3 MHz, DMSO-*d*$_6$) δ 177.2, 132.5, 129.3, 129.0, 128.0, 69.6, 13.5. $J^{\text{C-D}}$ was not assessed.

Phenyldideuterioacetamidine Hydrochloride. In a three-necked flask with a gas outlet and a dropping funnel topped with a nitrogen inlet, we placed 20 g of Mg$_3$N$_2$, which was moistened with 5 mL of EtOD. The gas outlet was connected to four traps, the middle two of which were filled with fresh KOH pellets. The whole apparatus was then purged with nitrogen for 10 min. D$_2$O (20 mL) was introduced into the dropping funnel, and the flask was cooled in a water bath. Slowly, three or four drops of D$_2$O were added to the magnesium nitride, causing a violent reaction. Again, nitrogen was passed through the apparatus in a very slow stream for 1–2 min. The end of the gas outlet was then connected to a 50-mL flask in which 16 mL of EtOD were stirred magnetically at 0 °C. D$_2$O (15–20 mL) was added slowly during 90 min to the Mg$_3$N$_2$, and ND$_3$ was bubbled through the EtOD as slowly as possible. When the hydrolysis reaction ceased to be violent, N$_2$ was passed through the apparatus from time to time to blow the remaining ND$_3$ into the EtOD. When the solution was saturated, phenyldideuterioacetimidic acid ethyl ester hydrochloride(3.2 g) was suspended in 4 mL of EtOD and added slowly to the ND$_3$ solution at 0 °C. The mixture was allowed to warm-up to room temperature, and the formed clear solution was stirred for another 2 h. The solvent was evaporated under reduced pressure, and the remaining oil was dried at 10^{-2} mbar over silica gel. Grinding with a drop of dry ether afforded the amidine hydrochloride as a white, crystalline solid in almost quantitative yield: mp 142–146 °C dec; ^{1}H NMR (200 MHz, DMSO-*d*$_6$) δ 7.54–7.48 (m, 2 H), 7.38–7.24 (m, 3 H); ^{13}C NMR (100.6 MHz, DMSO-*d*$_6$) δ 169.0, 134.2, 129.0, 128.6, 127.5. $J^{\text{C-D}}$ was not assessed.

3-Chloro-3-(phenyldideuteriomethyl)diazirine (4b) was prepared by the Graham oxidation of phenyldideuterioacetamidine hydrochloride and subsequent column chromatography on silica gel in 12% yield: ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.35–7.25 (m, 3 H), 7.22–7.18, (m, 2 H); ^{13}C NMR (100.6 MHz, CDCl$_3$) δ 132.7, 129.5, 128.8, 127.7, 48.3 (diazirine), 43.1 (quintet, *J* = 13.5 Hz); the product was contaminated by ca. 7% of monodeuterated diazirine; IR (Ar, 10 K) 555.3 (9.9), 557.8 (10.2), 573.2 (8.9), 619.5 (13.8), 624.3 (25.6), 660.5 (22.9), 698.5 (100), 717.3 (21.3), 727.5 (12.6), 735.7 (12.2), 743.9 (32.9), 795.4 (12.9), 874.5 (92.6), 920.3 (18.6), 984.4 (46.8), 985.4 (47.9), 989.3 (27.5), 996.5 (10.3), 1057.7 (28.2), 1061.1 (22.7), 1075.6 (24.2), 1078.0 (28.2), 1452.1 (31.5), 1453.5 (30.9), 1500.3 (49.6), 1566.8 (38.3), 1570.7 (36.6), 1576.5 (27.1), 1803.5 (11.1), 1946.7 (11.1), 2099.1 (7.8), 2167.5 (8.8), 2220.1 (8.3), 3013.2 (9.5), 3041.6 (24.3), 3063.3 (15.1), 3073.0 (18.5), 3097.1 (17.7), 3119.2 (11.7) cm^{-1} (rel intensity).

Dideuterio-(*Z*)-β-chlorstyrene (2b): IR (Ar, 10 K) 493.2 (49.8), 656.1 (19.8), 689.9 (100), 706.3 (53.6), 724.1 (35.9), 774.2 (57.9), 775.7 (65.7), 915.0 (14.3), 1027.8 (39.5), 1044.7 (59.1), 1219.7 (41.5), 1292.0 (13.1), 1447.7 (45.4), 1490.2 (15.4), 1495.0 (36.7), 1604.0 (34.0) cm^{-1} (rel intensity).

Dideuterio-(*E*)-β-chlorostyrene (3b): IR (Ar, 10 K) 489.3 (12.5), 580.9 (17.7), 661.9 (10.9), 692.8 (100), 789.7 (25.2), 792.1 (22.6), 909.2 (9.2), 929.0 (9.9), 933.3 (9.5), 1011.4 (17.1), 1032.6 (10.9), 1082.3 (12), 1226.0 (13.7), 1448.7 (39.3), 1495.5 (29.1), 1600.4 (34.0) cm^{-1} (rel intensity).

Benzylchlorocarbene-*d*$_2$ (1b): IR (Ar, 10 K) 472.9 (21.8), 522.1 (16.9), 527.9 (14.2), 645.0 (100), 648.4 (70.0), 733.7 (48.4), 737.1 (45.4), 872.2 (24.2), 880.8 (58.6), 899.6 (12.5), 1004.2 (43.3), 1007.6 (76.1), 1029.6 (14.5), 1076.5 (9.7), 1108.8 (53.4), 1450.9 (28.5), 1492.2 (33.3), 2133.3 (10.2) cm^{-1} (rel intensity).

Heptadeuteriobenzyl bromide was prepared by NBS bromination of toluene-*d*$_8$ in a smooth reaction in 75% yield.

Pentadeuteriophenylacetonitrile was prepared by means of a nucleophilic substition of heptadeuteriobenzyl bromide with NaCN in ethylene glycol at 110 °C. After separation of the organic phase, the dark solution was filtrated through silica gel and distilled to afford the product, which had undergone complete H/D exchange at the benzylic positions, in 61% yield.

3-Chloro-3-((pentadeuteriophenyl)methyl)diazirine (4c) was prepared from pentadeuteriophenylacetonitrile in the usual reaction sequence (Pinner synthesis, Graham oxidation) as indicated above: ^{1}H NMR (200 MHz, CDCl$_3$) δ 3.26 (s, 2 H); ^{13}C NMR (100.6 MHz, CDCl$_3$) δ 132.6, 129.1 (t, *J* = 24 Hz), 128.3 (t, *J* = 24.5 Hz), 127.2 (t, *J* = 24.5 Hz), 48.4 (diazirine), 43.5; IR (Ar, 30 K) 543.8 (100), 557.3 (26.5), 612.2 (32.5), 619.5 (34.3), 660.5 (14.2), 665.3 (15.6), 694.7 (25.8), 823.4 (18.9), 842.7 (17.8), 849.0 (47.9), 932.8 (58.5), 935.3 (57.5), 946.8 (40.4), 964.2 (23.1), 977.7 (19.2), 997.0 (18.4), 1008.1 (35.7), 1047.6 (8.3), 1053.4 (12.8), 1058.7 (22.7), 1143.5 (4.7), 1163.3 (13.9), 1171.0 (9.6), 1176.3 (12.2), 1313.2 (11.2), 1343.1 (7.8), 1349.4 (14.1), 1355.7 (9.9), 1392.3 (15.5), 1414.5 (7.9), 1429.4 (13.3), 1434.7 (11.6), 1442.9 (17.4), 1568.3 (61.4), 1580.3 (15.1), 2285.2 (21.6), 2298.7 (12.9), 2752.4 (4.3), 2859.9 (5.6), 2926.9 (10.2), 2959.7 (7.6) cm^{-1} (rel intensity).

Pentadeuterio-(*E*)-β-chlorostyrene (3c): IR (Ar, 10 K) 444.5 (26.1), 485.0 (72.1), 548.1 (100), 574.6 (44.6), 632.5 (22.4), 747.2 (27.2), 769.4 (32.8), 826.8 (70.0), 837.9 (82.8), 864.9 (34.8), 937.2 (85.4), 960.8 (10.2), 1159.0 (10.9), 1225.5 (28.6), 1289.1 (15.3), 1332.0 (13.7), 1337.3 (19.7), 1380.3 (14.3), 1542.7 (13.6), 1569.7 (20.6), 1617.5 (57.1), 2265.0 (6.0), 2282.3 (32.7), 2295.8 (23.2), 2966.9 (15.6), 3026.7 (18.6), 3077.8 (27.7) cm^{-1} (rel intensity).

Pentadeuterio-(*Z*)-β-chlorostyrene (2c): IR (Ar, 10 K) 485.4 (100), 548.6 (88.7), 657.6 (21.9), 700.5 (40.6), 712.5 (75.8), 783.4 (64.3), 807.5 (59.2), 858.6 (92.2), 1041.3 (14.9), 1132.4 (15.8), 1296.4 (17.1), 1629.0 (30.3), 1635.8 (23.2), 2281.8 (23.2), 2295.3 (16.4), 2311.7 (8.6), 2931.7 (9.7), 2966.9 (9.4), 3026.2 (12.3), 3078.3 (15.1), 3108.2 (13.7) cm^{-1} (rel intensity).

3-Benzyl-3-bromodiazirine (4d): ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.36–7.30 (m, 3 H), 7.23–7.21 (m, 2 H), 3.39 (s, 2 H); ^{13}C NMR (100.6 MHz, CDCl$_3$) δ 133.2, 129.5, 128.8, 127.7, 45.9, 39.8 (diazirine); IR (Ar, 10 K) 474.4 (2.9), 546.7 (11.1), 548.1 (13.7), 559.7 (2.7), 566.0 (9.1), 570.8 (33.1), 610.3 (9.2), 613.2 (12.6), 622.4 (5.8), 662.9 (24.9), 675.4 (1.8), 697.1 (66.9), 700.0 (100), 738.1 (9.4), 745.3 (7.2), 765.6 (9.89), 815.2 (12.3), 855.7 (2.6), 900.1 (50.1), 920.3 (20.7), 963.7 (5.0), 965.6 (6.8), 974.3 (6.2), 989.3 (20.5), 996.0 (16.3), 1005.6 (11.5), 1032.2 (11.4), 1079.9 (15.9), 1105.4 (1.1), 1159.9 (5.7), 1426.5 (3.5), 1433.3 (3.5), 1441.5 (5.8), 1457.4 (22.5), 1499.8 (38.4), 1556.7 (5.2), 1570.2 (23.6), 1573.6 (28.7), 2924.0 (3.7), 2961.1 (1.9), 3016.1 (1.5), 3042.1 (13.6), 3073.9 (7.3), 3097.5 (7.9), 3120.2 (3.9) cm^{-1} (rel intensity).

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(*Z*)-β-Bromostyrene (2d): IR (Ar, 10 K) 519.2 (38.4), 578.0 (39.3), 626.2 (13.5), 681.2 (63.4), 690.3 (57.9), 695.6 (57.6), 776.6 (100), 823.4 (37.8), 912.1 (5.9), 927.5 (9.5), 1030.7 (17.7), 1075.6 (8.6), 1158.0 (8.6), 1176.3 (7.1), 1300.7 (8.2), 1321.4 (25.3), 1332.5 (41.1), 1339.3 (43.6), 1346.0 (23.3), 1446.8 (40.9), 1451.1 (26.8), 1493.5 (42.5), 1504.2 (9.8), 1614.6 (21.5), 1620.8 (15.1), 3009.8 (9.9), 3031.5 (11.2), 3077.3 (14.3), 3099.0 (15.7) cm^{-1} (rel intensity).

(*E*)-β-Bromostyrene (3d): IR (Ar, 10 K) 493.2 (13.0), 568.8 (56.5), 689.9 (67.6), 732.8 (100), 754.0 (35.8), 942.0 (58.9), 1002.3 (5.1), 1074.1 (11.9), 1186.0 (5.1), 1197.5 (3.4), 1224.0 (30.6), 1282.4 (11.3), 1447.3 (ca. 50), 1498.9 (33.9), 1578.9 (14.6), 1607.3 (19.4), 1614.6 (47.7), 3010.3 (ca. 10), 3032.9 (ca. 15), 3077.8 (ca. 20) cm^{-1} (rel intensity).

Methylchlorodiazirine (4e): IR (Ar, 10 K) 604.0 (18.7), 607.9 (47.3), 882.7 (48.9), 1100.6 (100), 1201.4 (3.1), 1386.5 (16.7), 1437.6 (21.7), 1441.5 (12.9), 1461.2 (5.9), 1566.8 (17.9), 1572.1 (48.9), 1762.1 (2.9), 2944.2 (5.5), 2990.5 (6.8), 3004.0 (4.9) cm^{-1} (rel intensity).

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