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Adamantylchlorocarbene: characterization and rearrangement to chlorohomoadamant-3-ene

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Abstract: Adamantylchlorocarbene and its ring-expanded product, chlorohomoadamant-3-ene, have been characterized by matrix isolation spectroscopy combined with DFT calculations. © 1998 Elsevier Science Ltd. All rights reserved.

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Ring-expansion of bridgehead diazo compounds and related precursors has been a popular method for production of strained bridgehead olefins.[1,2] Until recent years, it has been generally assumed that such rearrangements proceed via 1,2-carbon migration of the corresponding carbenes. There has been, however, a growing awareness that diazo compounds and diazirines can undergo "direct" rearrangements concertedly with nitrogen loss. Although evidence for these carbene-mimicking reactions has been accumulating most rapidly in photochemically activated systems,[3-5] reports of similar behavior in thermal denitrogenations have begun to appear.[6,7] Because of this mechanistic imitation, investigators have begun to question the inherent tendency of bridgehead carbenes to undergo ring-expansion. In this context, we wish to report the direct low temperature characterization of 1-adamantylchlorocarbene (**6**), and a preliminary investigation of its chemistry. Under matrix isolation conditions, we can directly observe its rearrangement, albeit photochemically induced, to the bridgehead olefin chlorohomoadamant-3-ene (**8**). Inter alia, we also describe modifications on the standard synthesis of chlorodiazirines which may be of use to other workers in the field.

Moss and co-workers[8] have reported the reluctance of adamantane carbonitrile (**1**) to undergo the typical Pinner HCl/EtOH conversion to an imidate salt, from which would be produced the amidinium salt precursor **3** needed for Graham oxidation[9] to the corresponding chlorodiazirine. Although Moss applied Garigipati's[10] methylchloroaluminum amide method to this and a host of other sterically congested nitriles to produce amidiniums, we had developed another route to **3**. Judkins, et al.,[11] have shown that nitriles react readily with hydroxylamine to produce hydroxylamidines, and that these can be reduced readily to amidines. In our hands, this procedure conveniently converted **1** to **2** in 86% yield. As shown in Scheme 1, **2**

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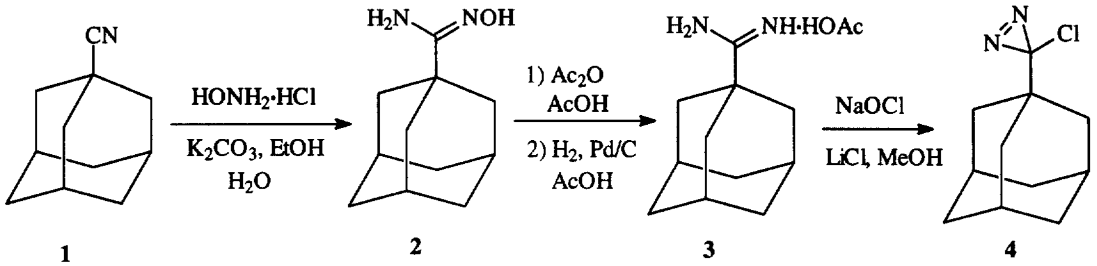
was subsequently acetylated and submitted to hydrogenolysis to give amidinium **3** (54% yield from **2**). We found Graham oxidation[9] of **3** also problematic. Repeated attempts at reaction with NaOCl (5.25% or 12.5%) under standard conditions gave little or no diazirine **4**, and mainly product consistent with N-chloroamidine. We found, however, that changing the reaction solvent from the usual DMSO to methanol gave chlorodiazirine **4** in 75 % yield after flash chromatography. The structure of the diazirine was confirmed by ^{1}HNMR, IR, and UV/vis spectroscopy.

Scheme 1

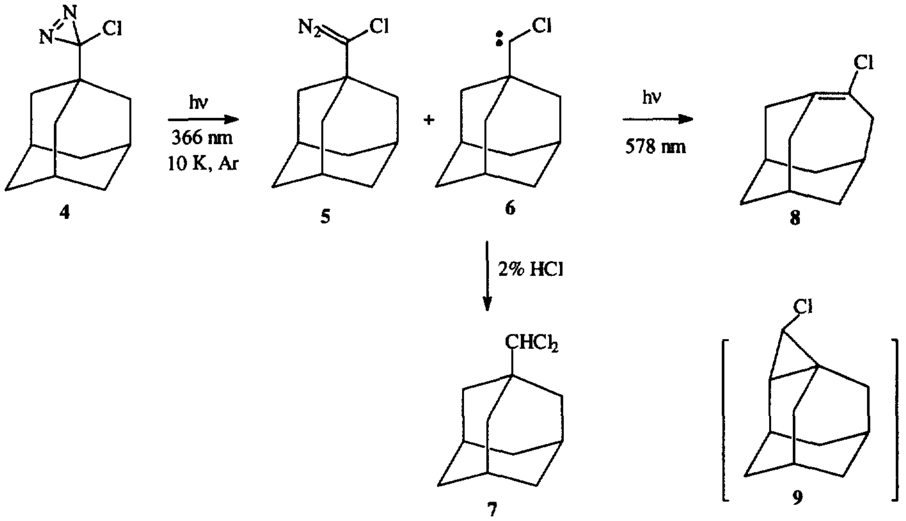


Diazirine **4** was evaporated directly onto a cold CsI window with a large excess of Ar. The 10 K matrix spectra showed IR (1560 cm^{-1}) and UV/vis (342, 348, and 359 nm) bands characteristic for the chlorodiazirine moiety.[12] Irradiation of the matrix at 366 nm caused the disappearance of the starting material IR bands, which were replaced by a set of new absorptions. At the same time, there emerged a broad absorption spanning wavelengths from 450 to 680 nm (λ_{max} 540 nm) in the visible. Although all of the IR bands simultaneously disappeared on subsequent photolysis (vide infra), in situ trapping demonstrated the presence of two photoproducts. Irradiation under the same conditions of an Ar matrix of **4** containing 2% HCl gave an IR which differed from the non-doped spectrum. One set of bands, dominated by a strong absorption at 2042 cm^{-1}, was common to both matrices. By analogy with related compounds, this product is assigned the ring-opened diazo structure **5**. The other IR bands in the HCl-doped spectrum were found to be identical with those of authentic dichloromethyladamantane **7**. Finally, the *absence* of a third set of IR spectra from the HCl-trapping matrix suggests their origin to be carbene **6** (major IR bands at 1452 m, 1142 m, 886 m, 857 m, 777 m, 756 s, 699 m cm^{-1}. These experiments are summarized in Scheme 2.

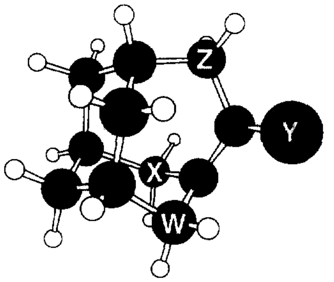
DFT calculations[13] confirmed the assignment of the IR spectra of carbene **6**. B3LYP/6-31G** geometry optimization gave a structure for **6** that was quite similar to that we have described previously[14] for *t*-butylchlorocarbene. In both, the carbenic centers tilt somewhat toward one adjacent CH bond. The UV/Vis spectra for both carbenes also span approximately the same wavelengths. The IR spectrum predicted by the calculations, with frequencies scaled by a factor of 0.96, gave an excellent fit to the experimental bands that disappeared on HCl trapping.

Irradiation of the argon matrix containing the diazo/carbene mixture with visible light caused the simultaneous disappearance of both compounds and the production of a new photoproduct with a medium intensity IR band at 1599 cm^{-1} (other major IR bands at 1452 s, 1268 m, 1061 m, 986 s, 718 s, 643 s, and 614 s cm^{-1}). Irrespective of wavelength of irradiation, no selective photodestruction of the IR absorptions of **5** or **6** could be discerned. B3LYP/6-31G** calculations predicted an IR spectrum for chlorohomoadamant-3-ene **8** that was satisfyingly congruent with the observed experimental intensity and frequencies. It is an open question whether diazo **5** gives carbene **6** in route to **8**.

Scheme 2



Containing a *trans*-cycloheptene ring structure, homoadamant-3-ene itself is unstable toward dimerization, and has only been observed at 77 K.[15] Others have shown, however, that steric protection[16] or conjugative stabilization[17] can render these strained compounds stable at or even above room temperature. The DFT calculations (Figure 1) indicate significant olefinic twisting/pyramidalization in the chlorocompound **8**, consistent with the observed C=C stretching frequency of 1599 cm^{-1} (similar to 1610 cm^{-1} in the parent homoadamantene).[15]



<WCCY = 37°
<WCCZ = 113°
<XCCY = 176°
<XCCZ = 34°

Figure 1. B3LYP/6-31G** calculated geometry for **8**, with olefinic dihedral angles listed.

We have reported previously that *t*-butylchlorocarbene undergoes intramolecular CH insertion via tunneling at even 10 K; only a small amount of methyl-shift was observed photochemically.[14] B3LYP calculations indicate that the corresponding CH-insertion product in this system, tetracycle **9**, should be only 9.8 kcal/mole higher in energy than **8**. Judging by the calculated IR spectrum, however, we do not observe **9** in matrix irradiations of the adamantyl carbene **6**, although it would be difficult to rule out the presence of minor amounts of this product. We speculate that the geometric constraints in **6** do not permit CH insertion to compete with ring expansion, despite the geometric similarities with *t*-butylchlorocarbene. This point, as well as the chemistry of homoadamantene **8**, is still under investigation.

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