The nucleophilicity of 3, coupled with the low C=C rotational barriers,[11] suggests that zwitterionic resonance forms $Re^+=CH-C^-HR$ contribute significantly to the ground state of 3. In view of the established geometry of the d donor orbital on rhenium,[5b] we propose that electrophilic attack occurs via the conformers I and II shown in Figure 1. These conformers would yield *ac* and *sc* Re=C isomers, respectively.

The feasibility of effecting 1,3-asymmetric induction was first assayed by treating *E*-**3b** with 1.03 equiv of CF_3SO_3D in CD_2Cl_2 at −75 °C. The relative NMR integrations of the β-hydrogens in the resulting *ac*-**2b**-β-d_1 indicated a (76 ± 5):(24 ± 5) ratio of diastereomers. Thus protonation occurs preferentially upon one C=C face of I. By analogy to the behavior of other $(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(X)$ compounds,[5b,6] we suggest that the face anti to the PPh_3 ligand is more reactive (Figure 1). However, analysis of the *E*-**3b**/CF_3SO_3D reaction is complicated by the formation of some *sc*-**2b**-β-d_1 (vide supra) and **2b**-β-d_2 (ca. 20%), so we sought a carbon–carbon bond-forming reaction in which to measure stereoselectivity.

Reaction of *E*-**3b** (0.1 M in CH_2Cl_2, −25 °C, 15 min) with 10 equiv of CH_3SO_3F gave, after workup at −25 °C, isobutylidene *ac*-$[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(=CHCH(CH_3)_2)]^+SO_3F^-$ (*ac*-**4**, only one Re=C isomer observed) as a thermally unstable oil of >95% ^1H NMR purity in 65% spectroscopic yield. Two CH_3 ^1H NMR resonances[9] were present. The corresponding reaction of *E*-**3b** with CD_3SO_3F was ^1H NMR monitored. Initial equilibration of *E*-**3b** to the 84:16 *E*/*Z* mixture occurred, followed by methylation to *ac*-**4**-γ-d_3 (Scheme I). Integration of the CH_3 ^1H NMR resonances indicated a (92 ± 2):(8 ± 2) ratio of diastereomers. The major diastereomer was assigned the (*SS*,*RR*) configurations by assuming (as reasoned above) the mode of attack upon I shown in Figure 1.

The isolation of **4** was complicated by two factors. First, as in enolate and enamine chemistry,[12] polyalkylation/proton transfer side reactions occurred when careful conditions were not followed. This problem could be circumvented by deprotonating (10 equiv $t\text{-}BuO^-K^+$) crude **4** to $(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CH=C(CH_3)_2)$ (**5**, 60% isolated).[9] Treatment of **5** with HBF_4·ether at −78 °C gave pure solutions of **4**. Second, **4** underwent a stereoselective isobutylidene → isobutylene (**6**, 73% isolated) rearrangement near room temperature (Scheme I).

The rearrangement **4** → **6** followed the rate law $d[\mathbf{4}]/dt = -k_{obsd}[\mathbf{4}]$. Data obtained in CD_2Cl_2 at 276, 288, 293, and 298 K gave $\Delta H^\ddagger = 20.4 \pm 1.4$ kcal/mol and $\Delta S^\ddagger = -2.7 \pm 0.3$ eu. Rearrangement of the 92:8 mixture of **4**-γ-d_3 diastereomers gave **6**-d_3 with 89 ± 3% of the CD_3 label in the upfield (^1H NMR)[5c,9] methyl site. Rearrangement of **4**-α-d_1 (prepared via **2b**-α-d_1;[5c] H* in Scheme I) gave **6**-d_1 with 91 ± 5% of the D label in the downfield =CHH′ site. Homonuclear NOE experiments on **6** showed the downfield CH_3 to be cis to the downfield =CHH′ hydrogen. Hence the hydrogen migrates to a position cis to the pro-*S* methyl group of **4**. The conversion **4** → **6** is reminiscent of a Wagner–Meerwein-like 1,2-hydrogen shift, but the high stereoselectivity suggests that $\pi_2s + \sigma_2a$ (Re=C/CH) or $\pi_2a + \sigma_2s$ mechanisms should be considered. Recently, several unstable alkylidene complexes have been observed to decompose similarly.[3c,d,13]

Vinyl complexes **3a–c** underwent reactions with other classes of electrophiles. Treatment of **3b** and **3c** with peracid *m*-$ClC_6H_4CO_3H$ in $CHCl_3/K_2CO_3$ gave carbon-bound rhenium enolates (or β-oxoalkyls) $(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2COR)$ (R = CH_3, **7b**; R = *n*-C_3H_7, **7c**)[9] in 40–50% yields. One possible pathway for this transformation would entail heterolytic opening of an epoxide intermediate to a $Re^+=CHCHRO^-$ species, followed by a 1,2-hydride migration similar to **4** → **6**. Complexes **3a–c** are also attacked by electrophilic olefins and metal alkylidenes; details of these reactions will be reported separately.

In summary, we have shown that chiral vinyl rhenium complexes can undergo electrophilic attack with appreciable 1,3-asymmetric induction. Although **3a–c** react only with strong electrophiles, it can be predicted that $L_nM_{asym}\text{-}C(X)=CHR$ species of greater nucleophilicity (e.g., X = oxygen substitutent)[14] should be of considerable value in synthesis. Finally, a two-step alkene → alkylidene rearrangement has recently been proposed as an initiating step in olefin metathesis.[15] In view of the microscopic reverse of **4** → **6**, such transformations could well be concerted and stereoselective.

Acknowledgment. We thank the Department of Energy and the NIH (GM 29026-01) for supporting the synthetic and stereochemical aspects of this study, respectively. FT NMR spectra were recorded on spectrometers obtained via NSF departmental instrumentation grants.

Supplementary Material Available: Tables of spectroscopic and other characterization of **3–7** (4 pages). Ordering information is given on any current masthead page.

---

[10] Neutral heteroatom-substituted carbenes such as $(CO)_5Cr=C(OCH_3)CH_3$ have acidities comparable to phenols: Casey, C. P.; Anderson, R. L. *J. Am. Chem. Soc.* **1974**, *96*, 1230.

[11] Facile C=C rotation has also been noted in $RCH=CHNR^-$ compounds ($\Delta G^\ddagger$ = 17–22 kcal/mol. Lee, J. Y.; Lynch, T. J.; Mao, D. T.; Bergbreiter, D. E.; Newcomb, M. *J. Am. Chem. Soc.* **1981**, *103*, 6215) and $(\eta\text{-}C_5H_5)Fe(CO)(PPh_3)(CR=CHR)$ complexes.[3a]

[12] House, H. O. "Modern Synthetic Reactions", 2nd ed.; W. A. Benjamin: Menlo Park, CA, 1972; pp 546–586.

[13] (a) Marsella, J. A.; Folting, K.; Huffman, J. C.; Caulton, K. G. *J. Am. Chem. Soc.* **1981**, *103*, 5596. (b) Brookhart, M.; Tucker, J. R.; Husk, G. R. *Ibid.* **1983**, *105*, 258.

[14] (a) Theopold, K. H.; Becker, P. N.; Bergman, R. G. *J. Am. Chem. Soc.* **1982**, *104*, 5250. (b) Aktogo, N.; Felkin, H.; Davies, S. G. *J. Chem. Soc., Chem. Commun.* **1982**, 1303. (c) Liebeskind, L. S.; Welker, M. E. *Organometallics* **1983**, *2*, 194.

[15] Iwasawa, Y.; Hamamura, H. *J. Chem. Soc., Chem. Commun.* **1983**, 130.

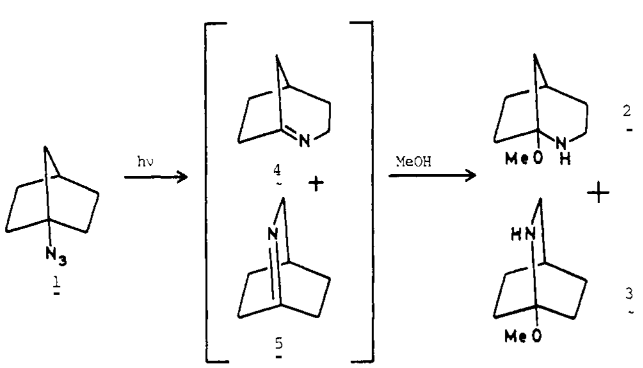
Observation of 2-Azabicyclo[3.2.1]oct-1-ene, a Highly Reactive Bridgehead Imine

Robert S. Sheridan*[1] and George A. Ganzer

S. M. McElvain Laboratories of Organic Chemistry
Department of Chemistry, University of Wisconsin
Madison, Wisconsin 53706

Received March 14, 1983

Interest in compounds containing bridgehead imine functionality has recently surged. In 1971 Reed and Lwowski[2] reported that irradiation of 1-azidobicyclo[2.2.1]heptane (**1**) in methanol gave adducts **2** and **3** in the ratio of 2:1, consistent with trapping of imines **4** and **5**. Whether or not a discrete nitrene is involved in these rearrangements is an open question, although some evidence points toward alkyl migration in concert with nitrogen loss.[3] In subsequent years similar evidence has accumulated for a number of anti-Bredt imines, generated by thermal and photo-



---

[1] Recipient of a Camille and Henry Dreyfus Foundation Grant for Newly Appointed Young Faculty in Chemistry.

[2] Reed, J. O.; Lwowski, W. *J. Org. Chem.* **1971**, *36*, 2864.

[3] Kyba, E. P.; Abramovitch, R. A. *J. Am. Chem. Soc.* **1980**, *102*, 735.

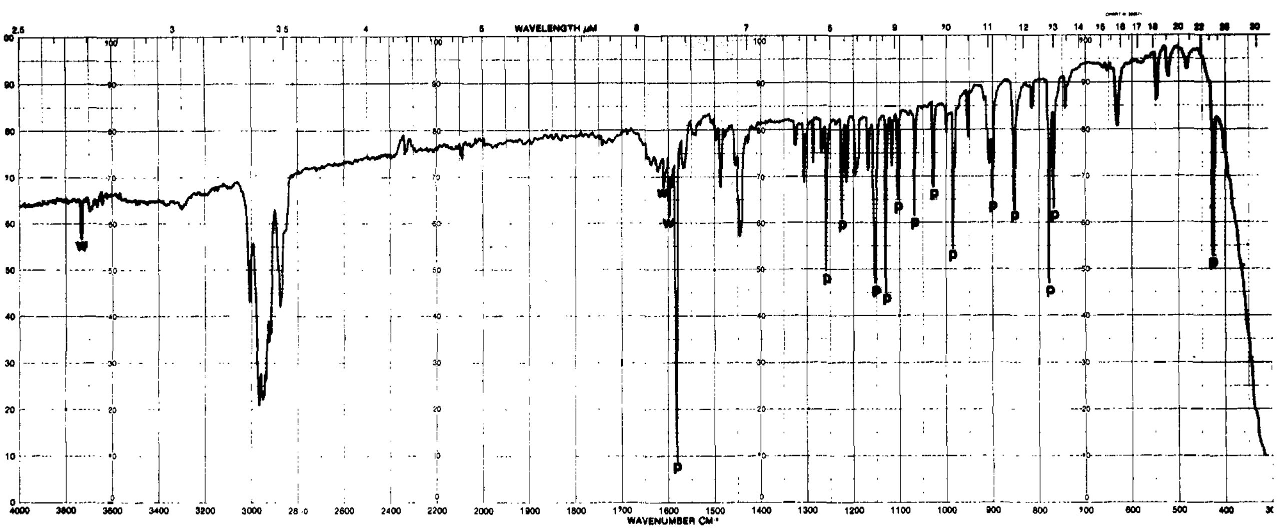


Figure 1. Infrared spectrum obtained on irradiation (λ >270 nm) of 1-azidobicyclo[2.2.1]heptane, matrix isolated in argon at 10 K. Absorptions marked P are tentatively assigned to 2-azabicyclo[3.2.1]oct-1-ene (**4**), those marked W are due to H_2O, and unlabeled absorptions are assigned to **4** or **5** (see text).

chemical decomposition of bridgehead azides.[4-8] The only bridgehead imines observed by conventional methods, however, have been those compounds formally comprising (*E*)-azacyclooctenes[7,9] (see, however, ref 16). We wish to report the first spectral characterization of 2-azabicyclo[3.2.1]oct-1-ene (**4**), a remarkably reactive imine.

Irradiation (λ >270 nm) of 1-azidobicyclo[2.2.1]heptane (**1**),[10] matrix isolated in argon (1:700)[11] at 10 K, produces an infrared spectrum with the most intense peak at 1585 cm^{-1} (Figure 1). A 1585-cm^{-1} absorption suggests the presence of a highly strained $C{=}N$ double bond. Trapping experiments confirm this possibility. Azide **1** was irradiated (λ >270 nm) in an argon matrix containing methanol (Ar:MeOH:**1** = 500:5:1). Although the methanol bands obscured several of the product absorptions in the IR spectrum, the major portion of the spectrum was identical with that obtained in the absence of methanol. Warming the window to 210 K to remove Ar and MeOH left neat material that exhibited IR bands closely matching those of independently synthesized **2**.[10] In addition, several small bands due to the isomeric product **3**[10] could be discerned. Gas–liquid-phase chromatography (7.5 ft × 0.32 cm Carbowax 20 M + 5% KOH on Chrom P; FID detection) of this material gave a ratio of **2** to **3** of 13/1, which was consistent with the ratio estimated by IR. The conversion of the 1585 cm^{-1} species to adduct **2** could be directly observed in a less volatile matrix. The photoproducts were generated photochemically at 65 K, by procedures similar to those above, in a 3-methylpentane matrix containing methanol. Warming to 100 K caused a slow decrease in the 1585 cm^{-1} band with concomitant growth of the bands of **2**.

The above results clearly show that the predominant species generated on photolysis of **1** is 2-azabicyclo[3.2.1]oct-1-ene (**4**). The most intense absorption of **4**, appearing at 1585 cm^{-1}, is ca. 80 cm^{-1} lower in energy than the $C{=}N$ stretch in monocyclic imines with similar substitution. For example, 1-aza-2-methylcyclohept-1-ene exhibits a $C{=}N$ stretch at 1665 cm^{-1}.[12] This shift to lower energy is similar to that reported for the $C{=}C$ stretch of homoadamant-3-ene[13] (1610 cm^{-1} vs. 1673 cm^{-1} in 1-methylcyclohept-1-ene) and is consistent with lowered π-overlap in the strained double bonds.

Our methanol trapping experiments indicate the presence of a minor amount of the isomeric compound **5**. All of the product IR absorptions were stable to further irradiation with shorter wavelength light, and none of the bands showed selective disappearance on warming. The bands of **4** and **5** (other than the 1585-cm^{-1} band) can thus not be distinguished on the basis of differing reactivity. It is possible, however, to attribute a number of the absorptions to imine **4**. Absorptions corresponding to analogous deformations in **4** and **5** would be expected to have similar molar absorptivities. Since the trapping experiment indicates a ratio of **4** to **5** of 13, the bands from **5** would be expected to be on the order of 1/13 of the intensity of corresponding bands from **4**. Hence, the most intense absorptions below 1400 cm^{-1}, including bands at 1260, 1225, 1155, 1150, 1130, 1105, 1070, 1030, 985, 900, 855, 780, 770, and 425 cm^{-1}, can be tentatively ascribed to title compound **4**. The absorptions at 1565, 1485, and 1445 cm^{-1} are of an appropriate intensity and in a reasonable energy region for the $C{=}N$ stretch of **5**, although more certain assignment cannot presently be made. The remaining bands in the spectrum cannot be assigned with confidence.

A major point of interest is the dramatic reactivity of **4** with methanol even at 100 K. This represents a striking contrast to the less-strained bridgehead imines 4-azatricyclo[5.3.1.1^{3,9}]dodec-3-ene and 5-azatricyclo[4.4.1.1^{3,9}]dodec-6-ene, which do not react with methanol at room temperature.[7] Maier and Schleyer[14] have noted an empirical correlation between the olefinic strain (OS) of bridgehead olefins and chemical reactivity. Olefins with OS values greater than or equal to 21 kcal/mol are predicted to be "unstable", requiring extremely low temperatures for observation. Although force-field calculations have not been reported for the bridgehead imines, Maier and Schleyer[14] calculate OS values of 28.6 and 40.4 kcal/mol for the hydrocarbons corresponding to **4** and **5**, respectively. These values are consistent with the high reactivity found for **4**. The olefinic strain energy for (*E*)-bicyclo[3.2.1]oct-1-ene is calculated to be 42 kcal/mol[14] and the inversion barrier for simple trisubstituted imines is estimated to be ca. 30 kcal/mol.[15] Since the strain of **4** should be similar

---

[4] 1-Azidobicyclo[2.2.2]octane: Quast, H.; Seiferling, B. *Liebigs Ann. Chem.* **1982**, 1553.

[5] 1-Azidoadamantane: Quast, H.; Eckert, P. *Liebigs Ann. Chem.* **1974**, 1727.

[6] 9-Azidotriptycene: Quast, H.; Eckert, E. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 168.

[7] 3-Azidohomoadamantane: Sasaki, T.; Eguchi, S.; Hattori, S.; Okano, T. *J. Chem. Soc., Chem. Commun.* **1981**, 1193.

[8] 1-Azidobicyclo[3.2.1]octane: Becker, K. B.; Gabutti, C. A. *Tetrahedron Lett.* **1982**, *23*, 1883.

[9] A polycyclic compound containing the 2-azabicyclo[3.3.1]non-1-ene system generated by oxidn. of an alkaloid has been reported by: Toda, M.; Hirata, Y.; Yamamura, S. *J. Chem. Soc., Chem. Commun.* **1970**, 1597.

[10] Synthesized by the procedure reported in ref 2.

[11] Matrix-isolated samples were prepared by gas-phase deposition onto a 2.54-cm CsI window cooled by an Air Products, Inc., Displex 202 refrigerator. Irradiations were performed with a Varian EIMAC 300-W high-pressure Xe arc illuminator, using appropriate cutoff filters.

[12] Bielawski, J.; Brandänge, S.; Lindblom, L. *J. Heterocycl. Chem.* **1978**, *15*, 97.

[13] Martella, D. J.; Jones, M., Jr.; Schleyer, P. v. R.; Maier, W. F. *J. Am. Chem. Soc.* **1979**, *101*, 7634.

[14] Maier, W. F.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1981**, *103*, 1891.

to that of the corresponding hydrocarbon, any (*E*)-**4** formed would isomerize to (*Z*)-**4**, even at 10 K. We thus suggest that the IR spectrum of **4** corresponds to the *Z* isomer. Further work to distinguish the spectra and properties of **4** and **5** is in progress.[16,17]

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the Camille and Henry Dreyfus Foundation for support of this work. The infrared spectrometer was purchased in part with funds from the National Science Foundation (Grant CHE-8117318). G.A.G. thanks Du Pont for a summer research assistantship. We also thank Professor C. P. Casey for the use of an analytical gas chromatograph.

---

(15) For ab initio calculations on methanimine's inversional barrier and pertinent references see: Lang, T. J.; Wolber, G. J.; Bach, R. D. *J. Am. Chem. Soc.* **1981**, *103*, 3275. The barrier for **4** may be higher, however, since only limited linearization at N can occur.

(16) As this work was completed we learned that Prof. J. Michl and co-workers have obtained similar results in the photolysis of 1-azidoadamantane to generate matrix-isolated 4-azahomoadamant-3-ene. The infrared spectrum of 4-azahomoadamant-3-ene exhibits a C=N stretch at 1602 cm^{-1}, ca. 15 cm^{-1} higher in energy than the corresponding stretch in **4**. This difference in stretching frequencies is gratifyingly consistent with the calculated differences in olefinic strain values calculated for the corresponding hydrocarbons;[14] OS = 20 kcal/mol for 3-homoadamantene, and OS = 29 kcal/mol for (*Z*)-bicyclo[3.2.1]oct-1-ene. Interestingly, azahomoadamantene is destroyed photochemically under matrix-isolation conditions, in contrast to **4** and **5**, which are photostable. The reason for this difference in excited-state behavior is not known. The above results have recently appeared: Michl, J.; Radziszewski, G. J.; Downing, J. W.; Wiberg, K. B.; Walker, F. H.; Miller, R. D.; Kovacic, P.; Jawdosiuk, M.; Bonacic-Koutecky, V. *Pure Appl. Chem.* **1983**, *55*, 315. We thank Prof. Michl for communicating these results to us prior to publication.

(17) A referee has questioned whether **4** might not be the corresponding nitrene. The nitrene, however, would not be expected to show a major absorption at 1585 cm^{-1} but would rather appear similar to the IR of 1-norbornylamine. Moreover, the addition product of methanol with **4** is not consistent with the chemistry expected for a nitrene.[2,3]

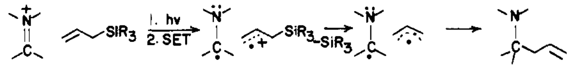
Sequential Electron-Transfer–Desilylation Pathways for *C*-Vinylazomethine Ylide Formation in the Photochemistry of (1-(Triethylsilyl)allyl)iminium Salts

Shyh-fong Chen, John W. Ullrich, and Patrick S. Mariano*

Department of Chemistry, University of Maryland
College Park, Maryland 20742

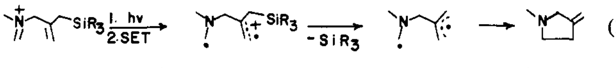
Received May 23, 1983

Studies in our laboratory over the past several years have concentrated on two interconnected aspects of iminium cation photochemistry concerned with the development of mechanistic principles for electron-transfer-initiated photoreactions and explorations for new and synthetically useful photochemical transformations.[1] Several observations made in our recent study of allylsilane–iminium salt systems have demonstrated the mechanistic features of photoaddition reactions initiated by electron transfer and driven by desilylation of allylsilane-derived cation radicals (eq 1).[2] Further investigations have shown that



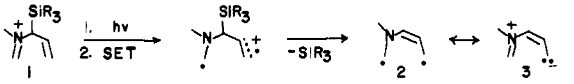
(1)

this process serves as the basis for a synthetically useful method for photocyclization (eq 2).[3] Our continuing interests in transformations that follow sequential electron-transfer–desilylation



(2)

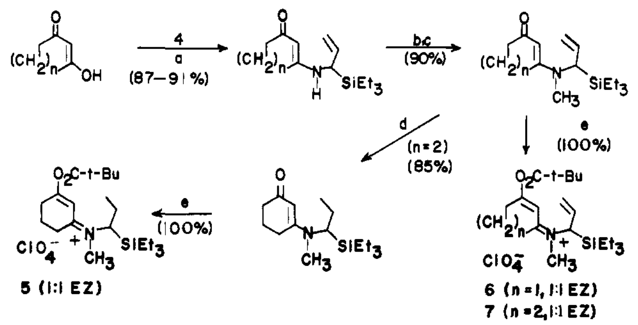
pathways are kindled by thoughts about the development of useful procedures for forming interesting reactive intermediates. With this aim in mind, we envisaged that the operation of pathways of this type in the excited-state chemistry of (1-(trialkylsilyl)-allyl)iminium salts **1** would serve to generate species that can be formulated as diradicals **2** or, if produced in the ground-state singlet manifold, as C-vinylazomethine ylides **3** (eq 3). Trans-



(3)

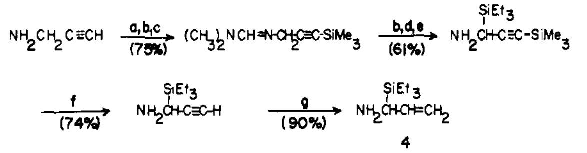
formations based upon this design would represent fundamentally important methods for the prepartion of conjugated ylides like **3** and would serve to further verify the generality of electron-transfer–desilylation pathways in excited-state chemistry. The hypothesis embodied in eq 3 has been successfully tested through studies with the β-enaminone-derived ((triethylsilyl)allyl)iminium perchlorates **6** and **7** and the saturated analogue **5**.

Scheme I



(a) C_6H_6, ref; (b) *n*-BuLi, THF, −78 °C; (c) CH_3I, 25 °C, 1 h; (d (d) H_2, Pd/C, EtOAc, 30 psi; (e) *t*-BuCOCl, $AgClO_4$, CH_3CN.

Scheme II



(a) $(CH_3)_2NCH(OCH_3)_2$, ref, 3 h; (b) *n*-BuLi, −78 °C TMSCl, 25 °C, 1 h; (d) TESCl, 25 °C, 1 h; (e) N_2H_4, *t*-BuOH, 25 °C, 15 h; (f) LiOEt, 25 °C, 10 h; (g) H_2, Pd/$CaCO_3$, Pb pois, THF, 1 atm.

Synthetic routes for preparation of the required allyliminium perchlorates are outlined in Scheme I.[4] The key starting material, and one that will find general use in the preparation of a variety of compounds in this class,[5] is the 1-(triethylsilyl)allylamine **4**. A short, efficient procedure for preparation of **4**, patterned after one employed by Barth and Kolb[6] for unsaturated amino acid synthesis, has been developed starting with propargylamine (Scheme II).[7] It should be noted that selection of the triethylsilyl rather than trimethylsilyl substituents in the iminium salts is dictated by the instability of substances containing the latter grouping under desilylation conditions used for terminal acetylene liberation (Scheme II).

Irradiations of acetonitrile solutions of the allyliminium perchlorates **6** and **7** with light of λ >280 nm followed by treatment of the photolysates with aqueous $NaHCO_3$ and silica gel chro-

---

(1) For a recent summary of these chemical studies see: Mariano, P. S. *Acc. Chem. Res.* **1983**, *16*, 130.

(2) Ohga, K.; Mariano, P. S. *J. Am. Chem. Soc.* **1982**, *104*, 617.

(3) Tiner-Harding, T.; Ullrich, J. W.; Chiu, F. T.; Chen, S. F.; Mariano, P. S. *J. Org. Chem.* **1982**, *47*, 3360.

(4) All new compounds have satisfactory spectroscopic properties and elemental compositions.

(5) Iminium salt preparation can occur by addition of electrophiles to nitrogen of imines derived by reaction of amine **4** with carbonyl compounds.

(6) Kolb, M.; Barth, J. *Tetrahedron Lett.* **1979**, 2999; *Angew. Chem.* **1980**, *19*, 725.

(7) Characteristic spectroscopic properties of the allyliminium perchlorates are as follows. **7**: UV (CH_3CN) λ_{max} 285 nm (ε 15 500); ^1H NMR ($CDCl_3$) δ 6.78, 6.70 (OC=CH), 4.53, 4.43 (NC*H*TES), 3.58, 3.49 (NCH_3). **6**: UV (CH_3CN) λ_{max} 279 nm (ε 20 200); ^1H NMR ($CDCl_3$) δ 6.82, 6.81 (OC=C-H), 4.49, 4.38 (NC*H*TES), 3.51, 3.45 (NCH_3).

0002-7863/83/1505-6160$01.50/0