Although both are highly strained, the latter is less so for here the natural bond directions from the norbornane subunit are more appropriately aligned to form the 4-membered ring. We are trying now to prepare and compare the two parent olefins.

Norrish type I photochemical cleavage of C3–C4 in ketone **10** might initiate loss of ketene.[9] Were this to occur, the other product could be the long-sought, but still unknown, anti-Bredt olefin $\Delta^{1(7)}$-norbornene. Ultraviolet irradiation of **10** in methylene chloride in fact gave a ketene, but this was identified as **14**. When the reaction was repeated in the presence of methanol the only isolable product was the corresponding ester. Clearly preferential cleavage occurred at C2–C3 rather than C3–C4. Perhaps additional substitution at C4, available via the ketone enolate, will reverse this in our favor.

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Arene–Iminium Salt Photochemistry. Dramatic Effects of Sequential Electron-Transfer–Desilylation Pathways on the Nature and Efficiency of Photoaddition and Photocyclization Processes

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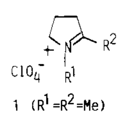
Previously, we have shown how photoinduced, sequential electron-transfer–desilylation pathways serve as a method for regioncontrolled generation of carbon radical and diradical species. We have provided examples of this process in routes for construction of heterocyclic systems.[1c–e,2] Recent efforts have focused on photoreactions of arene–iminium salt systems in which the aromatic electron donors contain benzylic hydrogens or trimethylsily groups[3] and where excitation of either the iminium salt or arene would initiate electron transfer. The resulting charged radical pairs possess the capability of being transformed to radical precursors of addition products by deprotonation or desilylation of the arene cation radical partners (Scheme I). Our preliminary investigations of inter- and intramolecular variants of toluene–pyrrolinium salt photoprocesses following electron-transfer mechanisms have provided results which show that (1) photoaddition and photocyclization reactions are initiated by excitation of either the arene or iminium salt chromophores, (2) relative rates of arene cation radical desilylation vs. deprotonation have a dramatic effect upon the nature and efficiency of reactions followed, and (3) photocyclizations of *N*-xylyliminium salts promoted by electron transfer are useful in the synthesis of N-heterocyclic substances.

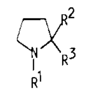
Qualitative and quantitative aspects of arene–iminium salt photoaddition reactions were explored with use of the pyrrolinium perchlorates **2**,[4] **3**,[1a,b] and **1**,[5] and the arenes, toluene (**4**) and benzyltrimethylsilane (**5**). Evidence for the operation of electron-transfer pathways in these systems derives from fluorescence quenching studies. Substituted benzenes, including **5**, and para-substituted toluenes serve as quenchers of iminium salts **2** and **3** fluorescence with quenching rate constants that parallel arene oxidation potentials[6] and approach diffusion control when $\Delta G_{SET} < 0$.[7] Likewise, the fluorescence of arenes such as **4** and **5** is quenched (k_q ca. 5×10^9 M^{-1} s^{-1}) by the nonconjugated iminium salt **1**.[6] Reverse electron transfer is the likely quenching mechanism in these cases since exchange energy transfer should be highly endoergic. Finally, the absence of phenylpyrrolinium salt and arene fluorescence in the xylylpyrroliium perchlorates **12–15** signals the operation of intramolecular electron transfer in their singlet manifolds.



1 ($R^1=R^2=Me$)
2 ($R^1=H$, $R^2=Ph$)
3 ($R^1=Me$, $R^2=Ph$)

$PhCH_2$-E

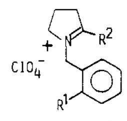
4 (E=H)
5 (E=TMS)



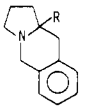
6 ($R^1=R^2=Me$, $R^3=PhCH_2$)
7 ($R^1=R^2=Me$, $R^3=H$)
8 ($R^1=R^2=Me$, $R^3=CH_2OH$)
9 ($R^1=H$, $R^2=Ph$, $R^3=PhCH_2$)
10 ($R^1=Me$, $R^2=Ph$, $R^3=PhCH_2$)

$PhCH_2CH_2Ph$

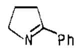
11



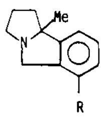
12 ($R^1=Me$, $R^2=Ph$)
13 ($R^1=CH_2TMS$, $R^2=Ph$)
14 ($R^1=Me$, $R^2=Me$)
15 ($R^1=CH_2TMS$, $R^2=Me$)
16 ($R^1=H$, $R^2=Me$)



17 (R=Ph)
18 (R=Me)



19



20 (R=Me)
21 (R=H)

Irradiation (λ > 240 nm) of either arene **4** or **5** in MeOH solutions containing iminium salt **1** followed by base treatment and chromatography leads to products, **6–8** and **11** (Table I), which appear to arise via the intermediacy of 1,2-dimethyl-2-pyrrolidinyl and benzyl radicals.[8] Similarly, photoreactions induced by irradiation (λ > 280 nm) of the salts **2** and **3** in MeOH solutions of arenes **4** or **5** result in formation of the respective radical coupling products **9**, **10**, and **11** (Table I).[8] A combination of fluorescence quenching and reaction quantum yield data has yielded information about the multiplicities of the reacting excited states. A close correspondence[9] exists between the Stern–Volmer quenching constants ($k_q\tau$) and intercept to slope ratios, obtained from plots of the reciprocals of product formation quantum yields vs. reciprocals of arene (for irradiation of **2**) or iminium salt **1** (for irradiation of **4** and **5**) concentrations. This suggests that the fluorescence quenching and photoaddition processes involve the same (i.e., singlet) excited states.

The nature and efficiencies of photoreactions of the *N*-xylylpyrrolinium perchlorates **12–15**[10] display a remarkable dependence

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(2) Brumfield, M. A.; Quillen, S. L.; Yoon, U. C.; Mariano, P. S., unpublished results.

(3) (a) The electron-transfer sensitized photochemistry of benzylstannanes has been probed by Eaton.[3b] (b) Eaton, D. F. *J. Am. Chem. Soc.* **1981**, *103*, 7235.

(4) Stavinoha, J. L.; Mariano, P. S. *J. Am. Chem. Soc.* **1981**, *103*, 3136.

(5) This salt was prepared by N-methylation with MeI followed by ClO_4^- exchange on Dowex-X-1.

(6) Rate constants (10^9 M^{-1} s^{-1}) for **2** fluorescence quenching (MeCN at 25 °C) by *p*-X-PhMe (OMe, 7.8; Me, 5.9; Br, 5.5; Cl, 4.8; H, 4.9; F, 4.4) and by X-Ph (Cl, 6.6; OMe, 6.6; H, 3.9; CF_3, 6.9; CH_2Me_3Si, 8.5) and for quenching by **1** of arene fluorescence ($PhCH_2Me_3Si$, 1.0; PhMe, 2.6; 2-Me-naphthalene, 4.3).

(7) (a) Free energies for electron transfer (ΔG_{SET}) are calculated[7b] by use of the following data: for **4** $E_{1/2}(+) = 1.98$ eV and $E_{0,0}^{S_1} = 4.6$ eV; for **5** $E_{1/2}(+) = 1.78$ eV and $E_{0,0}^{S_1} = 4.4$ eV; for **1** $E_{1/2}(-) = -2.2$ eV; for **2** $E_{1/2}(-) = -0.93$ eV and $E^{S_1} = 4.3$ eV. (b) Rehm, D.; Weller, A. *Isr. J. Chem.* **1970**, *8*, 259.

(8) All new compounds gave spectroscopic and molecular formula data in complete accord with the assigned structures.

(9) The intercept to slope ratios (*I*/*S*) from plots of [ϕ(bibenzyl formation)]$^{-1}$ from **2** vs. [**4**]$^{-1}$ and [**5**]$^{-1}$ are 91 ± 7 and 66 ± 3 M^{-1}, respectively, while quenching constants ($k_q\tau$) for these arenes are 78 ± 2 and 120 ± 8 M^{-1}, respectively. *I*/*S* from [ϕ(**2** disappearance)]$^{-1}$ vs. [**4**]$^{-1}$ and [**5**]$^{-1}$ are 204 and 165 M^{-1}, respectively. Finally, *I*/*S* from [ϕ(bibenzyl formation)]$^{-1}$ from **4** and **5** vs. [**1**]$^{-1}$ are 90 and 27, respectively, while k_q values are 87 and 100 M^{-1}.

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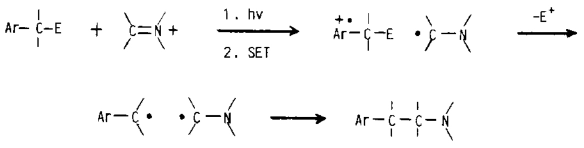
Scheme I



on the type of electrofugal group present at the arene benzylic positions. For example, irradiation ($\lambda \geq 280$ nm) of **12** in MeOH followed by basic workup and chromatography leads to formation of the benzoindolizidine **17**[8] (18%) and the phenylpyrroline **19** (15%). In contrast, the cyclization product **17** is produced *exclusively* (>40%) from photolysis (MeOH or MeCN) of the analogous trimethylsilyl-substituted pyrrolinium salt **13**. Mechanistic information for the transformation **13** → **17** is found in the observation that **13**-d_2, dideutereated at the N-C benzylic position, undergoes photocyclization to form **17**-d_2 with the two deuteriums located at the N-C benzylic position.

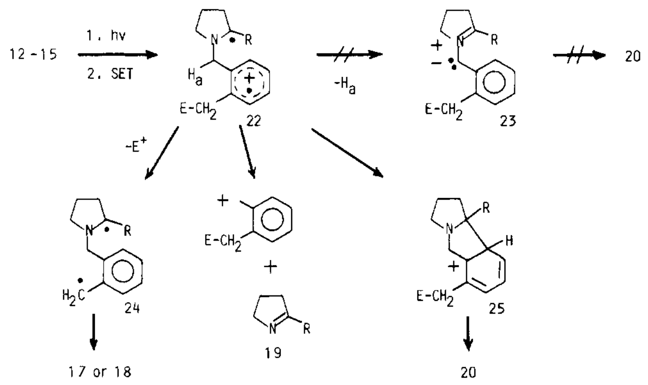
Another example of how trimethylsilyl substitution affects the nature of arene-iminium salt photochemistry is revealed in the photochemistry of pyrrolinium perchlorates **14** and **15**. Upon irradiation ($\lambda > 240$ nm) in MeCN followed by basic workup, **14** is converted to the dimethylbenzopyrrolizidine **20** (90%).[11] This novel pyrrolizidine ring-forming process is followed by the simple *N*-benzyl salt **16**, which undergoes efficient photocyclization (MeCN, 90%) to produce **21**. In order to gain evidence to rule out pathways involving the intermediacy of vinylazomethine ylides **23** (Scheme II) in this reaction, **14**-d_2 dideuterated at the N-C benzylic position was prepared and irradiated. The pyrrolizidine **12**-d_2 produced in this case contains both deuteriums at the N-C position, and, thus, is not produced via electrocyclization of **23**. In comparison, irradiation of the silicon-containing salt **15** (MeCN) leads to exclusive production (70%) of the benzoindolizidine **18**. Analysis of the crude photolysate revealed the absence of a Me_3Si analogue of **20** as a photoproduct.

Several aspects of the photocyclization reactions of pyrrolinium salts **12-16** deserve comment. The changes occurring upon replacement of hydrogen by the Me_3Si substituent at benzylic centers in these systems appear to be related to the relative rates of electrofugal group loss converting cation diradicals **22** to neutral diradicals **24** and of other processes open to **22** including C-N bond cleavage and radical coupling (Scheme II). The enhanced efficiency for benzoindolidine formation compared to photofragmentation by cleavage of **22** in the salts **13** is in accord with the greater rate for arene cation radical desilylation vs. deprotonation (Scheme II).[12] Moreover, when the cation diradicals **22** possess the more highly reactive methyl-rather than phenyl-substituted α-pyrrolidinyl radical center and a slow electrofugal group loss pathway (R = H), radical coupling occurs to generate the cation precursor **25** of the pyrrolizidine **20**. However, fast desilylation diverts reaction to indolizidine formation via diradical **24** (R = Me).[13]

Table I. Photoaddition Product Yields from Irradiation of Arene-Iminium Salt Systems in MeOH

pyrrolinium perchlorate	arene	photoproducts (yields)
1	**4**	**6** (2%) + **7** (23%) + **8** (35%) + **11** (1%)
1	**5**	**6** (40%) + **7** (26%) + **8** (10%) + **11** (16%)
2	**4**	**9** (24%) + **11** (15%)
2	**5**	**9** (22%) + **11** (20%)
3	**4**	**10** (20%) + **11** (21%)
3	**5**	**10** (24%) + **11** (24%)

Scheme II



The results summarized above demonstrate that the electron-transfer photochemistry of arene-iminium salt systems can be induced by irradiation of either the donor or acceptor component. This feature along with the control offered by the nature of benzylic-disposed electrofugal group on the type of the heterocyclic products formed suggests that photocyclization reactions of these systems will be synthetically significant.

Acknowledgment. We are pleased to acknowledge the support provided by NIH (GM-27251) and NSF (CHE-08240) for these studied. The technical assistance of Lori Klingler in accumulating a portion of the fluorescence quenching data is acknowledged.

Registry No. 1, 2730-96-3; **2**, 69105-60-8; **3**, 2826-88-2; **4**, 108-88-3; **5**, 770-09-2; **12**, 92014-43-2; **13**, 92014-45-4; **14**, 92014-47-6; **15**, 92014-49-8; **16**, 56519-58-5.

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[10] The *N*-xylylpyrollinium salts **12-16** were prepared by a sequence involving alkylation of the appropriate pyrrolines with either *o*-$MePhCH_2I$ or *o*-$Me_3SiCH_2PhCH_2I$ followed by perchlorate ion exchange.

[11] The ^1H NMR spectrum of pyrrolizidine **20** contains an AB quartet (3.86 and 4.44 ppm) for NCH_2 and a methyl singlet at 2.24 ppm, and its ^{13}C NMR spectrum indicates the presence of three quaternary aromatic carbons (132.7, 137.0, 147.8 ppm). In comparison, the ^1H NMR and ^{13}C NMR spectra of **18** resemble that of a indolizidine **17** and contain resonances for both sets of diastereotopic benzylic protons and only two quaternary aromatic carbons.

[12] An estimate of the relative rates of arene cation radical desilylation vs. deprotonation has been made through kinetic analysis[1b] of pyrrolinium salt **1** additions to **4** and **5**. This exceptionally inaccurate method suggests that desilylation is ca. 10 times faster than deprotonation.

[13] Perhaps another manifestation of the more rapid rate of arene cation radical desilylation vs. deprotonation might be found in the product spectra and yields from reaction of **4** and **5** with **1**. Thus, the much higher yield of benzylpyrrolidine **6** from **5** vs. **4** could reflect the faster rate of electrofugal group loss vs. cage collapse of the initially formed radical cation pair. This would lead to higher yields of the in-cage coupling product vs. materials generated by out-of-cage processes. However, this same trend is not seen for additions to the phenylpyrrolinium salts **2** and **3**.

Catalytic Versatility of Angiotensin Converting Enzyme: Catalysis of an α,β-Elimination Reaction

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We wish to report that angiotensin converting enzyme (ACE) catalyzes the α,β-elimination of *p*-nitrothiophenol from *N*-(3-benzoyl-2-((*p*-nitrophenyl)thio)propanoyl)-L-phenylalanine (**1**), a ketone substrate with a leaving group β to the ketone function. This substrate was employed in an effort to determine whether ACE can catalyze proton abstraction from an activated methylene group in a suitably designed ketone substrate. In earlier studies, carboxypeptidase (CPA), an exopeptidase containing an active site proposed to resemble that of ACE,[1] had been shown to catalyze stereospecifically proton incorporation into (*R*)-3,3-dideuterio-2-benzyl-3-(*p*-methoxybenzoyl)propionic acid (*R*-**2**-d_2),[2-4]

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