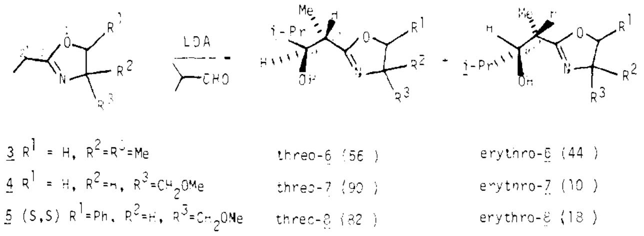
chemical control. From a synthetic point of view, these esters are readily purified by chromatography and the carboxylic acid obtained by simple acid hydrolysis (3 N HCl, THF, 25 °C, 12 h).

To further test the efficacy of internal lithium chelation toward enhanced threo-erythro selectivity, the 2-ethyl oxazolines **3**-**5**[7] were examined. Metalation of **3** (−78 °C, THF) followed by introduction of isobutyraldehyde gave diastereomeric **6** as a 56:44 mixture. However, when methoxy-substituted oxazoline **4** was similarly treated, a 9:1 ratio of threo: erythro adducts **7** was obtained.[8] Thus, the internal lithium chelation in lithiated oxazolines provides the necessary steric parameters for enhanced selectivity during C-C bond formation along with a high degree of selectivity in the deprotonation step.[9,10]

When the chiral, nonracemic oxazoline **5** was metalated and treated (−98 °C, THF) with isobutyraldehyde, four nonracemic diastereomers in the ratio of 18.3:1:2.4:2.2 were observed (LC). The four products were identified as 82% *S,S* and *R,R* enantiomers and 18% *S,R* and *R,S* enantiomers. The *S,S* enantiomer was present as 75% of the total mixture and could be readily isolated by preparative medium-pressure chromatography. The high selectivity observed is in contrast to a much lower selectivity (~1.5:1) reported[11] using the chiral 2-methyloxazoline **5** (methyl in place of the 2-ethyl group) and aldehydes to furnish 3-hydroxyalkanoic acids. The presence of C-2′,C-3′ substitution in **8** undoubtedly creates a more demanding steric array in the transition state. Since these oxazolines are easily hydrolyzed to the carboxylic acids,[12] a route is now available for the acquisition of *threo*-(2*S*,3*S*)-2-alkyl-3-hydroxy acids. Further studies involving internally chelated lithio enolates as reagents for stereoselective C-C-bond-forming reactions are continuing.



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(7) Preparation of **3** is described (Meyers, A. I.; Temple, D. L.; Nolen, R. L.; Mihelich, E. D. *J. Org. Chem.* **1974,** *39,* 2778); (*R,S*)-**4** and (*S,S*)-**5** were prepared from (*R,S*)-ethyl serinate and (1*S*,2*S*)-1-phenyl-2-amino-1,3-propanediol (Meyers, A. I.; Knaus, G.; Kamata, K.; Ford, M. E. *J. Am. Chem. Soc.* **1976,** *98,* 567; Meyers, A. I.; Whitten, C. E. *Heterocycles* **1976,** *4,* 1687).

(8) The oxazolines were hydrolyzed to the corresponding known acid[4] to confirm the threo-erythro assignment. Furthermore, the ^1H NMR spectra for **6**-**8** showed $J = 7$ Hz for C_2'-C_3' protons in the threo isomer and $J = 2.8$ Hz for C_2'-C_3' protons in the erythro isomer. This is in agreement with previous observations.[1]

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(10) It has been noted during this work that the stereoselectivity increases as the temperature of alkylation decreases. Thus, the stereoselectivity is not totally dependent upon the *E* or *Z* enolate ratio of the preformed enolate, but also on the nonbonded interactions in the transition state (cf. ref 2b, 5, and 7).

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(12) Hydrolysis has been accomplished using acidic media (1.5 N ethanolic sulfuric acid, reflux) or alkaline media (CH_3I, 2 N KOH, reflux, 2 h).

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Photoionization by Green Light

Sir:

In a recent communication[1] we showed that the photoionization of aminoperylene by green light (λ = 5300 Å) directly followed laser light intensity in the range 30-150 mJ/pulse. Some concern[2] has recently been exhibited with regard to the interpretation of the intensity dependence; attention was drawn[2] to another system where the yield of photoionization did not follow simple patterns. The system quoted, pyrene in anionic micellar solution, was not that reported in our communication,[1] although we have studied this system successfully a number of years ago[3-5] and find different mechanisms for these quite distinct systems. However, to avoid ambiguity we present two additional areas of experimental data: (a) an extension of our intensity data and (b) low intensity photoionization as measured by the SF_6 method.

Figure 1 shows the dependence of the yield of photoionization on the laser intensity, in which we present our original data together with an extension to lower intensities. An intensity range of 8-150 J/(cm^2/pulse) was covered. The data are linear and extrapolate through the origin. Photoionization of pyrene in NaLS micelles shows quite different behavior.[2,3] It is difficult to compare the aminoperylene data with the reported pyrene data,[2] in particular as the cross section of the laser beam and hence the irradiated volume are not given. However the aminoperylene data (Figure 1) again supported one-photon photoionization of aminoperylene in NaLS micelles.

To achieve extremely low light intensities we have photoionized aminoperylene in NaLS micelles with light (λ = 5300 Å) of 1-mW intensity, i.e. much lower than that used in the laser work. This light was obtained by passing the whole beam of a 450-W xenon lamp through an f 3.5 Bausch and Lomb monochromator which also had a filter at the exit slit. Solutions containing 5×10^{-5} M aminoperylene in 2×10^{-2} M NaLS together with O^2 ($[O_2] = 1.4 \times 10^{-4}$ M) and SF_6 ($[SF_6] = 1.3 \times 10^{-4}$ M) were photolyzed with this light. Fluoride ion was produced and measured on a fluoride sensitive electrode; no F^- was produced in absence of aminoperylene, or if NaLS was replaced by nonionic Igepal micelles. F^- results from the capture of e_{aq}^- produced in photoionization of aminoperylene by giving SF_6 $6F^-$ ions.[6] Excitation of aminoperylene leads to the excited singlet state and subsequently to the excited triplet. No reaction of the excited singlet or triplet state with SF_6 in SF_6 saturated solutions would be detected. The inclusion of O_2 which reacts at a diffusion-controlled rate with excited states of aminoperylene protects against two-photon photoionization of aminoperylene from the triplet state. Absorption by the foregoing solution of 0.31×10^{18} and 0.72×10^{18} quanta of light (λ = 5300 Å) produced 5.8×10^{16} and 12.0×10^{16} F^-, respectively. From the known rate constants for reaction of e_{aq}^- with O_2 ($k = 1.80 \times 10^{10}$ M^{-1} S^{-1}) and SF_6 ($k = 1.65 \times 10^{10}$ M^{-1} S^{-1}), and the fact that e_{aq}^- produces $6F^-$, the $[e_{aq}^-]$'s produced in photolysis are 2.1×10^{16} and 4.4×10^{16} molecules, respectively. The quantum yield for photoionization is thus 6.0×10^{-2}.

The above experiments support the observation of one-photon photoionization of aminoperylene in NaLS micelles

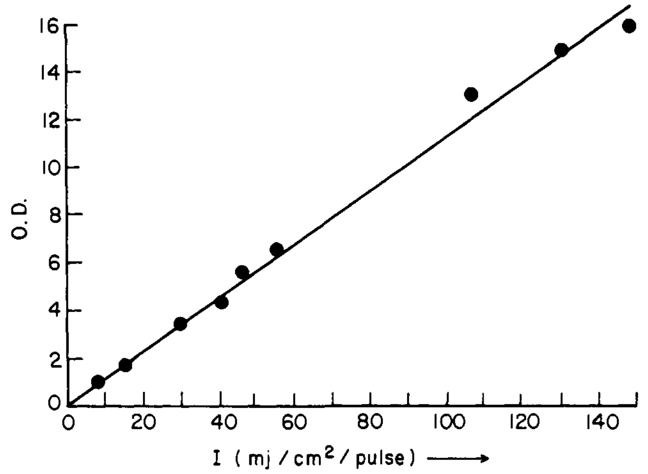

Figure 1. Dependence of photoionization yield of aminoperylene in NaLS on the laser intensity.

by green light. Several other molecules, tetramethylbenzidine,[7] phenothiazine,[8] etc., exhibit this unique effect, i.e., a substantial reduction in their photoionization potentials in NaLS micelles compared with the gas phase. Aminoperylene falls into this category and is quite unlike molecules such as pyrene, anthracene, etc., which follow two-photon photoionization in these systems. The difference in behavior is due to the location of the molecule in the micelle and hence its local micellar environment.[9]

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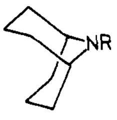
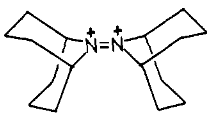
Adamantylideneadamantane Radical Cation, a Long-Lived One-Electron, Two-Center π-Bonded Species

Sir:

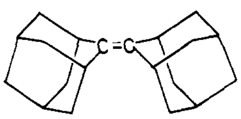
Simple trialkylamine cations have very short lifetimes in neutral or basic solutions, but are increasingly longer lived in more acidic solutions.[1] The only reason for short lifetimes in the absence of acid seems to be rapid deprotonation at carbons adjacent to nitrogen, because, when such C–H bonds are forced by bicyclic rings to be perpendicular to the N-centered p orbital in the cation, considerably longer lifetimes result. Thus 9-*tert*-butyl-9-azabicyclo[3.3.1]nonane cation radical ($\mathbf{1}^{+\cdot}$) lasts over an hour in acetonitrile, under conditions where its *N*-isopropyl analogue $\mathbf{2}^{+\cdot}$ has a submillisecond lifetime like other trialkylamine radical cations.[2] This Bredt's rule stabilization of cationic trisubstituted nitrogen species even extends to the hydrazine dication $\mathbf{3}^{2+}$, which has a lifetime of at least seconds,[3] in contrast to the submillisecond lifetime for the dications of all hydrazines studied which lack Bredt's rule stabilization of hydrogens on carbons attached to nitrogen. Given these results, we suspected that adamantylideneadamantane (**4**) might be reversibly oxidized to $\mathbf{4}^{+\cdot}$ and provide the first example of a long-lived monoolefin cation radical (a "one-electron π bond"). This proves to be the case.



1 R=tBu
2 R=iPr
5 R=H



3^{2+}



4

The cyclic voltammogram of **4** in acetonitrile shows an electrochemically reversible one-electron oxidation wave $E^{\circ\prime}$ = 1.45 V vs. SCE, even at 10-mV/s scan rates, requiring a lifetime of at least seconds for $\mathbf{4}^{+\cdot}$. Electrolytic oxidation in an ESR cell generates an air-sensitive radical, g = 2.0031, having a broadened multiplet for many hydrogens with a 3.0-G splitting constant, which we attribute to $\mathbf{4}^{+\cdot}$. The best model available for the proton splittings expected for $\mathbf{4}^{+\cdot}$ is $\mathbf{5}^{+\cdot}$, which was generated by photolysis of the *N*-chloro compound in trifluoroacetic acid, analogously to other dialkylamine radical cations.[4] The complex ESR spectrum of $\mathbf{5}^{+\cdot}$ was analyzed to give splittings $a(1\ \mathrm{H}) = 19.8_4$, $a(\mathrm{N}) = 17.3_4$, $a(8\ \mathrm{H}) = 3.9_6$, $a(2\ \mathrm{H}) = 0.9_9$, $g = 2.0034$. We attribute the eight hydrogen splitting to the two sets of four hydrogens on C_2, C_4, C_6, and C_8. The C_1C_2, C_1C_8, C_5C_4, and C_5C_6 bonds are held in excellent geometry for hyperconjugation with the half-filled p orbital on nitrogen and each pair of geometrically inequivalent methylene hydrogens is equivalently disposed with respect to one of these CC bonds. We presume that the rather large equal splittings for the two sets of four equivalent hydrogens γ to the formal spin-bearing orbital are a result of dominant spin polarization from hyperconjugation-generated spin at C_2, C_4, C_6, and C_8. By analogy one expects $\mathbf{4}^{+\cdot}$ to have a fairly large splitting for sixteen γ hydrogens, consistent with the ESR spectrum observed upon oxidation of **4**. Hyperconjugation in $\mathbf{4}^{+\cdot}$ is apparently significantly more efficient at delocalizing spin to the γ carbons than in $\mathbf{5}^{+\cdot}$, because $a(\mathrm{H}_\gamma)$ for $\mathbf{4}^{+\cdot}$ is ~50% larger than half $a(\mathrm{H}_\gamma)$ for $\mathbf{5}^{+\cdot}$. This effect could well be a result of a closer matching of the CC σ-bond energy with that of the carbon-centered π system of $\mathbf{4}^{+\cdot}$ than with the nitrogen-centered p orbital of $\mathbf{5}^{+\cdot}$. The positive "hole" of $\mathbf{4}^{+\cdot}$ is for a bonding electron, while that of $\mathbf{5}^{+\cdot}$ is formally (although not actually completely) nonbonding. Another piece of evidence which points to unusually important σ,π interaction in $\mathbf{4}^{+\cdot}$ is provided by its g factor, which is higher than for other hydrocarbon radicals; $\Delta g = g - g_e$ is 8×10^{-4} for $\mathbf{4}^{+\cdot}$, compared with the range of $2\text{–}4 \times 10^{-4}$ for polycyclic aromatic[5] and hexaalkylbenzene[6] cation radicals. The smaller π system for $\mathbf{4}^{+\cdot}$ should lower Δg slightly according to the Stone equation,[5,7] the opposite direction to the experimental observation. An unusually low energy $\sigma \rightarrow \pi$ transition has been predicted to increase Δg.[8]

The $E^{\circ\prime}$ value of 1.45 V for $\mathbf{4}/\mathbf{4}^{+\cdot}$ might be thought surprisingly low compared with the range of 2.27–3.20 V for irreversible $E_{1/2}$ values of ethylene and mono- and dialkyl olefins.[9] It is thermodynamically as easy to remove an electron in solution from the two-electron π system of **4** as it is from the eighteen-electron π system of benzanthracene. Miller and co-workers[9] have emphasized a linear relationship between the vapor phase ionization potential and the solution phase oxidation potential for many types of compounds. Such a line can now be established employing thermodynamically significant $E^{\circ\prime}$ values for polycyclic aromatic hydrocarbons in acetonitrile, using the electrochemical data of Parker[10] and vertical ionization potentials determined by photoelectron spectroscopy,

0002-7863/79/1501-2503$01.00/0