for the ^{111}Cd and ^{113}Cd NMR spectra, respectively, on the basis of a tetrahedral Cd_4 core with statistical populations[11] of $[(^{111}Cd)_n(^0Cd)_{4-n}]$ (n = 1-4), $[(^{111}Cd)_n(^{113}Cd)(^0Cd)_{3-n}]$ (n = 1-3), $[(^{113}Cd)_n(^0Cd)_{4-n}]$ (n = 1-4), and $[(^{111}Cd)(^{113}Cd)_n(^0Cd)_{3-n}]$ (n = 1-3) arising from a natural sample of cadmium,[12,13] assuming that the observed splitting of the major satellites, 47 ± 2 Hz in acetone and 45 ± 2 Hz in acetonitrile, is from two-bond coupling between ^{111}Cd and ^{113}Cd.

The assignment of $^2J(^{111}Cd-^{113}Cd)$ was confirmed by using ^{113}Cd enrichment. As expected, a sample of $(Me_4N)_2[(^{113}Cd)_4(SPh)_{10}]$ (^{111}Cd 0.2 and ^{113}Cd 91.7 atom %[14])showed, in the ^{113}Cd NMR spectrum, a singlet with no observable satellites, having the same values of δ_{Cd} and $\Delta\nu_{1/2}$ as a natural sample (see above). At 0.05 M total concentration in acetone, a mixture of natural and ^{113}Cd-enriched $[Cd_4(SPh)_{10}]^{2-}$ wherein $^{111}Cd:^{113}Cd:^0Cd$ = 0.13:1:0.85 gave the ^{111}Cd NMR spectrum shown in Figure 1b.[15] The seven-line spectrum is a superimposition of the singlet, doublet, triplet, and quartet spectra expected for isotopomers of the Cd_4 core containing ^{111}Cd and zero, one, two, and three ^{113}Cd nuclei, respectively. For the isotopic composition used, the statistical populations of $[(^{111}Cd)_n(^0Cd)_{4-n}]$ (n = 1-4), $[(^{111}Cd)_n(^{113}Cd)(^0Cd)_{3-n}]$ (n = 1-3), $[(^{111}Cd)_n(^{113}Cd)_2(^0Cd)_{2-n}]$ (n = 1 or 2), and $[(^{111}Cd)(^{113}Cd)_3]$ should be 2.7%, 8.7%, 9.5%, and 3.5%, respectively, from which the relative intensities of the seven lines in the ^{111}Cd NMR spectrum should be 0.047:0.32:0.77:1:0.77:0.32:0.047, close to the amplitudes of approximately 0.09:0.34:0.75:1:0.75:0:34:0.09 found.

Under our experimental conditions either inverse-gated or continuous-broad-band proton decoupling broadened the cadmium NMR spectra of **2** significantly. However, the temperature dependence of δ_{Cd} was appreciable, with $\Delta\delta/\Delta T$ averaging -0.19 ppm/K in the range 256-296 K, and so we attribute the line broadening caused by the proton decoupling to thermal inhomogeneity produced in the sample. Also, we find that, while our spectra are unaffected by small amounts of water, noticeable broadening of the resolved $^{111/113}$Cd NMR spectra of **2** is produced by small amounts (0.05 mol/mol $[Cd_4(SPh)_{10}]^{2-}$) of $Cd(NO_3)_2$[16] or $(Me_4N)_2[Cd(SPh)_4]$[9,17] or an equimolar amount of $(Et_3NH)(BF_4)$.[18] Consistent with the last observation, we observe that under conditions where acetonitrile solutions of **2** give well-resolved metal NMR spectra, corresponding solutions of **1** do not: the 295 K 44.37-MHz ^{113}Cd NMR spectrum of the latter is a broad line (δ_{Cd} 578, $\Delta\nu_{1/2} \approx 40$ Hz for a 0.05 M solution) with barely evident shoulders, in accord with the earlier report of a singlet ^{113}Cd resonance (see above).[19]

The value of 45-47 Hz found for $^2J(^{111}Cd-S-^{113}Cd)$ in $[Cd_4(SPh)_{10}]^{2-}$ leads to a value 4.6% higher for the corresponding $^2J(^{113}Cd-S-^{113}Cd)$,[12] which is not directly observable in our experiments. This two-bond $^{113}Cd-^{113}Cd$ coupling is within the range found for ^{113}Cd-MT (see above) and hence provides strong support for the interpretation[1,2] that $^{113}Cd-^{113}Cd$ coupling in the protein is between CdS_4 kernels linked by a bridging cysteinyl thiolate group. In addition, our results show that the Cd_4 core of $[Cd_4(SPh)_{10}]^{2-}$ remains intact on the NMR time scale under conditions where rapid exchange of the attached bridging and terminal thiolate groups is known to occur[6] and hence is consistent with the mechanistic scheme proposed[6] to account for this exchange.

Note Added in Proof: Since the submission of our manuscript we have learned of independent work[20] in which Cd-Cd nuclear spin-spin coupling has been observed in $[E_4Cd_{10}(SPh)_{10}]^{4-}$ (E = S or Se) and $[Cd_4(SPh)_{10}]^{2-}$.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada for support in the form of an Operating Grant to P.A.W.D. and a Strategic Grant in Environmental Toxicology to P.A.W.D. jointly with Professors M. G. Cherian and M. J. Stillman of the Departments of Pathology and Chemistry, respectively, of the University of Western Ontario.

Registry No. 2, 84493-87-8; ^{111}Cd, 14336-64-2; ^{113}Cd, 14336-66-4.

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[11] Calingaert, G.; Beatty, H. A. *J. Am. Chem. Soc.* **1939**, *61*, 2748-2754.

[12] ^{111}Cd (spin $I = 1/2$, $\mu = -0.5922\ \mu_m$), 12.75%; ^{113}Cd (spin $I = 1/2$, $\mu = 0.6195\ \mu_m$), 12.26%; zero-spin Cd, 74.99% natural abundance.

[13] Expected statistical populations are the following: $[(^{111}Cd)_n(^0Cd)_{4-n}]$, 27.6%; $[(^{111}Cd)_n(^{113}Cd)(^0Cd)_{3-n}]$, 12.4%; $[(^{113}Cd)_n(^0Cd)_{4-n}]$, 26.3%; $[(^{111}Cd)(^{113}Cd)_n(^0Cd)_{3-n}]$, 12.3%.

[14] The isotopic ratio in the metallic cadmium used as starting material was determined using SIMS. We are indebted to Dr. R. R. Martin of this department for this analysis.

[15] Scrambing of the ^{113}Cd label is complete within the time of ca. 20 min needed to prepare the mixture and measure initial spectra.

[16] Addition of $Cd(NO_3)_2$ leads to formation of a white precipitate of, presumably, $Cd(SPh)_2$.

[17] Carson, G. K.; Dean, P. A. W. *Inorg. Chim. Acta* **1982**, *66*, 157-161.

[18] The complications caused by the Et_3NH^+ cation probably result from proton-assisted dissociation of coordinated PhS^-. For a recent example of this general phenomenon, see: Rabenstein, D. L.; Reid, R. S. *Inorg. Chem.* **1984**, *23*, 1246-1250.

[19] It should be emphasized, however, that the ^{113}Cd NMR spectra reported in ref 6 were measured at a higher frequency and concentration than used here.

[20] Dance, I. G.; Saunders, J. K., personal communication.

The 1,7-Cyclobutanonorbornane System[1]

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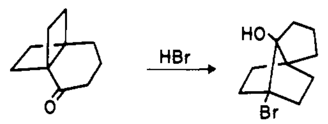
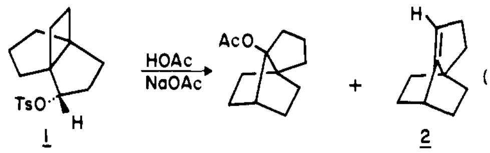
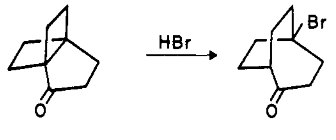
In an undistorted norbornane the bonds to substitutents at C1 and C7 lie in orthogonal planes. If the substituents are carbon, the equilibrium distance between them is about 3.2 Å (Figure 1a). Bridging C1,C7 with a three-carbon chain, the 1,7-cyclopentanonorbornane system, necessitates some warping of the parent skeleton (Figure 1b). The strain energy is calculated to be 33 kcal/mol (cf. norbornane, ~18 kcal/mol).[2] The system is fairly well-known; direct access is available via rearrangements of [4.2.2]propellanes (eq 1)[3] and [3.3.2]propellanes (eq 2).[4]



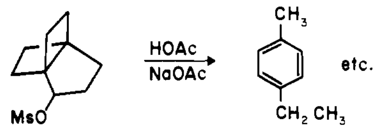
(1)



(2)



(3)



(4)

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[1] IUPAC nomenclature: tricyclo[3.2.2.0^{1,4}]nonane.

[2] The molecular mechanics (MM2) program used was written by N. Allinger and Y. H. Yuh, University of Georgia (1980) and obtained from the Quantum Chemistry Program Exchange, University of Indiana. See: Allinger, N. L. *J. Am. Chem. Soc.* **1977**, *99*, 8127. Initial coordinates were introduced using a structure input program written and kindly provided by M. Saunders, Yale University.

[3] Eaton, P. E.; Jobe, P. G. *J. Am. Chem. Soc.* **1980**, *102*, 6636.

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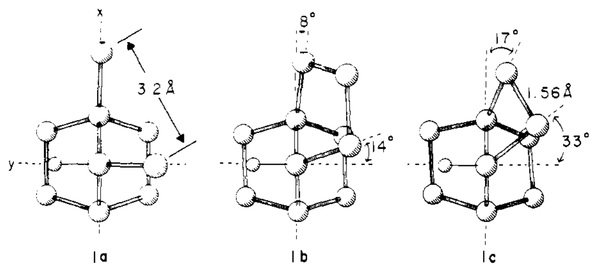
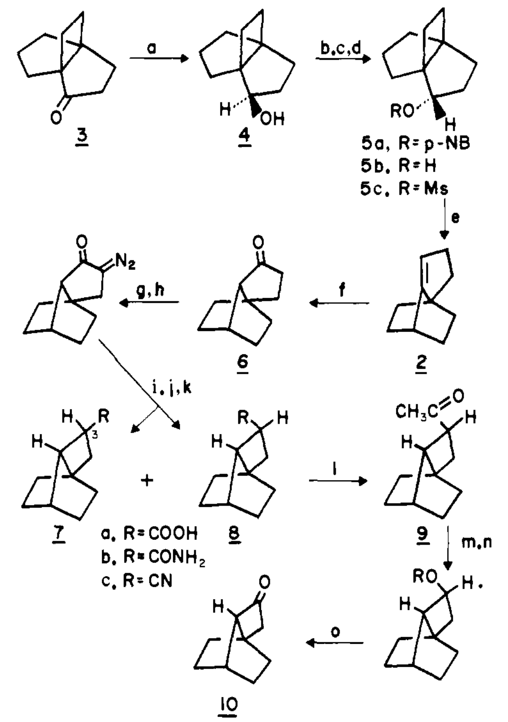


Figure 1. PLUTO projection down *z* of MM2 structures for (a) 1,7-dimethylnorbornane, (b) 1,7-cyclopentanonorbornane, and (c) 1,7-cyclobutanonorbornane. Distances are internuclear; angles are between bonds and the *xz* or *yz* plane as appropriate.

Chart I[a]



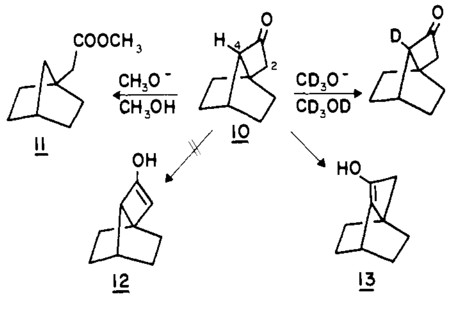
[a] (a) Reference 6; (b) p-NO_2PhCO_2H, DEAD, Ph_3P, PhH → **5a**, 80%; (c) 15% aqueous NaOH → **5b**, 82%; (d) MsCl, Et_3N, CH_2Cl_2, 0 °C, 15 min → **5c**, quantitative; (e) quinoline, 100 °C, overnight, steam distill; (f) BH_3·THF, Et_2O, reflux, 15 min, then $H_2Cr_2O_7$, reflux, 7 h, 54% from **5c**; (g) EtOCHO, NaOMe, overnight, 81%; (h) TsN_3 Et_3N, CH_3CN, 86%; (i,j) Hg arc (Pyrex filter); THF, H_2O → **7a**,**8a**, 84%; THF, NH_4OH → **7b**,**8b**, 68%; (k) $POCl_3$ on **7b**,**8b**, 80 °C, 90 min → **7c**,**8c**, 92%; (l) CH_3Li on **7c**,**8c**, 97%; (m) m-$ClPhCO_3H$, CH_2Cl_2 → R = Ac, 71%; (n) $LiAlH_4$ → R = H, 98%; (o) Me_2SO, TFAA, Et_3N, −65 °C → room temperature, 97%.

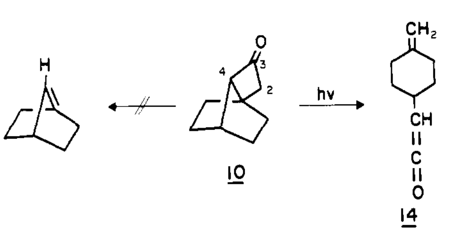
Bridging C1,C7 of the norbornane with a two-carbon chain, as in the title system, is much more difficult and requires substantial distortion of the norbornane skeleton (Figure 1c). The calculated strain energy is 59 kcal/mol. Attempts to prepare the system from [3.2.2]propellane reactions analogous to those in eq 1 and 2 fail; eq 3[5] and 4 pertain instead.

We have now obtained the title system successfully and present here its first synthesis and characterization. Satisfyingly, we were able to use a [3.3.2]propellane rearrangement to provide a suitable starting material. Tobe, Odaira, and co-workers had earlier shown (eq 2) that buffered acetolysis of *endo*-tosylate **1** gave 44% yield of the 1,7-cyclopentenonorbornane (**2**).[4] We envisioned (Chart I) conversion of **2** to ketone **6** and then photochemical Wolff contraction of its α-diazo derivative, the latter reaction providing sufficient energy to access the desired system. First, it was essential to improve on the original synthesis of **2**, for the key precursor, *endo*-alcohol **5b**, was obtained therein only after a difficult separation from its exo isomer **4**.[4] We chose instead to start with this exo isomer since it is available stereoselectively from hydride reduction of the well-known ketone **3**.[6] Mitsunobu[7] inversion of **4** by treatment with diethyl azodicarboxylate, triphenylphosphine, and *p*-nitrobenzoic acid gave pure *endo*-*p*-nitrobenzoate **5a** from which the synthesis proceeded expeditiously as outlined in Chart I.

The title ring system was produced by this route epimerically substituted at position 3 (IUPAC numbering).[1] It is apparent from models and calculations that the trans epimers are sterically the more favored. As treatment of the cis nitrile **7c** ($\delta_{C3\,H}$ 3.08, t d, J = 8 and 2 Hz) with KO-*t*-Bu/*t*-BuOH gave the trans isomer **8c** ($\delta_{C3\,H}$ 2.89, t d, J = 9 and 6 Hz), the geometries could be assigned as stated. Other assignments were made similarly. For each of the trans compounds the C3 H resonance appears about 0.2 ppm upfield from that of the cis isomer. The nuclear coupling constants of C3 H to its neighbors are fairly regular in the trans series, while in the cis, in which the substituent is awkwardly crowded, the couplings vary reflecting the different geometric demands of different substituents.

Reaction of a mixture of nitriles **7c** and **8c** with methyllithium gave, after acidic workup, only the trans methyl ketone **9**. Oxidative degradation of **9** via the acetate and alcohol gave the ketone **10**: IR (gas) ν 1800 cm^{-1}; ^{1}H NMR δ ($CDCl_3$, 500 MHz) C2 H 2.87 (br s), C4 H 2.43 and 3.06 ppm (doublet pair, J = 14 Hz). This cyclobutanone is a liquid, reasonably stable at room temperature when pure. It is, however, labile to nucleophilic cleavage; reaction with dilute sodium methoxide in methanol at room temperature gave ester **11** rapidly. Under similar conditions but with deuteriated reagents it could be shown that exchange of the C4 proton of **10** occurred somewhat faster than cleavage of the 4-membered ring. Heating ketone **10** at 100 °C in CD_3CO_2D containing a trace of CF_3CO_2H resulted in slow D-for-H exchange at C4. There was no significant deuterium incorporation at C2 prior to ultimate degradation of the structure in either the acid- or base-catalyzed exchange reactions. This seems to fit well with MM2 predictions for the relative stabilities of the unsubstituted cyclobutenonorbornanes corresponding to enols **12** and **13**.[8]





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(4) Tobe, Y.; Hayauchi, Y.; Sakai, Y.; Odaira, Y. *J. Org. Chem.* **1980**, *45*, 637.

(5) Observation by K. Nyi, The University of Chicago.

(6) Tobe, Y.; Doi, A.; Kimura, K.; Odaira, Y. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 639.

(7) Mitsunobu, O.; Eguchi, M. *Bull. Chem. Soc. Jpn.* **1971**, *44*, 3427.

(8) As a caveat to this interpretation we note that the favored (but not exclusive!) direction of exchange in ketone **6** is the same as for **10**, but MM2 calculations indicate the difference in stability of the corresponding 1,7-cyclopentenonorbornanes is greater and opposite that of the 1,7-cyclobutenonorbornanes.

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.

Acknowledgment. We are grateful to the National Science Foundation (CHE-8118391) for support of his work. The NSF and the NIH (CA 14599) also provided substantial funding for the Department NMR facilities. I.D.R. thanks Middlebury College for a sabbatical leave.

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[9] (a) Turro, N. J.; Bauer, D. *Adv. Photochem.* **1974**, *9*, 197. (b) Miller, R. D.; Abraitys, V. Y. *J. Am. Chem. Soc.* **1972**, *94*, 663. (c) Lee-Ruff, E.; Hopkinson, A. C.; Kazarians-Moghaddam, H. *Tetrahedron Lett.* **1983**, *24*, 2067.

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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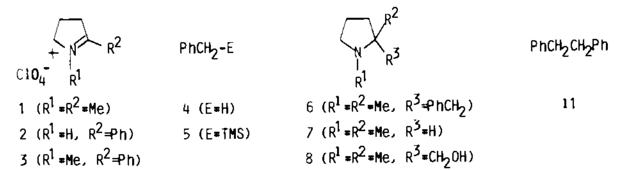
Previously, we have shown how photoinduced, sequential electron-transfer–desilylation pathways serve as a method for regiocontrolled generation of carbon radical and diradical species. We have provided examples of this process in routes for construction of heterocyclic systems.[1c–e,2] Recent efforts 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 $\Delta G_{\mathrm{SET}} < 0$.[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 ($R^1=Me$, $R^2=Ph$)

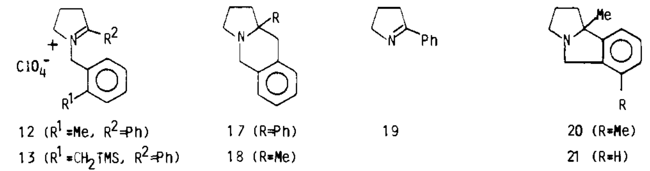
$PhCH_2-E$

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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[1] (a) Ohga, K.; Mariano, P. S. *J. Am. Chem. Soc.* **1982**, *104*, 617. (b) Ohga, K.; Yoon, U. C.; Mariano, P. S. *J. Org. Chem.* **1984**, *49*, 213. (c) Ullrich, J. W.; Chiu, F. T.; Harding, T. *Ibid.* **1984**, *49*, 220. (d) Chen, S. F.; Ullrich, J. W.; Mariano, P. S. *J. Am. Chem. Soc.* **1983**, *105*, 6160. (e) Chiu, F. T.; Ullrich, J. W.; Mariano, P. S. *M. Org. Chem.* **1984**, *49*, 228.

[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}.

0002-7863/84/1506-6439$01.50/0