cleophiles in approaches to oxygen and nitrogen heterocycles,[7] the present furan synthesis considerably extends those original observations, as it documents the participation of (*E*)-crotylsilanes in the asymmetric addition to aldehydes promoting a silicon-directed heterocyclization which results in the formation of tetrahydrofurans.[8] The formation of the isolated 2,5-cis-substituted furans is consistent with the well-precedented stereochemical course of Lewis acid-promoted additions of chiral crotylsilanes and stannanes to aldehydes and activated acetals and the fact that the heterocyclization proceeds with inversion of configuration at the C2 center.[3,5,9] An intriguing aspect of the furan synthesis is that the 1,2-silyl migration competes favorably with elimination of the dimethylphenylsilyl (DMPS) group after condensation with the aldehyde. As illustrated in Scheme I with the (2*S*,3*S*)-diastereomer **1a**, a diastereoface selective addition to the si face of the aldehyde simultaneously generates two new stereocenters and a β-silyl carbocation stabilized through the $\sigma \rightarrow \pi$ conjugation of the adjacent C–Si bond. A 1,2-cationic migration of the DMPS group[10] is followed by heterocyclization producing the 2,5-cis tetrahydrofuran **3**. The process is further enhanced by the fact that the tetrahydrofurans are equipped with a DMPS group, a known hydroxyl group synthon, and functionalized at C2 and C5 for further synthetic transformations.[11]

The results of the asymmetric furan synthesis are summarized in Table I. For these examples, $BF_3{\cdot}OEt_2$ was determined to be the most effective Lewis acid for efficient conversion to the tetrahydrofuran. In the reactions with α-benzyloxy acetaldehyde (**2a**) both syn and anti α-methyl (*E*)-crotylsilanes **1a** and **1c** exhibited excellent levels of diastereoselection producing the tetrahydrofurans **3a** and **3c** with de's reaching 96% as determined by NMR analysis. The condensation reactions with the β-benzyloxy aldehyde **2b** showed similar levels of selectivity; however, the reaction temperature was necessarily increased to −30 °C to ensure the efficient conversion to the furan product. The tetrahydrofurans **3b–e** were subjected to a Hg^{II} oxidation [$Hg(OAc)_2$/32% AcOOH/AcOH/cat. H_2SO_4/RT][11] to give the diastereomerically pure alcohols **4b–e**, thus establishing the synthon equivalency of the DMPS group.

In conclusion, the asymmetric additions of chiral (*E*)-crotylsilanes to α- and β-benzyloxy aldehydes constitute a remarkably simple procedure for the construction of nearly optically pure tetrahydrofurans. The distinguishing features of this Lewis acid-mediated tetrahydrofuran synthesis are the high levels of diastereoface selection and the facility of the 1,2-silyl migration allowing heterocyclization. Further studies of these organosilane reagents in asymmetric transformations are in progress.

Acknowledgment. This work has been financially supported by the National Institutes of Health (CA47249).

Supplementary Material Available: Experimental procedures and spectral data for all reaction products (5 pages). Ordering information is given on any current masthead page.

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(7) (a) Danheiser, R. L.; Kwasigroch, C. A.; Tasi, Y.-M. *J. Am. Chem. Soc.* **1985**, *107*, 7233–7235. (b) Related allenylsilane additions see: Danheiser, R. L.; Carini, D. J., Basak, A. *J. Am. Chem. Soc.* **1981**, *103*, 1604–1606. (c) Allyltrimethylsilane addition to a chiral aldehyde with furan formation see: Sugimura, H. *Tetrahedron Lett.* **1990**, *31*, 5909–5912.

(8) All new compounds were isolated as chromatographically pure materials and exhibited acceptable ^1H NMR, ^{13}C NMR, IR, MS, and HRMS spectral data.

(9) $S_{E'}$ additions: (a) Hayashi, T.; Konishi, M.; Ito, H.; Kumada, M. *J. Am. Chem. Soc.* **1982**, *104*, 4962–4963. For Lewis acid catalyzed intramolecular additions of certain allylsilanes and stannanes to aldehydes, a synclinal arrangement of the reacting olefins has been postulated, [cf. Denmark, S. E.; Weber, E. J. *Helv. Chim. Acta* **1983**, *66*, 1655–1560]. (b) These findings are consistent with a stereospecific anti $S_{E'}$ process as previously reported for cases involving intermolecular additions of chiral allyl- and crotylsilanes, allylstannanes, and recently chiral allenylstannanes [cf. Marshall, J. A., Wang, X. *J. Org. Chem.* **1991**, *56*, 3211–3213].

(10) Brook, A. G.; Bassindale, A. R. In "Rearrangements in the Ground and Excited States"; de Mayo, P., Ed.; Academic Press; New York, 1980, Vol. II, pp 190–192.

(11) Fleming, I.; Sanderson, P. E. J. *Tetrahedron Lett.* **1987**, *28*, 4229–4232.

Use of Sterically Hindered Sensitizers for Improved Photoinduced Electron-Transfer Reactions

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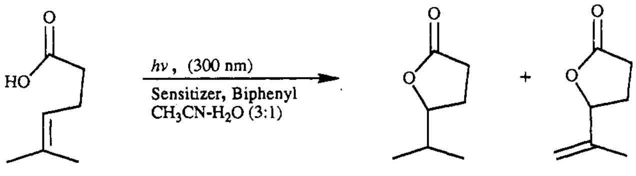
Photoinduced single-electron-transfer (SET) reactions are potentially of great value to synthetic organic chemists.[1] Unfortunately, low quantum yields and/or poor product yields often prevent these photoinduced SET reactions from being widely used in organic synthesis. Both strained and unsaturated organic molecules are known to form cation radicals as a result of electron transfer to photoexcited sensitizers (excited-state oxidants).[1] The resulting cation radical–anion radical pairs can undergo a variety of reactions including back electron transfer, nucleophilic attack on the cation radical, electrophilic attack on the anion radical, reduction of the anion radical, and addition of the anion radical to the cation radical. Because of our interest in the use of photoinduced SET reactions to achieve anti-Markovnikov addition of nucleophiles to carbon–carbon multiple bonds,[2,3] we sought to minimize side reactions and to maximize quantum yields. We felt that sterically hindering the photosensitizer might accomplish these goals. In particular, we desired to minimize coupling reactions between the cation radical and the anion radical, which can be a major side reaction.[4,5] We now report that our overall goals of increasing both product yields and quantum yields can be accomplished through the use of sterically encumbered photosensitizers.

The anti-Markovnikov lactonization of 5-methyl-4-hexenoic acid (**1**) to **2** and **3**, a photoinduced SET reaction which has been studied in detail,[2] was chosen as the model reaction for the evaluation of a series of sensitizers. The sensitizers studied were 1,4-dicyanobenzene (**4**),[5] 4,4′-dicyanobiphenyl (**5**),[6] 4,4′-dicyano-3,3′,5,5′-tetramethylbiphenyl (**6**),[7,8] 1-cyanonaphthalene (**7**),[9] 1,4-dicyano-2,3,5,6-tetramethylbenzene (dicyanodurene) (**8**),[10] 9,10-dicyano-1,2,3,4,5,6,7,8-octahydroanthracene (**9**),[7,8] and 1,4-dicyano-2,3,5,6-tetraethylbenzene (**10**).[7,8] Table I lists the



1 2 3

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(1) For leading references to photoinduced SET reactions, see: *Photoinduced Electron Transfer*; Fox, M. A., Chanon, M., Eds.; Elsevier: Amsterdam, 1988; Part C.

(2) Gassman, P. G.; Bottorff, K. J. *J. Am. Chem. Soc.* **1987**, *109*, 7547.

(3) Gassman, P. G.; Bottorff, K. J. *Tetrahedron Lett.* **1987**, *28*, 5449.

(4) For selected examples of cation radical–anion radical coupling reactions, see: McCullough, J. J.; Miller, R. C.; Wu, W.-S. *Can. J. Chem.* **1977**, *55*, 2909. Borg, R. M.; Arnold, D. R.; Cameron, T. S. *Can. J. Chem.* **1984**, *62*, 1785. Lewis, F. D.; DeVoe, R. J.; MacBlane, D. B. *J. Org. Chem.* **1982**, *47*, 1392. Kojima, M.; Sakuragi, H.; Tokumaru, K. *Tetrahedron Lett.* **1981**, *22*, 2889. Albini, A.; Fasani, E.; Sulpizio, A. *J. Am. Chem. Soc.* **1984**, *106*, 3562. Pac, C.; Nakasone, A.; Sakuri, H. *J. Am. Chem. Soc.* **1977**, *99*, 5806. Mizuno, K.; Ogawa, J.; Otsuji, Y. *Chem. Lett.* **1981**, 741. Yamada, S.; Nakagawa, Y.; Watabiki, O.; Suzuki, S.; Ohashi, M. *Chem. Lett.* **1986**, 361. Gassman, P. G.; Carroll, G. T. *Tetrahedron* **1986**, *42*, 6201.

(5) Arnold, D. R.; Wong, P. C.; Maroulis, A. J.; Cameron, T. S. *Pure Appl. Chem.* **1980**, *52*, 2609.

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(7) Satisfactory elemental analyses and/or exact mass molecular weights were obtained for all new compounds. All compounds gave spectral data consistent with the assigned structures.

(8) 4,4′-Dicyano-3,3′,5,5′-tetramethylbiphenyl was prepared through an Ullmann coupling[11] of 4-bromo-2,6-dimethylbenzonitrile. 9,10-Dicyano-1,2,3,4,5,6,7,8-octahydroanthracene and 1,4-dicyano-2,3,5,6-tetraethylbenzene were prepared by iodination[10] of the appropriate alkylated benzene followed by replacement of the iodide by cyanide using copper cyanide.[10]

(9) Maroulis, A. J.; Arnold, D. R. *J. Am. Chem. Soc.* **1976**, *98*, 5931.

(10) Suzuki, H.; Nakamura, K.; Goto, R. *Bull. Chem. Soc. Jpn.* **1966**, *39*, 128. Suzuki, H.; Hanafusa, T. *Synthesis* **1974**, *1*, 53.

(11) Colon, I.; Kelsey, D. R. *J. Org. Chem.* **1986**, *51*, 2627.

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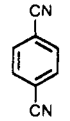
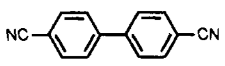
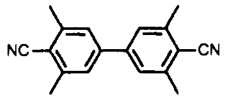
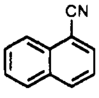
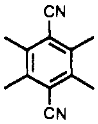
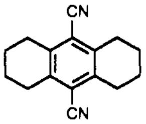
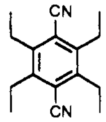
Table I. Photoinduced SET Anti-Markovnikov Lactonization of 5-Methyl-4-hexenoic Acid (**1**) to **2** and **3**: Properties of Electron-Acceptor Photosensitizers and Reaction Results

sensitizer	$E_{1/2}$* (red),^{a,b} V	K_{SV},^{c} L/mol	Φ_s^{d}	Φ_2^{e}	Φ_3^{e}	time,^{e} min	equiv of sensitizer consumed	yields^e 2, %	yields^e 3, %	total yield,^{e} %
 **4**	2.50	150	0.882	0.018	0.003	245	0.38	31	5	36
				[0.042	0.011	135		27	5	32]^f
		[161	0.889]^a							
 **5**	2.27	89	0.817	0.029	0.010	180	0.22	37	10	47
				[0.043	0.016	120		31	9	40]^f
		[89	0.816	0.022	0.009	270		33	11	44]^a
				[0.044	0.019	150		27	11	38]^{a,f}
 **6**	2.00	[81	0.801	0.022	0.008	480	*g*	42	10	52]^a
				[0.044	0.019	170	*g*	33	11	44]^{a,f}
 **7**	1.78	96	0.828	0.039	0.006	180	0.25	46	6	52
		[94	0.825]^a							
 **8**	1.91	76	0.792	0.152	0.017	60	0.08	76	8	84
		[79	0.798]^a							
 **9**	1.84	63	0.758	0.168	0.017	70	0.03	79	7	86
		[64	0.763]^a							
 **10**	1.89	46	0.696	0.167	0.016	60	0.05	83	6	89
		[46	0.695]^a							

[a] Measurements made in pure acetonitrile. [b] Excited-state oxidizing potential. For calculation, see ref 12 and supplementary material. [c] Measurements made in 75% acetonitrile–25% water. The average correlation coefficient for the Stern–Volmer plots was 0.995. [d] Quantum yield for sensitization of **1**. Defined by the equation $\Phi_s^{-1} = 1 + (k_q\tau[\mathbf{1}])^{-1}$, where k_q = rate of fluorescence quenching by **1** and τ = excited-state lifetime of the sensitizers ($k_q\tau = K_{SV}$). [e] Preparative photochemistry was carried out in acetonitrile (1.5 mL)–water (0.5 mL) containing 0.10 mmol of **1**, 0.015 mmol of biphenyl, and the following quantites of photosensitizer: **4**, 0.05 mmol; **5**, 0.04 mmol; **6**, 0.04 mmol (not completely soluble even in pure acetonitrile, relatively insoluble in acetonitrile–water); **7**, 0.04 mmol; **8–10**, 0.015 mmol. All other measurements were carried out on solutions of the same molar ratios on a smaller scale, unless otherwise specified. [f] Irradiation carried out in quartz tubes. [g] Loss not evaluated because of insolubility of the sensitizer.

data for each of the sensitizers relative to $E_{1/2}$*(red) (excited state),[12-14] the Stern–Volmer quenching constant (k_{SV}), the quantum yield for sensitization of **1**, quantum yields for formation of **2** and **3**, the time for complete reaction, equivalents of sensitizer consumed, yields of **2** and **3**,[15] and the combined yield of **2** and **3** (material balance).[15]

As can be noted from Table I, yields of products and quantum yields of products both improved as one progressed from **4** to **9** and **10**. At the same time, consumption of sensitizer decreased. Thus, the major goal of minimizing the side reactions of the sensitizer (anion radical) and the substrate (cation radical) have been achieved with the net result of improved yields.[16]

While the impact of steric hindrance on a bimolecular coupling reaction is readily rationalized, the role of steric encumbrance on quantum yields is less obvious.[17] As can be seen from Table I, the quantum yields for quenching of the excited-state sensitizers

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(12) Ultraviolet spectra were recorded on a Varian Cary 118 spectrophotometer; excitation and emission spectra were recorded on a Spex-Fluorolog F112X spectrofluorometer.

(13) Cyclic voltammetry was carried out using a Princeton Applied Research Model 273 potentiostat/galvanostat.

(14) Calculated as $E_{1/2}$*(red) = $E_{0,0}$ + $E_{1/2}$(red); see: Jones, G., II; Chiang, S.-H.; Becker, W. G.; Greenberg, D. P. *J. Chem. Soc., Chem. Commun.* **1980**, 681. $E_{1/2}$(red) values were obtained by cyclic voltammetry using platinum working and auxiliary electrodes vs a saturated calomel electrode and were referenced to ferrocene/ferrocenium couple at 0.31 V vs SCE. $E_{0,0}$ values correspond to the energy at the intersection of the excitation and emission spectra (see supplementary material).

(15) Yields were determined via GLC using acetophenone (added after completion of the photochemical experiment) as an internal standard. In those cases where the products were isolated and separated by preparative chromatography, the yields were slightly lower.

(16) When **4** was used as photosensitizer, the coupling product dihydro-5-[1-(4-cyanophenyl)-1-methylethyl]-2(3*H*)-furanone was isolated in 21% yield. Bottorff, K. J. Ph.D. Thesis, University of Minnesota, 1986, p 214.

(17) For selected references to steric effects and distance effects in photoinduced single-electron-transfer reactions, see: Jones, G., II; Chatterjee, S. *J. Phys. Chem.* **1988**, *92*, 6862. Yorozu, T.; Hayashi, K.; Irie, M. *J. Am. Chem. Soc.* **1981**, *103*, 5480. Oliver, A. M.; Paddon-Row, M. N. *J. Chem. Soc., Perkin Trans. 1* **1990**, 1145. See, also: Gould, I. R.; Ege, D.; Moser, J. E.; Farid, S. *J. Am. Chem. Soc.* **1990**, *112*, 4290. Finckh, P.; Heitele, H.; Volk, M.; Michel-Beyerle, M. E. *J. Phys. Chem.* **1988**, *92*, 6584. Bunce, N. J.; Safe, S.; Ruzo, L. O. *J. Chem. Soc., Perkin Trans. 1* **1975**, 1607.

($\Phi_{\text{sensitization}}$) remains relatively constant, while the quantum yields for the formation of **2** increase by a factor of 9 as one progresses from **4** to **9** and **10** as sensitizer. Quenching rate constants (k_q, $M^{-1}\ s^{-1}$) for **4**, **7**, **8**, and **9** were 1.66×10^{10}, 1.06×10^{10}, 1.09×10^{10}, and 9.8×10^{9}, respectively, for the quenching of sensitizer fluorescence by **1** in acetonitrile.[18] Thus, electron transfer from the substrate, **1** [$E_{1/2}(\text{ox}) = 1.77$ V], to the excited-state oxidant would appear to be diffusion controlled. This indicates that there is little, if any, observable steric hindrance to the initial electron transfer from **1** to the excited-state oxidant. Thus, the major influence of the bulky substituents must be on back electron transfer. This is consistent with the hypothesis that back electron transfers are "very sensitive to small structural changes."[19,20]

In summary, we have demonstrated the advantages which can accrue through the use of sterically encumbered sensitizers in photoinduced SET reactions.

Acknowledgment. We are indebted to the National Science Foundation for a grant which supported this investigation.

Registry No. 1, 5636-65-7; **2**, 38624-29-2; **3**, 22616-89-3; **4**, 623-26-7; **5**, 1591-30-6; **6**, 137396-51-1; **7**, 86-53-3; **8**, 2619-37-6; **9**, 137396-52-2; **10**, 137396-53-3; dihydro-5-[1-(4-cyanophenyl)-1-methylethyl]-2(3*H*)-furanone, 137396-54-4.

Supplementary Material Available: Properties of the sensitizers **4–10** including UV absorption, fluorescence emission, quantum yield for fluorescence, and ground-state reduction potentials (1 page). Ordering information is given on any current masthead page.

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(18) The excited-state lifetimes of **4**, **7**, **8**, and **9** were 9.70,[5] 8.92,[9] 7.22, and 6.53 ns, respectively. We thank Dr. K. Tominaga for measuring the lifetimes of **8** and **9**.

(19) Gould, I. R.; Moser, J. E.; Ege, D.; Farid, S. *J. Am. Chem. Soc.* **1988**, *110*, 1991.

(20) The role of biphenyl in these reactions is not completely evident. In the absence of biphenyl, reaction times increase dramatically, although overall yields decrease only slightly.

Spectroscopic Detection of Ammonium Ylides from Arylchlorocarbenes and Amines

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The reactions of carbenes with amines have been extensively studied[1-4] and the subject has been recently reviewed.[5] In most cases an ammonium ylide is invoked as an intermediate for this reaction. The spectroscopic detection of this intermediate has only been reported for the reaction of 1-naphthylcarbene and triethylamine,[6] and the role of an ammonium ylide in the mechanism of carbene insertion into the N–H bond of amines has never been demonstrated. Laser flash photolysis (LFP) of 3-chloro-3-aryldiazirines in the presence of diethylamine (DEA) make possible direct observation of the UV spectrum of ammonium ylide, and therefore the formal insertion into N–H bonds is classified as a two-step process.

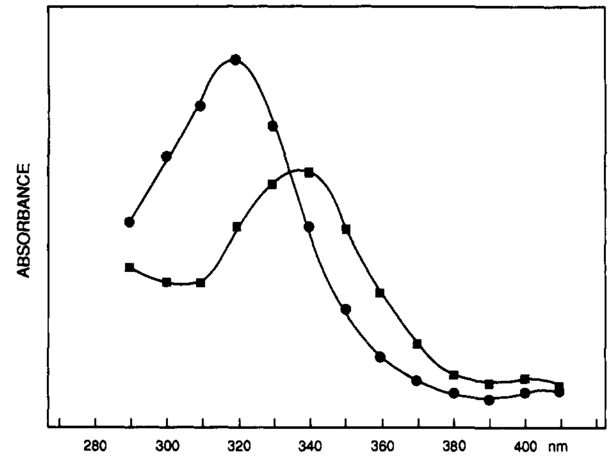

Figure 1. Transient absorption spectra for a solution of 3-chloro-3-(*p*-chlorophenyl)diazirine (0.015 M) and DEA (0.048 M) in isooctane. Time (t) after 200-ps excitation at 355 nm is (●) 0 and (■) 16 ns.

Photolysis of 3-chloro-3-aryldiazirines in the presence of DEA yielded *N,N,N′,N′*-tetraethylbenzylidenediamines as observed by Tomioka et al.[7] These authors suggested that the free arylchlorocarbene reacts with the N–H bond of the amine to afford the α-chlorobenzylamine which should easily undergo attack by a second DEA to give the final product. 3-Chloro-3-(*p*-chlorophenyl)diazirine (PCPD) (10^{-2} M) in isooctane was flashed with a 200-ps, 355-nm pulse from a frequency tripled mode-locked Nd-YAG laser. The quenching rate constant of the carbene **1**, *p*-Cl-Ph$\ddot{\text{C}}$Cl, monitored at 310 nm, by DEA was obtained in the usual manner by plotting the observed pseudo-first-order rate constant ($k_{\text{obs}} = k_0 + k_q[\text{amine}]$ where k_0 is the rate constant of carbene decay in the absence of quencher) for the carbene decay vs [DEA] from 0.5–10 mM. The linear plot yielded a rate constant for the reaction of **1** with DEA at 27 °C of $k_q(\mathbf{1}, \text{DEA}) = (2.33 \pm 0.10) \times 10^{9}\ M^{-1}\ s^{-1}$.

For DEA concentrations less than 10 mM, no new transient other than that of the carbene was detected.[8] When the DEA concentrations are sufficiently high (20–400 mM), an additional transient ($\lambda_{\text{max}} = 340$ nm) was observed (Figure 1). It can easily be seen from this figure that during the first 16 ns after excitation there is a growth of a new transient in the 340–400-nm region. We attribute this transient to the absorption of the ammonium ylide because (1) this transient is absent in the absence of DEA and (2) its rate of growth matches the rate of decay of the carbene as extrapolated from data at low [DEA]. These results are given in a log–log plot of k_{obs} vs [DEA]. In the 20–400-mM DEA range, k_{obs} vs [DEA] deviates from linearity which can be explained by the increasing contribution of ylide absorption to the measured signal. At low [DEA], a slope of unity is obtained in agreement with $k_{\text{obs}} = k_0 + k_q[\text{amine}] \simeq k_q[\text{amine}]$, which leads to $\log k_{\text{obs}} = \log k_q + \log[\text{amine}]$, whereas at high [DEA], the slope is not unity but not zero. The spectrum of the ylide was made at $[\text{DEA}] = 4.8 \times 10^{-2}$ M which is indicated by point A in Figure 2. A lifetime around 26 ns at point A was obtained by a first-order analysis of the decay of the transient absorption at 310 nm. In fact, this absorption is the sum of the carbene and the ylide absorptions so that the decay is not simply first order. The carbene lifetime extrapolated from data at low [DEA] is 9 ns. Also, if a first-order analysis is performed at 360–380 nm, where carbene absorption is low compared to that of the ylide, the decay time of the ylide is 32 ns. Figure 3 shows the analysis of the transient absorption at 340 nm as the sum of the absorptions of the carbene and of the ylide with lifetime of 10 and 32 ns, respectively. The

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(1) Johnson, A. W. *Ylide Chemistry*; Academic Press: New York, 1966.

(2) Hata, Y.; Watanabe, M. *Tetrahedron Lett.* **1972**, 4659.

(3) Tomioka, H.; Suzuki, K. *Tetrahedron Lett.* **1989**, 6353.

(4) Kirmse, W.; Arold, H. *Chem. Ber.* **1968**, *101*, 1008.

(5) Padwa, A.; Hornbuckle, S. F. *Chem. Rev.* **1991**, *91*, 263.

(6) Barcus, R. L.; Hadel, L. M.; Johnston, L. J.; Platz, M. S.; Savino, T. G.; Scaiano, J. C. *J. Am. Chem. Soc.* **1986**, *108*, 3928.

(7) Tomioka, H.; Haya, F.; Suzuki, K. *J. Chem. Soc., Chem. Commun.* **1988**, 1090.

(8) Gould, I. R.; Turro, N. J.; Butcher, J., Jr.; Doubleday, C., Jr.; Hacker, N. P.; Lehr, G. F.; Moss, R. A.; Cox, D. P.; Guo, W.; Munjal, R. C.; Perez, L. A.; Fedorynski, M. *Tetrahedron* **1985**, *41*, 1587.

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