Table I. Isotropic Hyperfine Coupling Constants (±0.01 MHz) from ENDOR Spectra of Flavin Radical Cations in Toluene/CF_3COOH at 265 K[a]

				position				
radical	H-6α	CH_3-7β	CH_3-8β	H-9α	H-5α	CH_2/CH_3-10β	N-5	N-10
1	−4.07	(−)0.80	+10.35	+1.60	−23.30	+7.33	(+)21.16	(+)13.00
2	−4.03	(−)0.86	+9.95 (9.53)	+1.53	−22.70 (32.24)	+13.83 (13.17)	+20.73 (23.83)	+13.19 (12.05)
3	+1.06	+3.18	+6.30	(+)0.32	−	+14.06	−	+13.08

[a] For numbering scheme refer to Figure 1. The signs of the smallest couplings are uncertain due to lack of resolution. Simulations of the ESR spectra using the ENDOR data gave satisfying agreements. Hyperfine data for **2** in brackets are taken from ref 21. For assignments see text and ref 5, 6, 14.

In Figure 1 the resolution achieved in our ENDOR experiments is demonstrated for flavin radical cations **1–3**. From the ENDOR spectrum of **3** six hyperfine couplings can be evaluated arising from five different sets of protons and from one ^{14}N nucleus, respectively. For **1** and **2** six proton and two nitrogen hyperfine coupling constants could be detected. An improved ENDOR response of the signals belonging to the larger ^{14}N hyperfine coupling occurred at higher temperatures (see, e.g., insert in Figure 1).[19] The relative signs of the hyperfine coupling constants were measured by electron nuclear nuclear TRIPLE resonance.[20] All isotropic couplings are collected in Table I. Only for **2** some hyperfine coupling constants are already known from ESR simulations.[21]

Since no further ^{14}N ENDOR lines could be detected, spin populations within the pyrimidine moiety of the flavin skeleton seem to be negligibly small. We therefore feel that our ENDOR results present the complete set of isotropic proton and nitrogen hyperfine coupling constants larger than 0.3 and 1 MHz, respectively.

One of the drawbacks of the ENDOR method is the fact that ENDOR line intensities normally do not reflect the number of nuclei belonging to a particular hyperfine coupling. Hence, unambiguous assignments of the couplings to specific molecular positions often call for isotopic labeling of the compound under study. We are currently synthesizing some partially deuterated derivatives of the flavin system. In the present studies some of the assignments could be established from the following facts: For **3** the discrimination between the methyl proton couplings of positions 7 and 8 is based on a comparison with similar radicals bearing only one methyl group in position 7 or 8 respectively.[22] The largest (negative) proton coupling of **1** and **2** has to be assigned to the proton attached to the nitrogen in the 5 position, because the respective ^{1}H ENDOR lines do not show up when using deuterated trifluoroacetic acid for the sample preparation. Comparison of **3** with **1** or **2** shows that the smaller nitrogen coupling can be ascribed to position 10. Thus in **1** and **2** the larger nitrogen coupling can be assigned to position 5. Since even the nitrogen in position 10 has relatively large spin population, the largest methyl proton coupling of 14 MHz can be assigned to the methyl group at this nitrogen. This assignment is supported by comparison of **2** with **1** because substitution of the methyl by the ribityl group results in a decrease of the respective hyperfine coupling of almost 50%. It should be mentioned that all the other couplings, including those of the nitrogen at position 10, remain essentially unaffected by this substitution. On the other hand, substitution of N by S in position 5 causes a considerable redistribution of the spin density within the benzene fragment (Table I).

As has recently been demonstrated, it is possible to study protein bound organic π radicals under physiological conditions by ENDOR spectroscopy in aqueous solution.[23] We therefore feel encouraged to extend our ENDOR experiments to the investigation of naturally occurring flavoenzymes in order to get a better understanding of structures, bondings, and functions of flavins in biological systems.

Stereoselective Carbonyl Olefination via Organosilicon Compounds

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Of the many reactions available for carbonyl olefination, the silicon method, which is known as Peterson olefination,[1] has been shown in several cases to be superior to the conventional Wittig reaction due to the higher reactivity of α-silyl carbanions.[2] The significant limitation on the broad utility of these reagents often arises from the lack of stereoselectivity of the reactions.[1] In order to circumvent this problem, several indirect approaches were reported.[3] We report here an efficient silicon-mediated alkene synthesis which directly produces (Z)-alkenyl derivatives almost exclusively.

We have found that 1,3-bis(trimethylsilyl)propyne (**1**)[4] may be rapidly metalated at −78 °C in dry tetrahydrofuran (THF) with *tert*-butyllithium in essentially quantitative yield.[5] Our observation that the produced anion reacts with cyclohexanone to furnish the enyne **2** in 83% yield, accompanied by a very small amount (<3%) of the corresponding cumulene derivative,[6] es-
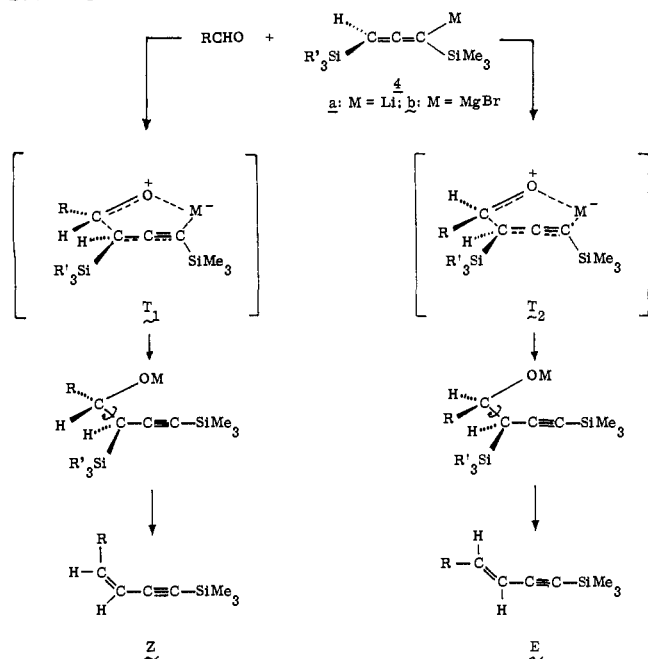
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(21) Müller, F.; Hemmerich, P.; Ehrenberg, A. In "Flavins and Flavoproteins"; Kamin, M., Ed; University Park Press: Baltimore, 1971.
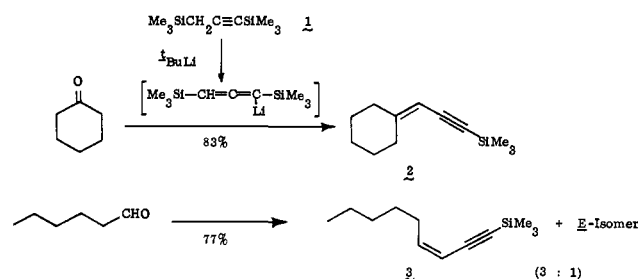
(22) Bock, M., unpublished results.

(23) Lendzian, F.; Lubitz, W.; Scheer, H.; Bubenzer, C.; Möbius, K. *J. Am. Chem. Soc.*, in press.

(1) For an excellent review, see: (a) Chan, T.-H. *Acc. Chem. Res.* **1977**, *10*, 442. (b) See also: Jarvie, A. W. P. *Organomet. Chem. Rev., Sect. A* **1970**, *6*, 153.

(2) Boeckman, R. K.; Silver, S. M. *Tetrahedron Lett.* **1973**, 3497. Shimoji, K.; Taguchi, H.; Oshima, K.; Yamamoto, H.; Nozaki, H. *J. Am. Chem. Soc.* **1974**, *96*, 1620. *Bull. Chem. Soc. Jpn.* **1974**, *47*, 2529.

(3) (a) Hudrlik, P. F.; Peterson, D. *Tetrahedron Lett.* **1974**, 1133. *J. Am. Chem. Soc.* **1975**, *97*, 1464. (b) Chan, T.-H.; Mychajlowskij, W.; Ong, B. S.; Harpp, D. N. *J. Organomet. Chem.* **1976**, *107*, C1.

(4) Prepared from 1-(trimethylsilyl)propyne (Corey, E. J.; Kirst, H. A. *Tetrahedron Lett.* **1968**, 5041) by the following procedure: Treatment of 1-(trimethylsilyl)propyne in ether at −5 °C with tetramethylethylenediamine and an equivalent amount of *n*-butyllithium under argon led to complete metalation. After 30 min, chlorotrimethylsilane (1 equiv) was added, and the mixture was stirred at room temperature for 12 h. After extractive workup followed by distillation [bp 75–76 °C (34 mmHg)], 1,3-bis(trimethylsilyl)propyne was obtained as a colorless liquid in 70–75% yield; ^{1}H NMR (CDCl$_3$) δ 0.17 and 0.24 (2s, 9 H each), 1.61 (s, 2H). For another preparation of the compound, see: Jaffe, F. *J. Organomet. Chem.* **1970**, *23*, 53.

(5) Metalation may be also carried out with *n*-butyllithium and tetramethylethylenediamine (1:1) at −78 °C for 1 h.

(6) Cumulene derivatives, which have the higher R_f values on TLC assay, are the major byproducts from this reaction and may be readily removed by simple column chromatography. The preparation of cumulene under different conditions will be published in due course.

Communications to the Editor

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Scheme I

Table I. Enyne Synthesis from Disilylpropynes and Carbonyl Compounds[a]

entry	carbonyl compd	R'$_3$Si	counterion	yield,[b] %	olefin ratio[c] (Z/E)
A		Me$_3$Si	Li	83	
			MgBr	88	
		Et$_3$Si	MgBr	93	
B		Me$_3$Si	Li	77	3:1
			MgBr	75	7:1
		Et$_3$Si	Li	78	6:1
			MgBr	89	31:1
		t-BuMe$_2$Si	MgBr	65	>50:1
C		Me$_3$Si	Li	69	8:1
			MgBr	84	20:1
		Et$_3$Si	Li	88	10:1
			MgBr	96	23:1
		t-BuMe$_2$Si	Li	55[d]	12:1
			MgBr	75	30:1
D		Me$_3$Si	Li	53	1:1
			MgBr	76	3:1
		Et$_3$Si	Li	63	1:1
			MgBr	78	2:1
		t-BuMe$_2$Si	MgBr	55	1:1
E	Ph	Me$_3$Si	MgBr	88	2:1
		t-BuMe$_2$Si	MgBr	90	7:1

[a] All reactions were performed as described in detail in the text. [b] Values reported are isolated yields. [c] Olefin ratio was determined by GLC (SE-30). Pure E and Z isomers were separated by medium pressure liquid chromatography (Lobar column, hexane), and the structures were determined by ^{1}H NMR and IR analyses.[18] [d] A relatively large amount of the regioisomeric product[6] was produced in this particular case.

tablishes the site selectivity of this ambient anion in the reaction with carbonyl compounds. In a similar reaction of **1** with hexanal, the corresponding enyne **3** was produced in 77% yield with moderate stereoselectivity ($Z/E = 3:1$).

Since the syn elimination of the β-oxido trialkylsilyl derivative is well established,[7] an explanation for the observed stereoselectivity must be attributed to the diastereoselective addition of the α-silyl carbanion to the carbonyl compound (Scheme I). Given the reasonable postulate that the reaction proceeds via a pericyclic process,[8] the influence of variable steric parameters may be analyzed to determine their effects upon the relative heats of formation of diastereoisomeric transition states. Thus, for the allenyl anion **4**,[9] one might anticipate that the transition state T$_2$ might be destabilized relative to T$_1$ by maximizing the R ↔ R'$_3$Si steric parameter. To achieve greater stereochemical regulation in the kinetically controlled condensation process, we have studied the counterion[10] and steric effects conferred upon these reactions. Thus, the allenylmagnesium reagent **4b**, prepared by the addition of 1 equiv of magnesium bromide in ether to **4a**, reacts with hexanal to give the enyne **3** with higher stereoselectivity ($Z/E = 7:1$). Excellent diastereoselection was finally attained in the formation of the Z isomer by changing both the counterion (Li

→ Mg) and the silyl group (Me$_3$Si → t-BuMe$_2$Si),[11] and (Z)-**3** was obtained almost exclusively ($Z/E > 50:1$).

It is apparent from the data in Table I that the consequence of counterion and steric effects may well be generalizable (cf. entries B, C, and E). Clearly, this synthetic transformation provides a simple route to many natural products hitherto accessible only by lengthy or complicated syntheses.[12] For example, it should be especially useful in the field of anticholinergic alkaloids, histrionicotoxin and gephyrotoxin.[13]

In contrast to aliphatic or α,β-unsaturated aldehydes, the modest levels of stereoselectivity observed with benzaldehyde (entry D) were surprising. In fact, we have observed that the trend of the geometric ratio is opposite to what one would predict based upon the above condensation study. This change in ratio may not be fully answerable at present but is possibly due to an acyclic transition state or other electronic factors.[14]

The representative carbonyl olefination summarized in Table I was carried out according to the following general procedure: To a solution of 2.0 mmol of the disilyl derivative in 6 mL of dry THF was added dropwise with stirring at −78 °C a solution of

(7) Hudrlik, P. F.; Peterson, D.; Rona, R. J. *J. Org. Chem.* **1975**, *40*, 2263.

(8) Rautenstrauch, V. *Helv. Chim. Acta* **1974**, *57*, 496. A similar mechanism was suggested for the stereoselective generation of *erythro*-acetylenic diol from the allenyl Grignard reagent and carbonyl compounds. See: Mercier, F.; Epsztein, R.; Holand, S. *Bull. Soc. Chim. Fr.* **1972**, 690.

(9) Propargyl Grignard reagent has been shown to exist in the allenyl form. See: Prevost, C.; Gaudemar, M.; Miginiac, L.; Bardone-Gaudemar, F. *Bull. Soc. Chim. Fr.* **1959**, 679.

(10) For counterion-dependent processes of ambident anions, see: (a) Lau, P. W. K.; Chan, T. H. *Tetrahedron Lett.* **1978**, *27*, 2383. For a general review, see: (b) Seebach, D.; Geiss, K.-H. "New Applications of Organometallic Reagents in Organic Chemistry"; Elsevier: Amsterdam, 1976; p 22.
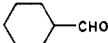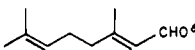
(11) Prepared from 1-(trimethylsilyl)propyne by the following procedure: Treatment of 1-(trimethylsilyl)propyne in ether at −5 °C with *tert*-butyllithium (1 equiv) for 1 h led to complete metalation. The resulting pale yellow solution was treated with chlorotriethylsilane or *tert*-butylchlorodimethylsilane (1 equiv) and the mixture was stirred for 12 h. After extractive workup followed by distillation the disilylated propyne was obtained in 40–60% yield. 3-(Triethylsilyl)-1-(trimethylsilyl)propyne: bp 106–108 °C (31 mmHg); ^{1}H NMR (CDCl$_3$) δ 0.15 (s, 9 H) 1.60 (s, 2 H, CH$_2$C≡C). 3-(*tert*-Butyldimethylsilyl)-1-(trimethylsilyl)propyne: bp 106 °C (31 mmHg); ^{1}H NMR (CDCl$_3$) δ 0.14 and 0.19 (2s, 15 H), 0.98 (s, 9 H, *t*-Bu), 1.63 (s, 2 H, CH$_2$C≡C). The *n*-butyllithium–TMEDA method may cause the rearrangement of acetylenic bond in some cases.

(12) Holmes, A. B.; Raphael, R. A.; Wellard, N. K. *Tetrahedron Lett.* **1976**, 1539. Corey, E. J.; Ruden, R. A. *Ibid.* 1973, 1495.

(13) For a recent synthesis, see: Fujimoto, R.; Kishi, Y.; Blount, J. F. *J. Am. Chem. Soc.* **1980**, *102*, 7154.

(14) An acyclic extended transition state in which electrostatic repulsion is minimized was proposed for diastereoselection of aldol-type condensation. See: Murata, S.; Suzuki, M.; Noyori, R. *J. Am. Chem. Soc.* **1980**, *102*, 3248.

Table II. RCHO → RCH=CHCN[a]

entry	aldehyde	reagent	yield,[b] %	olefin ratio[c] (Z/E)
A	⬡—CHO	t-BuMe₂SiCH₂CN[d]	76	6:1
		Ph₃SiCH₂CN[d]	80	9:1
B	∿∿CHO	t-BuMe₂SiCH₂CN	62	3:1
		Ph₃SiCH₂CN	63	5:1
C	(branched)—CHO[e]	t-BuMe₂SiCH₂CN	79	2:1
		Ph₃SiCH₂CN	85	2:1

[a] All reactions were performed as described in the text.
[b] Values reported are isolated.   [c] Olefin ratio was determined by GLC (Carbowax 20 M). Vicinal olefinic coupling constants of Z-unsaturated nitriles: entry A, 11 Hz; B, 11 Hz; C, 11 Hz.   [d] See ref 21.   [e] Ca. 93% pure (E)-citral was used.

2.0 mmol of *tert*-butyllithium in pentane (1.8 M) under an argon atmosphere. [After 1 h at −78 °C, a freshly prepared ethereal solution (6 mL) of magnesium bromide (2.2 mmol)[15] was added and the stirring continued for an additional 15 min.[16]] The carbonyl compound (1.6 mmol) was then added. After 5 min, the solution was gradually warmed to 50 °C and stirred there for 2–3 h to complete the elimination.[17] The product was extracted with ether repeatedly, washed with dilute hydrochloric acid and water, dried, and concentrated in vacuo. The residual liquid was subjected to column chromatography on silica gel (hexane) to give the enyne.[18]

Due to the observed high stereoselectivities in our enyne synthesis, we have sought to extend the investigation to other systems, with the object of finding the generality of Scheme I. An interesting and synthetically important result was obtained with the carbanion derived from α-silylated acetonitrile,[19] which in principle is capable of reacting with carbonyl compounds in a similar mechanism as reagent **1**.[20] Thus, (triphenylsilyl)acetonitrile[21] was treated first with lithium diisopropylamide (1.0 equiv, −20 °C, THF, 30 min) and then with magnesium iodide[22] (1.1 equiv, 0.3 M solution in ether, −20 °C, THF, 5 min). To the resulting milky white suspension at −78 °C was added cyclohexanecarboxaldehyde (1.0 equiv), and the mixture was stirred at −78 °C for 5 min, 20 °C for 15 min, and 50 °C for 1 h. After the usual workup followed by column chromatography the α,β-unsaturated nitrile **5** was obtained in 80% yield (Z/E = 9:1). The examples cited in Table II illustrate the synthesis of unsaturated nitriles using the indicated reagents and reactants.

(15) Prepared from ethylene dibromide and magnesium in ether.
(16) This procedure was omitted in the case of lithium reagent. Thus, after 1 h at −78 °C, the carbonyl compound was introduced.
(17) We have observed that magnesium salts of β-hydroxysilanes undergo elimination more readily when the silyl group is trimethylsilyl than when it is *tert*-butyldimethylsilyl.
(18) The (Z)-enyne was characterized by an infrared absorption at ~14 μm and a coupling constant between the vicinal olefinic hydrogens of ~11 Hz observed in the ¹H NMR spectrum. On the other hand, the (E)-enyne was characterized by an infrared absorption at ca. 10.4 μm and a coupling constant of ~16 Hz. See ref 12 and 13.
(19) (a) Ojima, I.; Kumagai, M.; Nagai, Y. *Tetrahedron Lett.* **1974**, 4005. (b) Matsuda, I.; Murata, S.; Ishii, Y. *J. Chem. Soc., Perkin Trans. 1* **1978**, 26.
(20) For the stereospecific epoxy nitrile cyclization, the cyano anion in which the metal is located on the nitrogen atom was proposed as a possible structure for transition states. See: Stork, G.; Cama, L. D.; Coulson, D. R. *J. Am. Chem. Soc.* **1974**, *96*, 5268. Stork, G.; Cohen, J. F. *Ibid.* **1974**, *96*, 5270. Recently, monolithiated acetonitrile was reported to have three local singlet potential-energy surface minima, corresponding to three different structures, from minimal basis ab initio calculations, and the most stable of the three forms is the lithium atom acting as a bridge to compress the carbon–carbon bond. See: Moffat, J. B. *J. Chem. Soc., Chem. Commun.* **1980**, 1108. With this proposed structure the similar five-membered-ring transition state shown in Scheme I may also be considered.
(21) Prepared from lithiated acetonitrile and chlorosilanes; see ref 19b and references cited therein. (Triphenylsilyl)acetonitrile (56% yield): mp 135.5–136 °C (acetone); ¹H NMR (CDCl₃) δ 2.35 (s, 2 H), 7.43 (br s, 15 H). (*tert*-Butyldimethylsilyl)acetonitrile (50%): bp 102 °C (30 mmHg); mp 71–72 °C; ¹H NMR (CDCl₃) δ 0.29 (s, 6 H), 1.04 (s, 9 H), 1.68 (s, 2 H).
(22) Freshly prepared from magnesium and iodine in ether.

5 (Z/E = 9 : 1)
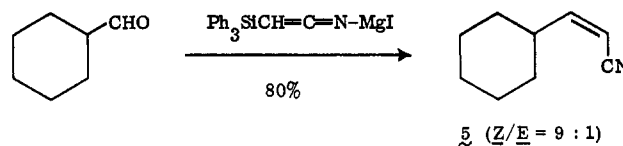
Although the mechanistic considerations given here can only be considered tentative, the present examples point to the importance of counterion and steric effects in the stereochemical course of the reaction. We believe that examination of other allenyl anions in this context will reveal similar stereochemical regulations.

Photoinduced Alkylation of Five-Membered Heteroaromatic Compounds via Electron-Transfer Reaction: Heterodimer Cation Radical Intermediacy

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Photoinduced intermolecular interactions between electron donor and acceptor molecules are a subject of current interest in connection with photochemical and photophysical processes involving exciplexes and radical ions.[1-5] Photocyclodimerization of electron-rich aromatic olefins proceeds via dimer cation radicals.[2] Nucleophiles such as methanol and cyanide ion can add to photochemically generated cation radicals.[3] However, little is known about the photocrossed addition between two different electron-rich unsaturated compounds,[4,5] which may occur through electron transfer. We now report a novel photocrossed addition between 1,1-diarylethylenes (D) and five-membered heteroaromatic compounds (D′) such as furans and 1-methylpyrrole. A key step of this photoreaction was the reaction of photochemically generated cation radicals of diarylethylenes (D⁺·) with neutral heteroaromatic compounds (D′) to give heterodimer cation radicals (DD′⁺·).

Irradiation of an acetonitrile solution of 1,1-diphenylethylene (**1a**) (20 mmol) and 2-methylfuran (**2b**) (200 mmol) containing a small amount of 1-cyanonaphthalene (**3a**) (2 mmol) gave 5-(2,2-diphenylethyl)-2-methylfuran (**5**) mp 38.5–39.5 °C, in 87% yield with 70% recovery of **3a**.[6,7] Irradiation of a mixture of **1a**

1a   **2b**   **5**
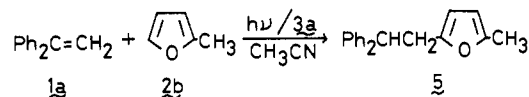
(1) For review articles, see: Davidson, R. S. *Mol. Assoc.* **1979**, *1*, 215–334. Mataga, N.; Ottolenghi, M. *Ibid.* **1979**, *2*, 1–78. Caldwell, R. A.; Creed, D. *Acc. Chem. Res.* **1980**, *13*, 45. Lewis, F. D. *Ibid.* **1979**, *12*, 152.
(2) (a) Ledwith, A. *Acc. Chem. Res.* **1972**, *5*, 133. (b) Neunteufel, R. A.; Arnold, D. R. *J. Am. Chem. Soc.* **1973**, *95*, 4080. (c) Farid, S.; Shealer, S. E. *J. Chem. Soc., Chem. Commun.* **1973**, 677. (d) Kuwata, S.; Shigemitsu, Y.; Odaira, Y. *J. Org. Chem.* **1973**, *38*, 3803. (e) Yamamoto, M.; Asanuma, T.; Nishijima, Y. *J. Chem. Soc., Chem. Commun.* **1975**, 53.
(3) Maroulis, A. J.; Shigemitsu, Y.; Arnold, D. R. *J. Am. Chem. Soc.* **1978**, *100*, 535. Shigemitsu, Y.; Arnold, D. R. *J. Chem. Soc., Chem. Commun.* **1975**, 407. Rao, V. R.; Hixson, S. S. *J. Am. Chem. Soc.* **1979**, *101*, 6458. Mizuno, K.; Ogawa, J.; Otsuji, Y. Annual Symposium on Photochemistry in Japan, Tokyo, Japan, 1979; pp 116.
(4) Farid, S.; Hartman, S. E.; Evans, T. R. "The Exciplex", Gordon, M., Ware, W. R., Eds.; Academic Press: New York, 1975; pp 327–343. Maroulis, A. J.; Arnold, D. R. *J. Chem. Soc., Chem. Commun.* **1979**, 351. Arnold, D. R.; Borg, R. M.; Albini, A. *Ibid.* **1981**, 138.
(5) Mizuno, K.; Kaji, R.; Otsuji, Y. *Chem. Lett.* **1977**, 1027. Mizuno, K.; Kaji, R.; Okada, H.; Otsuji, Y. *J. Chem. Soc., Chem. Commun.* **1978**, 594.
(6) Irradiation was carried out with a high-pressure mercury arc using a Pyrex filter (>280 nm) at ambient temperature.