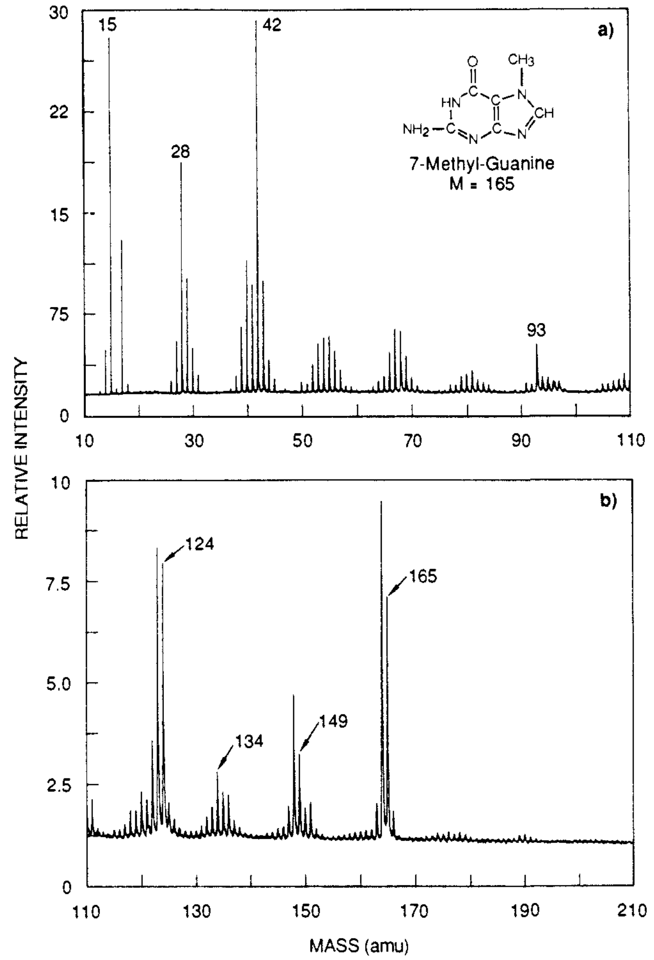

Figure 2. Mass spectrum of 7-methylguanine. The spectrum was accumulated over 1000 pulses. Main fragment peaks referred to in the text are indicated.

and water, respectively) to dry before introduction into the UHV chamber; small crystallites were observed.

Figure 1 displays the mass spectrum of TCDD taken with 200 pulses of Ar^+ bombardment and VUV laser ionization. While characteristic fragments are seen in the low mass region, notably m/e = 50 amu (CH_3Cl) and 84 amu (CH_2Cl_2), the high mass part of the spectrum shows parent molecules (m/e 320–328) in a clear fashion with the characteristic isotope pattern. Decomposition by loss of Cl and COCl is evidenced to be a minor process by the low intensity of the mass peaks at 286–292 and 257–264 amu, respectively. The signal of the parent molecule obtained with one single pulse had S/N of 10. Assuming a desorption yield of 1–10 molecules per incident ion, a detection limit of 3×10^{-17}–3×10^{-16} mol is estimated corresponding to the amount of compound removed in a single pulse; a much larger amount of material was on the sample mount for these initial experiments. Thus this is an extrapolated limit. Note this sensitivity can be improved with better spatial dispersion of the sample on the substrate and with a higher intensity VUV source. For the current 1-mm diameter focus of the light (passing about 1 mm above the sample), the estimated ionization efficiency is about 1%; an efficiency too high would lead to multiple absorption and excessive fragmentation. We also note that with multiphoton ionization at 248 and 308 nm no parent molecular ion or even structurally significant fragment were observed.

The spectrum of the purine 7-methylguanine shown in Figure 2 also exhibits a strong parent ion signal (165 amu) as well as with the loss of hydrogen (164 amu) and highly characteristic fragment peaks at m/e = 149 and 134 amu due to the loss of the NH_2 and CH_3 groups. The fairly strong feature at m/e = 124 amu is likely due to the decomposition of the imidazole ring leaving a pyrimidine ring with an NH group attached; the peak at 93 amu then corresponds to the further loss of NH_2 and NH groups. The sensitivity here is the same as for the dioxin, that is, S/N of about 10 for a single pulse.

The extent of fragmentation from the ion bombardment versus the photoionization is not presently known though future comparative studies with laser desorption and photoionization at slightly longer wavelengths will help to clarify this issue. Additional structural information for unknown molecules can be obtained by photofragmentation with the addition of variable amounts of a second laser beam.[19] The approach reported here is also being applied to the surface analysis of bulk structural polymers.[14]

Acknowledgment. We thank NSF-Division of Materials Research and Perkin-Elmer Corp. Physical Electronics Division for financial support. U.S. thanks Deutsche Forschungsgemeinschaft for a fellowship.

Registry No. TCDD, 1746-01-6; 7-methylguanine, 578-76-7.

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(19) Hunt, D. F.; Shabanowitz, J.; Yates, J. R., III. *J. Chem. Soc., Chem. Commun.* **1987**, 548.

Accelerating Symmetry Forbidden Reactions: The Vinylcyclopropane → Cyclopentene Cation Radical Rearrangement

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Woodward–Hoffmann forbidden reactions represent perhaps the most general class of organic transformations which remain unrealized. Thus the discovery of general ways to accelerate these reactions is an important experimental goal. One-electron oxidation may be a simple and useful strategy for this purpose.[1] We describe herein the successful application of this idea to the [1,3] sigmatropic rearrangement of vinylcyclopropanes to cyclopentenes.

The accelerating effect of one-electron oxidation on the rate of a symmetry-forbidden reaction has been most clearly demonstrated for the dimerization of substituted ethylenes to cyclobutanes.[2] In one instance, for the cation radical dimerization of *trans*-4-propenylanisole, the activation enthalpy for the cycloaddition reaction has been reported to be only 0.7 kcal/mol.[3]

It remains unclear, however, whether one-electron oxidation will have a similarly dramatic effect for other symmetry-forbidden reactions. For example, recent calculations on the degenerate [1,3] sigmatropic rearrangement of the propene cation radical predict a rather substantial barrier, ca. 30 kcal/mol.[4] We decided to test the viability of the cation radical [1,3] sigmatropic rearrangement by using the vinylcyclopropane → cyclopentene rearrangement as a model reaction.[5]

Our initial attempt at the cation radical ring expansion reaction utilized *cis*-1-*p*-anisyl-2-vinylcyclopropane (**1**) as a substrate and

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(1) For theoretical treatments of odd-electron pericyclic reactions, see: (a) Bauld, N. L.; Cessac, J. *J. Am. Chem. Soc.* **1977**, *99*, 23. (b) Haselbach, E.; Bally, T.; Lanyiova, Z.; Baertschi, P. *Helv. Chim. Acta* **1979**, *62*, 583. (c) Bauld, N. L.; Bellville, D. J.; Pabon, R.; Chelsky, R.; Green, G. *J. Am. Chem. Soc.* **1983**, *105*, 2378. (d) Pabon, R. A.; Bauld, N. L. *J. Am. Chem. Soc.* **1984**, *106*, 1145.

(2) For reviews, see: (a) Mattes, S. L.; Farid, S. *Acc. Chem. Res.* **1982**, *15*, 80. (b) Mattes, S. L.; Farid, S. In *Organic Photochemistry*; Padwa, A., Ed.; Marcel Dekker: New York, 1983; Vol. 6, p 233. (c) Julliard, M.; Chanon, M. *Chem. Rev.* **1983**, *83*, 425.

(3) Lorenz, K. T.; Bauld, N. L. *J. Am. Chem. Soc.* **1987**, *109*, 1157.

(4) Clark, T. *J. Am. Chem. Soc.* **1987**, *109*, 6838.

(5) For a review of the vinylcyclopropane → cyclopentene rearrangement, see: Hudlický, T.; Kutchan, T. M.; Naqvi, S. M. *Org. React.* **1985**, *33*, 247.

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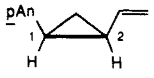
p-BrPh$_3$N$^{\bullet+}$SbF$_6^-$ or O$_2^{\bullet+}$SbF$_6^-$ as catalytic one-electron oxidants.[6] Although **1** underwent rapid cis → trans isomerization in the presence of these catalysts, neither it nor the trans isomer **2** ring expanded to 4-p-anisylcyclopentene. Isotopic labeling experiments suggested that the isomerization mechanism involved cleavage of the C1–C2 cyclopropane bond to provide the s-trans and/or the s-cis trimethylene cation radicals, **3** and **4**, as intermediates.



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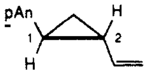

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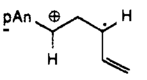

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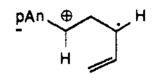
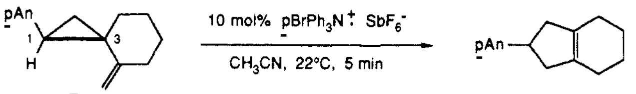


4

The lack of cyclopentene formation might be accommodated by these results in one of three ways. First, cleavage of $1^{\bullet+}$ or $2^{\bullet+}$ produces only the s-trans cation radical **3**, which, of course, is incapable of forming the cyclopentene cation radical. Second, cleavage of $1^{\bullet+}$ or $2^{\bullet+}$ produces the s-cis cation radical **4**, but it does not close for stereoelectronic reasons, e.g., it may be viewed as a disfavored 5-*Endo-Trig* reaction in Baldwin's[7] nomenclature. Third, ring closure of **4** to the cyclopentene cation radical might not occur for thermodynamic reasons, i.e., the 4-p-anisylcyclopentene cation radical might be less stable than the more delocalized cation radicals $1^{\bullet+}$ and $2^{\bullet+}$.

Only the first of these hypotheses provided an optimistic experimental prediction: a vinylcyclopropane with a double bond constrained to produce an s-cis trimethylene cation radical should ring expand upon one-electron oxidiation. Toward this end we prepared the spirocyclic vinylcyclopropane **5**.[8] Gratifyingly, it does ring expand under very mild conditions by using aminium ion catalysis. Apparently the first hypothesis is correct.



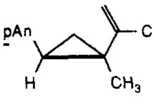
5 **6**

The rearrangement was achieved by the addition of **5** to 10 mol % p-BrPh$_3$N$^{\bullet+}$SbF$_6^-$ in acetonitrile at 22 °C for 5 min. Cyclopentene **6** was isolated as the sole product in 86% yield. For comparison, the thermal isomerization of **5** occurred with a convenient rate only above 200 °C. Extrapolating the thermal isomerization rate to 22 °C, gives $t_{1/2} \approx 10^{12}$ min.[10] Using $t_{1/2} \leq 1$ min for the aminium-catalyzed reaction provides a rate enhancement of $\geq 10^{12}$.

One possible explanation for the dramatic rate enhancement of the aminium ion catalyzed ring expansion reaction has a thermodynamic origin—perhaps the cation radical rearrangement is more exothermic than the neutral molecule rearrangement. This hypothesis was easily ruled out by comparing the oxidation potentials[11] of **5** (E_p = 1.06 V) and **6** (E_p = 1.48 V). The difference $\Delta H(5^{\bullet+} \rightarrow 6^{\bullet+}) - \Delta H(5 \rightarrow 6)$ is equal to IP (**6**) - IP (**5**). Thus the cation radical isomerization reaction is, in fact, less favorable than that of the neutral molecules by 0.42 V (ca. 10 kcal/mol). The low activation barrier for the cation radical isomerization must therefore be due to other factors. One satisfying explanation lies in the strength of the C1–C3 bond of **5** versus its cation radical. Thermodynamic cycle calculations[12] predict that the C1–C3 bond energy will be lowered by ca. 25 kcal/mol upon removal of an electron.

There has been a recent concern that aminium ion salts can lead to Brønsted acid-catalyzed reactions.[13,14] To test this possibility for the rearrangement of **5** → **6**, we examined the effect of added 2,6-di-*tert*-butylpyridine (**7**) on the aminium ion catalyzed reaction. By using the same conditions as above, except with an aminium ion solution containing 19 mol% of **7**, cyclopentene **6** was produced in 88% yield. A control experiment demonstrated that 25 mol % of 2,6-di-*tert*-butylpyridinium hexafluoroantimonate did not cause isomerization of **5**. These results argue strongly against an acid catalyzed isomerization mechanism.

Doubtless, if only conformationally rigid vinylcyclopropanes ring expanded the utility of the cation radical rearrangement would be limited. Fortunately, it is not. We have discovered that cyclopropanes **8** and **9** both cleanly ring expand to cyclopentene **10** under aminium ion catalysis.



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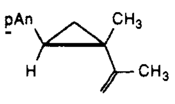

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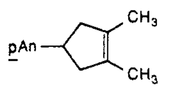

10

Addition of **8**[15] or **9**[15] to 11 mol % of p-BrPh$_3$N$^{\bullet+}$SbCl$_6^-$ in acetonitrile at 59 °C for 10 min provided **10** in 86% yield. The thermal isomerization of **8** and **9**, on the other hand, proceeded conveniently only above 200 °C. The rate enhancement of the aminium-catalyzed reaction was estimated to be $\geq 10^9$ at 59 °C.[16] As before, addition of 2,6-di-*tert*-butylpyridine (23 mol %) did not suppress cyclopentene formation; **10** was produced in 95% yield. The oxidation potentials of **8** (E_p = 1.09 V), **9** (E_p = 1.10 V), and **10** (E_p = 1.54 V) serve a similar purpose to that above. They reveal that the cation radical isomerization is thermodynamically less favorable than that of the neutral molecules by 0.45 V (10 kcal/mol).

The detailed mechanisms of the aminium ion catalyzed ring expansion reactions of **5**, **8**, and **9** remain uncertain. The two contenders, however, are clear: (1) stepwise isomerization via trimethylene cation radical intermediates or (2) concerted isomerization via odd-electron pericyclic transition states. Less clear is why **8** and **9** smoothly ring expand under aminium ion catalysis but **1** and **2** do not.[17] This issue as well as the distinction between the mechanistic pathways is currently under investigation.

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(6) Dinnocenzo, J. P.; Schmittel, M. *J. Am. Chem. Soc.* **1987**, *109*, 1561.

(7) Baldwin, J. E. *J. Chem. Soc., Chem. Commun.* **1976**, 734.

(8) **5** was prepared in four steps from (E)-2-(p-methoxybenzylidene)-cyclohexanone.[9] This substance was first reduced (LiAlH$_4$, Et$_2$O; 78%) to the allylic alcohol followed by cyclopropanation (CH$_2$I$_2$, ZnEt$_2$; 92%). The cyclopropyl alcohol so obtained was oxidized (pyridinium dichromate, N,N-dimethylformamide; 55%) to the cyclopropyl ketone and, finally, converted to **5** by Wittig olefination (Ph$_3$P=CH$_2$, Et$_2$O; 92%). Parallel synthetic work with the Z isomer of the starting material demonstrated that stereochemical integrity was maintained throughout the synthetic transformations.

(9) Billimoria, J. D. *J. Chem. Soc.* **1955**, 1126.

(10) The thermal isomerization half-life of **5** → **6** is ≈46 min at 211 °C. Using an activation entropy of -0.35 eu for the ring expansion (Simpson, J. M.; Richey, H. G., Jr. *Tetrahedron Lett.* **1973**, 2545) provides a half-life of 3 × 10^{12} min at 22 °C.

(11) The oxidation potentials (E_p versus SCE) were obtained by cyclic voltammetry (150 mV/s) at a platinum electrode in acetonitrile with ca. 0.1 M tetrabutylammonium hexafluorophosphate as the supporting electrolyte and were irreverible for **5**, **6**, **8**, **9**, and **10**.

(12) (a) The difference in the C1–C3 bond dissociation energies of **5** and $5^{\bullet+}$, ΔBDE, can be calculated from the equation,[12b] ΔBDE = BDE(**5**) - BDE($5^{\bullet+}$) = IP (**5**) - IP(TB), where IP(**5**) is the ionization potential of **5** (1.06 V)[11] and IP(TB) is the ionization potential of the trimethylene biradical produced by homolytic cleavage of the C1–C3 bond in **5**. The latter was approximated by the ionization potential estimated[12b] for the p-methoxybenzyl radical, -0.04 V versus SCE. Thus ΔBDE = 1.10 V or 25 kcal/mol. (b) Dinnocenzo, J. P., manuscript in preparation.

(13) (a) Gassman, P. G.; Singleton, D. A. *J. Am. Chem. Soc.* **1984**, *106*, 6085. (b) Gassman, P. G.; Singleton, D. A. *J. Am. Chem. Soc.* **1984**, *106*, 7993.

(14) See, however: Dinnocenzo, J. P.; Schmittel, M. *J. Am. Chem. Soc.*, submitted for publication.

(15) Compounds **8** and **9** were prepared as a separable mixture by cyclopropanation (Olofson, R. A.; Dougherty, C. M. *J. Am. Chem. Soc.* **1973**, *95*, 581) of 2,3-dimethyl-1,3-butadiene.

(16) The thermal isomerization half-life of **8**/**9** → **10** in nitrobenzene-d_5 is ≈40 min at 211 °C. Using an activation entropy of -0.35 eu for the ring expansion[10] provides a half-life of 2 × 10^9 min at 59 °C. Using $t_{1/2} \leq 2$ min for the aminium-catalyzed reaction provides a rate enhancement of $\geq 10^9$.

(17) The previously reported[6] aminium ion catalyzed rearrangement of **1** to **2** was carried out at low temperature (-40 °C) in acetonitrile. The failure to form 4-p-anisylcyclopentene under these conditions is *not* due to the low temperature. We have shown that the aminium ion catalyzed **1** → **2** rearrangement similarly occurs at elevated temperature (60 °C) but that no cyclopentene is formed.

In summary, the results presented here demonstrate the remarkable catalytic effect that one-electron oxidation can have on the rearrangement of vinylcyclopropanes to cyclopentenes.

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Electron-Transfer Reactions in Cyanine Borate Ion Pairs: Photopolymerization Initiators Sensitive to Visible Light

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Photoinitiation of polymerization is a process of immense practical, economic, and theoretical importance. In typical examples the polymerization of an acrylate or styrene-derived monomer is initiated by irradiation of a sensitizer with ultraviolet light. The excited state of the sensitizer may dissociate directly to form active free radicals as in the case of the benzoin ethers,[3] or it may first undergo a bimolecular electron-transfer reaction whose products initiate polymerization as is the case in the benzophenone–dimethylaniline system.[4] Efforts to extend the range of useful photoinitiators of free-radical polymerization to the visible region of the spectrum have heretofore met with only modest success.[5] These special initiators typically are sensitive only to blue light or suffer from thermal instability and have low quantum efficiencies. We report herein the discovery that triphenylalkylborate salts of cyanine dyes (Chart I) are photoinitiators of free-radical polymerization whose sensitivity throughout the entire visible spectral region is the result of a novel intra-ion-pair electron-transfer reaction.

The absorption spectra of the di-*n*-butyltetramethylindocarbocyanines (**1a–c**) in ethyl acetate, di-*n*-butyl suberate (DBS), or *n*-butyl acrylate solution exhibit modest solvatochromic shifts with maxima at ca. 556 nm ($\epsilon_{max} = 1.8 \times 10^5$ M^{-1} cm^{-1}) that are essentially independent of the identity of the counter ion. In acetonitrile solution, this absorption maximum shifts to 545 nm ($\epsilon_{max} = 1.0 \times 10^5$ M^{-1} cm^{-1}). Solutions of cyanine borate (**1c**) in butyl acrylate are stable in the dark, but polymerization occurs rapidly when they are irradiated with visible light. In contrast, irradiation of butyl acrylate solutions of the cyanine bromide (**1a**) or the hexafluorophosphate (**1b**) does not initiate polymerization. Other cyanine dyes absorbing at various wavelengths throughout the visible spectral region behave similarly.

The mechanism for operation of these cyanine borate initiators was investigated by steady-state and time-resolved methods. Irradiation of cyanine borate **1d** in N_2-purged ethyl acetate solutions containing increasing amounts of tri-*n*-butylstannane gives propylbenzene in 45% yield with a quantum efficiency of ca. 0.14 at extrapolated infinite stannane concentration. This finding signals generation of the phenylpropyl radical in this case and, by implication, the *n*-butyl radical from cyanine borate **1c**. Etter and co-workers[6] likewise inferred radical formation from bleaching studies of cyanine borates in the absence of traps. A related process operates in the reaction of these borates with excited-state cyanoarenes.[7]

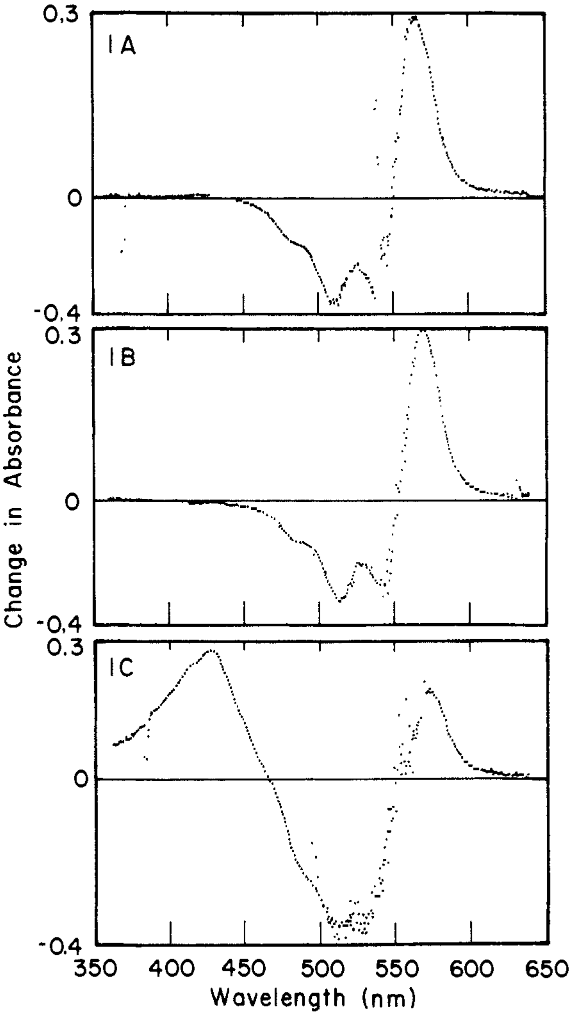
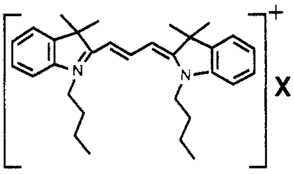


Figure 1. Transient absorption spectra recorded 1 μs after irradiation of the cyanine dyes at 532 nm: (1A) irradiation of cyanine borate (**1c**) in acetonitrile solution; (1B) irradiation of cyanine hexafluorophosphate (**1b**) in ethyl acetate solution; (1C) irradiation of cyanine borate (**1c**) in ethyl acetate solution.

Chart I



1a: X = Br
1b: X = PF_6
1c: X = $[n\text{-}C_4H_9B(Ph)_3]$
1d: X = $[Ph(CH_2)_3B(Ph)_3]$

Cyanines **1** fluoresce with quantum yields and lifetimes that vary with the nature of the solvent but, surprisingly, are essentially independent of the identity of the anion, Table I. The emission in the ester solutions, solvents of relatively low dielectric constant, has maxima at ca. 583 nm and efficiencies and lifetimes that clearly depend on the solvent viscosity. In acetonitrile solution,

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(1) University of Illinois.

(2) Mead Imaging.

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(4) Block, H.; Ledwith, A.; Taylor, A. R. *J. Polym. Sci.* **1972,** *10,* 3137. Bevington, J. C. *Radical Polymerization*; Wiley: New York, 1966.

(5) Eaton, D. F. *Adv. Photochem.* **1985,** *13,* 427.

(6) Etter, M. C.; Holmes, B. N.; Kress, R. B.; Filipovich, G. *Isr. J. Chem.* **1985,** *25,* 264.

(7) Lan, J. Y.; Schuster, G. B. *Tetrahedron Lett.* **1986,** *27,* 4261. Lan, J. Y.; Schuster, G. B. *J. Am. Chem. Soc.* **1985,** *107,* 6710.