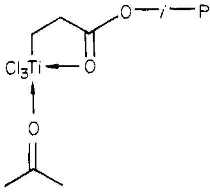
compound that is stable at room temperature for several months under vacuum and decomposes very slowly in solution ($t_{1/2}$ = 4 months; 26 °C, 0.1 M benzene). It melts at 90–95 °C with color change to reddish brown and sublimes with some decomposition at 90–110 °C (0.005 mmHg). Molecular weight by cryoscopy is 560–620, indicating a dimeric structure. Several lines of evidence suggest that **4** has the basic β-acylalkylmetal structure shown.[8] The ^{13}C NMR (proton noise decoupled) spectrum exhibits two nonequivalent methylene carbons, the broad signal at 100.6 ppm being assigned to the carbon bound to the metal. The ^{1}H NMR spectrum, showing a pair of A_2B_2-type triplets, resembles the spectrum of alkyl 3-(trichlorostannyl)propionate, which has a chelate structure similar to the one proposed here.[4b] The downfield shift of the carbonyl carbon (^{13}C NMR) and the weakening of the C=O bond (IR)[9] are also found for the stannylpropionate.[10] Undoubtedly, the internal coordination of the carbonyl group to the metal is responsible for the unusual thermal stability of **4**.[11] Bromine reacts with **4b** to give ethyl 3-bromopropionate, and oxidation of **4c** with molecular oxygen gives isopropyl 3-hydroxypropionate in good yield (Scheme I). Attempts to obtain diffractable crystals in order to get further information about the structure are in progress.

Having established the preparation of **4**, we then examined their reactivities with organic electrophiles. To our great satisfaction, the titanium alkyls smoothly transferred their propionate unit to aldehydes above 0 °C in methylene chloride (Scheme II).[12] Aliphatic aldehydes reacted cleanly with **4** to give the γ-hydroxy esters. The reaction provides a very efficient synthesis of this potentially useful class of compounds. Benzaldehyde initially gave the γ-hydroxybutyrate in moderate yield, but the product suffered in situ chlorination toward the end of the reaction. Chlorinated products were also obtained from p-nitrobenzaldehyde and crotonaldehyde. Ketones do not serve as reactive electrophiles for the titanium homoenolate. Addition of acetone to **4c** in benzene at once gave the monomeric addition complex **5**,[13] which remained quite stable. The reaction of acetophenone with **4c** gave the γ-hydroxy ester only in low yield. Chlorination of the initial adduct was a side reaction observed. Interestingly, **4** is inert to either benzoyl chloride or its more electrophilic derivative, the aluminum chloride complex. This inertness suggests that the trichlorotitanium alkyl **4** is substantially different in nature from the usual Grignard reagents.



5

We have demonstrated that the purple powder of the trichlorotitanium homoenolate has considerable potentialities as a novel reagent for organic synthesis. Various points of interest including the modification of the reactivities by ligand exchange as well as the preparation of other metal complexes are under further study.

Acknowledgment. We thank Professor Takakazu Yamamoto for helpful discussions and for provision of an IR facility and Dr. Yoko Kaizu for the measurement of the resonance Raman spectra.

Registry No. **3a**, 84098-43-1; **3b**, 27374-25-0; **3c**, 84098-44-2; **4a**, 84098-51-1; **4b**, 84098-52-2; **4c**, 84098-53-3; **5**, 84098-54-4; $TiCl_4$, 7550-45-0; Me_3SiCl, 75-77-4; $BrCH_2CH_2COOEt$, 539-74-2; $HOCH_2CH_2COO$-i-Pr, 84098-45-3; $PhCH_2CH_2CH(OH)$-CH_2CH_2COO-i-Pr, 84098-46-4; $PhCH(Cl)CH_2CH_2COOEt$, 2125-35-1; O_2N-p-$C_6H_4CH(OH)CH_2CH_2COOEt$, 84098-47-5; O_2N-p-C_6H_4CH-$(Cl)CH_2CH_2COOEt$, 84098-48-6; $PhCH{=}CHCH(OH)$-CH_2CH_2COOEt, 84098-49-7; $PhC(OH)(CH_3)CH_2CH_2COO$-i-Pr, 84098-50-0; $PhCH_2CH_2CHO$, 104-53-0; $CH_3CH_2CH(CH_3)CHO$, 96-17-3; PhCHO, 100-52-7; O_2N-p-C_6H_4CHO, 555-16-8; $CH_3CH{=}CHCHO$, 4170-30-3; $PhCOCH_3$, 98-86-2; $PhCH{=}CHCHO$, 104-55-2; acetone, 67-64-1; isopropyl (trichlorostannyl)propionate, 70508-46-2; 1-methylpropyl-2-oxotetrahydrofuran, 77755-97-6; ethyl chloroheptenoate, 84129-71-5.

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[8] **4c**: ^{1}H NMR (0.3 M $CDCl_3$) δ 1.51 (d, 6 H, J = 6 Hz), 2.40 (CH_2Ti) and 3.38 (A_2B_2 t, 2 H, J = ca. 7 Hz), 5.65 (qq, 1 H, J = 6, 6 Hz); ^{13}C NMR ($CDCl_3$) δ 21.6 (q), 44.1 (t), 77.7 (d), 100.6 (br, $w_{1/2}$ = ca. 45 Hz on PND), 189.8 (s); IR (0.1 M benzene) 2930 (s), 1603 (vs), 1425 (s), 1330 (m), 1260 (m), 1095 (s), 895 (m), 800 cm^{-1} (m); IR (0.02 M CL_4) 1608 cm^{-1}; IR (KBr) 1610 (br s), 1465 (m), 1390 (sh), 1375 (m), 1325 (s), 1095 (s), 880 (v br), 360 cm^{-1} (v br); resonance Raman (514.5 nm, solid) 360 (s), 285 (sh), 280 (br s), 265 (br s), 120 cm^{-1} (m). Anal. Calcd for $C_6H_{11}O_2Cl_3Ti$: C, 26.75; H, 4.12. Found: C, 26.59; H, 4.22. We owe the description of the homoenolate complex as **4** partly to a referee.

[9] (a) Driessen, W. L.; Groeneweld, W. L.; van der Wey, F. W. *Recl. Trav. Chim. Pays-Bas* **1970**, *89*, 353. (b) Brun, L. *Acta Crystallogr.* **1966**, *20*, 739.

[10] Isopropyl (trichlorostannyl)propionate: ^{1}H NMR ($CDCl_3$) δ 1.30 (d, 6 H, J = 6 Hz), 2.13 and 2.83 (A_2B_2 t, 2 H, J = ca. 7 Hz), 5.15 (qq, 1 H, J = 6, 6 Hz); ^{13}C NMR ($CDCl_3$) δ 21.53 (q), 24.22 (t), 28.20 (t), 75.00 (d), 180.54 (s); IR (0.03 M CCl_4) 2960 (w), 1665 (vs), 1388 (s), 1330 (m), 1265 (m), 1230 (m), 1105 (s), 900 cm^{-1} (w). Anal. Calcd for $C_6H_{11}O_2Cl_3Sn$: C, 21.18; H, 3.26. Found: C, 21.32; H, 3.24.

[11] Cf.: Wailes, P. C.; Coutts, R. S. P.; Weigold, H. "Organometallic Chemistry of Titanium, Zirconium, and Hafnium"; Academic Press: New York, 1974; Chapter 2. Schrock, R. R.; Parshall, G. W. *Chem. Rev.* **1976**, *76*, 246.

[12] We thank H. Oshino for some experimental help.

[13] **5**: IR (0.1 M benzene) 2940 (m), 1675 (s), 1605 (s), 1420 (m), 1370 (m), 1325 (m), 1250 (sh), 1240 (m), 1090 (m), 860 cm^{-1} (s). Molecular weight by cryoscopy is 310.

Photosensitized [4 + 2] Cyclodimerization of 1,3-Cyclohexadiene

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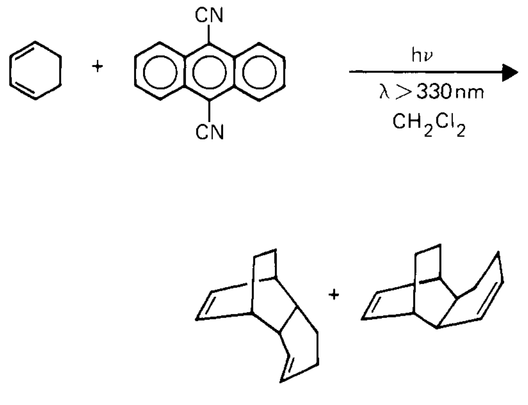
IBM Research Laboratory, San Jose, California 95193

Received June 21, 1982

Excited state complexes (excimers and exciplexes) and/or photoinduced electron-transfer processes have been implicated in a variety of photochemical reactions.[1] One interesting consequence of these phenomena is that the course of the photoreaction may be drastically altered from that of excited singlet and/or triplet pathways. We have found that 1,3-cyclohexadiene (CHD), when irradiated through a uranyl oxalate filter (λ >330 nm) in CH_2Cl_2 at room temperature in an inert atmosphere in the presence of 9,10-dicyanoanthracene (DCNA), produces almost exclusively the [4 + 2] adducts *endo*- and *exo*-dicyclohexadiene (**1** and **2**; 4:1) in >60% isolated yield[2] (eq 1). This constrasts



(1)

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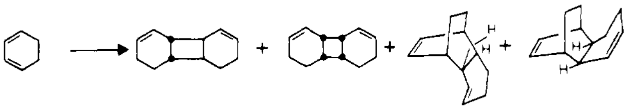
[1] Several reviews which include numerous references are as follows: (a) Mattes, S. L.; Farid, S. *Acc. Chem. Res.* **1982**, *15*, 80. (b) Caldwell, R. A.; Creed, D. *Ibid.* **1980**, *13*, 45–50. (c) Davidson, R. S. In "Molecular Association"; Foster, R., Ed.; Academic Press: London, 1975; p 215.

Table I. Photodimerization of Cyclohexadiene



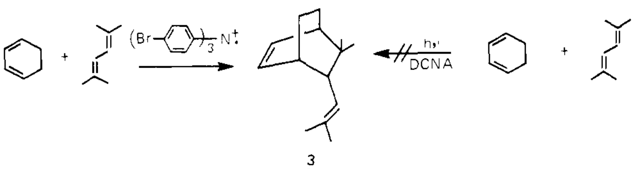
6 7 1 2

	overall dimer yield, %	relative yields			
		6	7	1	2
hν, direct[4] (quartz)		0.5	0.5		0.5
hν, direct[4] (>330 nm)		44	23		40
hν, triplet[3a]	92	60	20	trace	20
thermal[3]	32			80	20
DCNA, *hν* (>330 nm)	60			77	23

with the thermal reaction which produces **1** and **2** in low to moderate yields after 20 h at 200 °C[3] and with the singlet[4] and triplet-sensitized[3] dimerizations of cyclohexadiene, which produce predominately [2 + 2] products (Table I).

However, these results are strikingly similar to those reported by Libman several years ago.[5] In that work the [4 + 2] dimerization of several dienes including CHD in the presence of octafluoronaphthalene in CH_3CN was reported. Dramatic differences in product formation upon going from CH_3CN to cyclohexane were observed. Dimerization was suppressed in cyclohexane. On the basis of the strong role solvent played in the reaction, it was proposed that dimerization was preceded by the formation of excited-state charge-transfer complexes or ion pairs.[5] The intermediacy of ion pairs or free radical cations is further supported by work recently reported by Bauld and co-workers, who found that dimerization of CHD to **1** and **2** could be effected in good yield in the dark by oxidation of CHD with a triarylamine radical cation in CH_2Cl_2.[6]

The similarity between the photochemical and dark oxidative reaction ends, however, with CHD. When we extended the reaction to mixed systems such as 2,5-dimethylhexadiene (DMHD) and CHD identical with Bauld's experiment,[7] we found absolutely no evidence for the formation of the mixed dimer **3** (eq 2). Furthermore, the formation of the CHD dimer was completely quenched.

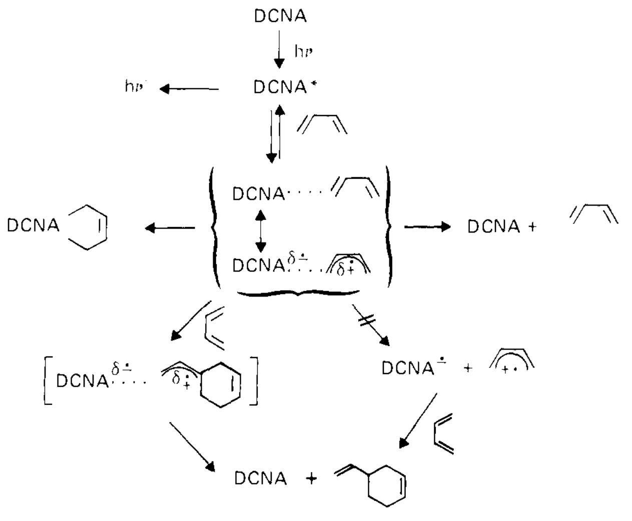


3

(2)

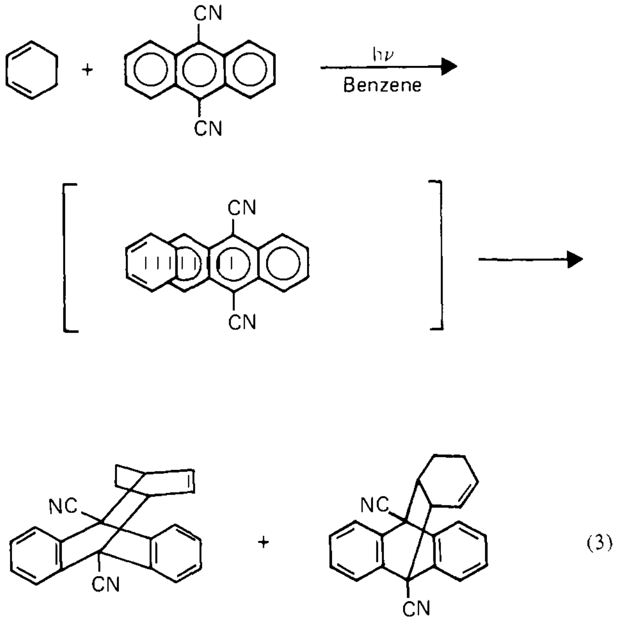
This was quite surprising since our initial simple conclusion was that after initial contact and formation of an excited-state complex, DCNA and diene underwent electron transfer to generate a radical cation/radical anion pair. It was then that the diene radical cation acting as an electron-poor dienophile underwent a [4 + 2] cycloaddition with available neutral diene. CHD and DMHD both quench DCNA fluorescence at similar diffusion-controlled rates, and one might expect to find as did Bauld that DMHD would be preferentially oxidized and the major product would be an adduct of that diene and CHD. Although the reaction may be inhibited by steric interactions, this particular reaction was demonstrated to proceed quite smoothly.[6]

Scheme I



Several possibilities exist for the striking difference in product observations between the thermal oxidation and photochemical experiments upon which we can speculate. Scheme I summarizes these possibilities.

In the photochemical experiment, at least one competing pathway, adduct formation between sensitizer and diene, prevails (eq 3). These products have been observed and reported earlier by Yang, who found them to be major products in benzene.[9] However, in CH_2Cl_2, this competition is not strong since adducts **4** and **5** are only observed[10] after prolonged irradiation of CHD and DCNA, whereas **1** and **2** are rapidly produced at much shorter irradiation times. Similarly, for DMHD and CHD with DCNA, little DCNA was consumed to give adduct under similar irradiation conditions and times. Interestingly, **1** and **2** are also produced upon irradiation of CHD and DCNA in benzene, though to a lesser extent.[11]



4 5

(3)

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(2) The products were isolated by distillation and identified by ^1H and ^{13}C NMR. Samples were also analyzed by GC (OV-1) and compared against authentic samples prepared by the method of Bauld.[6]

(3) (a) Valentine, D.; Turro, N. J.; Hammond, G. S. *J. Am. Chem. Soc.* **1964**, *86*, 5202–5208. (b) Alder, K., Stein, G. *Justus Liebigs Ann. Chem.* **1932**, *496*, 197–203.

(4) Schenck, G. O.; Mannsfield, S.-P.; Schomburg, G.; Krauch, C. H. *Z. Naturforsch., B* **1964**, *19B*, 18–22.

(5) Libman, J. *J. Chem. Soc., Chem. Commun.* **1976**, 361–362.

(6) Bellville, D. J.; Wirth, D. O.; Bauld, N. L. *J. Am. Chem. Soc.* **1981**, *103*, 718–720.

(7) Equimolar CHD and DMHD, 0.1 M.

(8) In CH_2Cl_2, for CHD, $k_q\tau = 151$; for DMHD, $k_q\tau = 232$.

(9) Yang, N. C.; Srinivasan, K. *J. Am. Chem. Soc.* **1975**, *97*, 5006–5008.

(10) Authentic samples were obtained as described by Yang,[9] isolated, and identified by NMR.

The differences may arise from the differences in the intermediates generated in the two experiments. In Bauld's thermal experiment, presumably radical cations of the dienes are first generated which subsequently react with available cisoid diene. However, in the photochemical experiment, free radical cations may not form, but rather a tightly bound complex, either an exciplex or radical cation/radical anion pair, reacts directly with cisoid diene to form dimer products, perhaps through an intermediate such as a "triplex" or "exterplex".[1b,12] Although radical cations and anions are known to form in sufficiently polar solvents such an CH_3CN, CH_2Cl_2 is much less polar and presents an intermediate polarity where the degree of solvent penetration and dissociation of the exciplex could be far less. Thus, differences in the structures of the dienes might mean differences in the structure of the subsequently formed complex, which could lead to very different reactivities with another diene. Current data, however, cannot rule out the possibility that identical intermediates form in both the photochemical and thermal oxidative experiments and that although DMHD efficiently quenches DCNA fluorescence, the lifetime of any intermediate complex formed may be too short to undergo subsequent dissociation and bimolecular chemistry.

We are currently studying the mechanism of this reaction in greater depth. Our preliminary findings are that the lack of reactivity and quenching behavior of DMHD is the exception rather than the rule, and other olefins and dienes do undergo [4 + 2] cycloadditions.

Registry No. 1, 703-35-5; **2**, 703-36-6; DMHD, 764-13-6; CHD, 592-57-4; DCNA, 1217-45-4.

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(11) Unpublished results.

(12) "Triplexes" have been proposed in authracene dimerizations in the presence of aromatic amines and dienes: (a) Saltiel, J.; Townsend, D. E.; Watson, D. D.; Shannon, P.; Finson, S. L. *J. Amer. Chem. Soc.* **1977**, *99*, 884-896. (b) Yang, N. C.; Shold, D. M.; Kim, D. *J. Am. Chem. Soc.* **1976**, *98*, 6587-6596. (c) Saltiel, J.; Townsend, D. C.; Watson, B. D.; Shannon, P. *J. Am. Chem. Soc.* **1975**, *97*, 5688-5695. (d) Saltiel, J.; Townsend, D. D. *J. Am. Chem. Soc.* **1973**, *95*, 6140-6142. (e) Campbell, R. O.; Lie, R. S. *Mol. Photochem.* **1974**, *6*, 207-223.

(13) Beens, H.; Knibbe, H.; Weller, A. *J. Chem. Phys.* **1967**, *47*, 1183.

Halonium-Initiated Cyclizations of Allylic Urethanes: Stereo- and Regioselectivity in Functionalizing the Olefinic Bond[1]

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Received August 19, 1982

Studies of relative asymmetric induction in acyclic systems have served as the basis of conceptually new strategies for synthesis.[2] We viewed a stereo- and regiospecific addition to the olefinic bond of an acyclic allylamine as the key step in an approach to some highly functionalized alkaloids, for example, naphthyridinomycin.[3] We have now shown that the halonium-initiated cyclization of urethane **1** gives the cyclic urethanes **2**[4] and/or **3** (R^1 = H, R^2 = Ar or R^1 = Ar, R^2 = H). Each process (**1** → **2** and **1** → **3**) is stereospecific. Furthermore, the regioselectivity of the cyclization depends on the electronic properties of the olefinic substituents (R^1 and R^2).

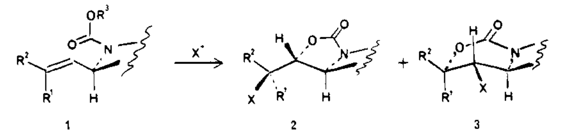
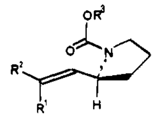
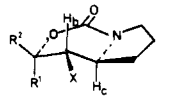


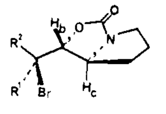
Chart I



7a, R^1 = H; R^2 = C_6H_5; R^3 = CH_3
7b, R^1 = C_6H_5; R^2 = H; R^3 = CH_3
8a, R^1 = H; R^2 = C_6H_5; R^3 = *t*-Bu
8b, R^1 = C_6H_5, R^2 = H; R^3 = *t*-Bu
9a, R^1 = H; R^2 = *o*-C_6H_4CN; R^3 = *t*-Bu
9b, R^1 = *o*-C_6H_4CN; R^2 = H; R^3 = *t*-Bu
10a, R^1 = H; R^2 = *p*-$C_6H_4NO_2$, R^3 = *t*-Bu
10b, R^1 = *p*-$C_6H_4NO_2$, R^2 = H; R^3 = *t*-Bu



11a, R^1 = H; R^2 = C_6H_5
11b, R^1 = C_6H_5; R^2 = H
12a, R^1 = H, R^2 = *o*-C_6H_4CN
12b, R^1 = *o*-C_6H_4CN; R^2 = H
13a, R^1 = H; R^2 = *p*-$C_6H_4NO_2$
13b, R^1 = *p*-$C_6H_4NO_2$; R^2 = H

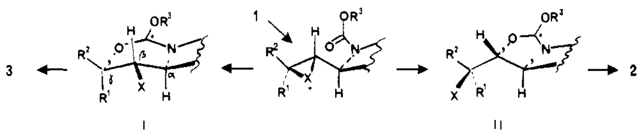


12c, R^1 = *o*-C_6H_4CN; R^2 = H
13c, R^1 = *p*-$C_6H_4NO_2$; R^2 = H

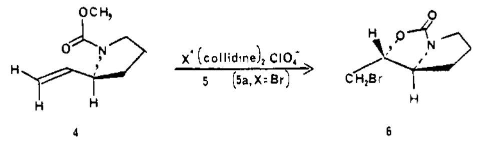
Table I. Product Distributions as a Function of Olefin Geometry and Aryl Substituent

allylic urethane	reagent	product(s) (yield, %)	ratio
8a	5b	11a, X = I (73)	
8b	5b	11b, X = I (60)	
9a	5a	12a, X = Br (62)	
9b	5a	12b + 12c, X = Br (40)	1:2
10a	5a	13a, X = Br (60)	
10b	5a	13b + 13c, X = Br (70)	1:5

Scheme I



The cyclization of allylic methyl urethane **4**[5] with brominium dicollidine perchlorate (**5a**)[6] proceeded in refluxing methylene chloride (3 h) to afford an 82% yield of a single oxazolidone, IR 1750 cm^{-1}. This product was shown to be the trans-isomer **6**.[7]



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(1) These studies were reported at the Chemical Society Symposium on Synthesis, Oxford, England, July, 1981.

(2) Bartlett, P. A. *Tetrahedron* **1980**, *36*, 3.

(3) (a) Sygusch, J.; Brisse, F.; Hanessian, S.; Kluepfel, D. *Tetrahedron Lett.* **1974**, 4021; **1975**, errata no. 3. (b) Sygusch, J.; Brisse, F.; Hanessian, S. *Acta Crystallogr., Sect. B* **1976**, *B32*, 1139.

(4) (a) Fraser-Reid has reported the cyclization of an ethyl allyl urethane with iodonium dicollidine perchlorate to afford the oxazolidone product; in the system described, the allyl urethane moiety was part of a ring system and could give only one stereoisomer. See: Pauls, H. W.; Fraser-Reid, B. *J. Am. Chem. Soc.* **1980**, *102*, 3956. (b) Bartlett has observed an iodonium-initiated urethane closure of an acyclic-protected amino acid; however, the stereochemistry of cyclization was not reported. See: Bartlett, P. A.; Tanzella, D. J.; Barstow, J. F. *Tetrahedron Lett.* **1982**, *23*, 619. (c) The bromonium-initiated cyclizations of a urethane that resembles our substrate **4** have been studied by Overman (Overman, L. E.; McCready, R. J. *Tetrahedron Lett.* **1982**, *23*, 4887). We are grateful to Professor Overman for sharing his results with us prior to publication.

(5) The structure of each new compound was assigned by IR and NMR spectroscopy. With the exception of **13a** and **13b**, which were obtained only in minute amounts, each new compound was also characterized by elemental analysis and/or high-resolution mass spectroscopy.

(6) Lemieux, R. V.; Morgan, A. R. *Can. J. Chem.* **1965**, *43*, 2190.