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Studies of Photochemical Reactions of 7,8-Digermabicyclo[2.2.2]octadienes by Steady-State and Laser Flash Photolysis Techniques

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The photochemistry of 1,4-diphenyl-2,3-benzo-7,7,8,8-tetraalkyl-7,8-digermabicyclo[2.2.2]-octadienes in solution has been studied in detail by steady-state, nanosecond laser flash photolysis, and matrix isolation techniques. Photolysis of 7,8-digermabicyclo[2.2.2]octadienes in solution resulted mainly in the formation of tetraalkyldigermenes and 1,4-diphenylnaphthalene in the triplet excited state. The 7,8-digermabicyclo[2.2.2]octadiene also photochemically isomerized to 1,4-diphenyl-2,3-benzo-6,6,7,7-tetraalkyl-6,7-digermatricyclo[3.3.0.0]-octane as minor product. The reactions of tetraalkyldigermenes with butadienes (2,3-dimethylbuta-1,3-diene and 2-methylbuta-1,3-diene), carbon tetrachloride, and methanol gave the corresponding digermene trapped products: 1,2-digermacyclohex-4-enes, 1,2-dichlorodigermanes together with hexachloroethane, and methoxydigermanes, respectively, in good yields. The transient bands of tetraalkyldigermenes using nanosecond laser flash photolysis appeared at ca. 380 nm. The rate constants for the quenching reactions of the digermene with oxygen, polyhalomethanes, alcohols, 2,3-dimethylbuta-1,3-diene, 1-hexyne, and triethylsilane were also measured under various conditions. The quenching reactions of digermenes with carbon tetrachloride and ethanol ($k = \sim 10^7$ M^{-1} s^{-1}) are 100 times faster than that with 1,3-butadiene ($k = \sim 10^5$ M^{-1} s^{-1}). The digermenes were very rapidly quenched with oxygen ($k = \sim 10^8$ M^{-1} s^{-1}), but very slowly with 1-hexyne and triethylsilane ($k < 10^4$ M^{-1} s^{-1}) under reaction conditions. The UV absorption bands of tetraalkyldigermenes generated from 7,8-digermabicyclo[2.2.2]octadienes in matrix at 77 K were also observed at 370−380 nm. The mechanism of digermene formation was also discussed.

Introduction

In recent decades much interest has been focused on the chemistry of stable group 14 elements (silicon, germanium, and tin) in low coordination states because of their unique structure and reactivities.[1−4] However, there have been few reports on the mechanism of generation of doubly bonded species of group 14 elements and their abstraction and addition reactions of substrates.[2j,5−10] Especially, information on the generation and reaction mechanism of reactive digermenes has not yet been reported. It is very important to investigate the generation and reactivities of the reactive doubly

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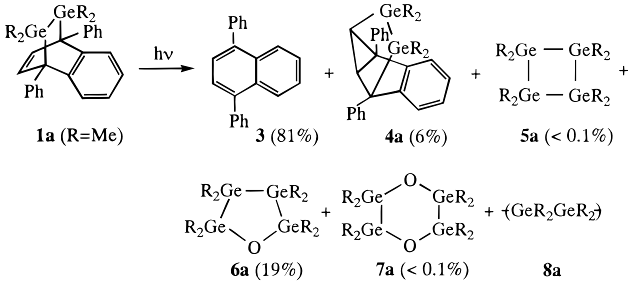
bonded species of the group 14 elements for characterization of the transition states and elucidation of the reaction mechanism. In this paper, we report a study of the photochemistry of 1,4-diphenyl-2,3-benzo-7,7,8,8-tetraalkyl-7,8-digermabicyclo[2.2.2]octadienes in solution by steady-state, nanosecond laser flash photolysis, and matrix isolation techniques. The 7,8-digermabicyclo[2.2.2]octadienes act as convenient photochemical sources for reactive digermene species. Together with interesting results of reactive digermenes with substrates, studies of the first kinetics of digermenes with laser flash photolysis techniques are demonstrated. The first clear evidence of substituent effect on electronic properties of digermenes is also given.

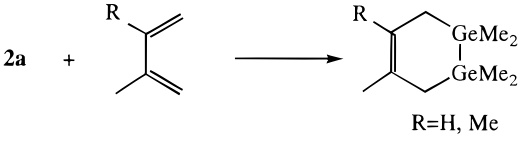
Results and Discussion

Photolysis of a benzene solution of 1,4-diphenyl-2,3-benzo-7,7,8,8-tetramethyl-7,8-digermabicyclo[2.2.2]octadiene [4q] (**1a**, ca. 0.07 M) through a quartz tube with a low-pressure Hg arc lamp under argon at room temperature resulted in the formation of 1,4-diphenylnaphthalene (**3**, 81%), a rearranged product (**4a**, 6%), 2,2,3,3,4,4,5,5-octamethyl-1-oxa-2,3,4,5-tetragermacyclopentane (**6a**, 19%), and unidentified oligo(tetramethyldigermene)s (**8a**, $M_w = 1400$, $M_w/M_n = 1.1$), together with very small amounts of octamethylcyclotetragermane (**5a**) and 2,2,3,3,5,5,6,6-octamethyl-1,4-dioxa-2,3,5,6-tetragermacyclohexane (**7a**). The products **3** and **4a** after ca. 80% conversion were isolated and purified by rapid chromatography with a short silica column. The rearranged product **4a** was characterized in ^{1}H NMR spectroscopy, showing two doublets at 1.63 ppm (J = 8.6 Hz, H_8) and 2.69 ppm (J = 8.6 Hz, H_5) except for signals of Ge−Me and phenyl groups. They were identified by their GC−MS and NMR spectra by comparison with spectral data of an authentic sample of **3** and similar silicon compounds for **4a**.[11−14] The oligogermanes **5a** and **7a** were characterized by their GC−MS spectra by careful comparison with those of authentic and similar germanium compounds.[15,16] The oligomer **6a** was also characterized by its GC−MS and NMR spectra using the crude photolysates.[15] The formation of oligogermane **6a** and **7a** may be ascribed to an accidental oxidation of compound **5a** by oxygen[15] and the dimerization of the oxidant of digermene, respectively. Oxygen could not be completely excluded during photolysis and/or a subsequent workup. The molecular weight and its distributions of the oligogermanes **8a** were determined by gel-permeation chromatography (GPC) analysis using polystyrene samples for calibration. The ^{1}H NMR spectra of **8a** showed resonances in the range of δ 0.2−0.6 ppm assigned to Ge−Me. The product yields were determined by ^{1}H NMR and GC analyses.

The presence of 1,4-diphenylnaphthalene **3** and oligogermanes **5a**−**8a** strongly indicates that photolysis of **1a** leads to the formation of tetramethyldigermene, $Me_2Ge{=}GeMe_2$, **2a**.



To trap possible reactive intermediate **2a**, irradiation of a benzene solution of **1a** containing a large amount (10−20 times) of butadienes (2,3-dimethylbuta-1,3-diene and 2-methylbuta-1,3-diene), effective digermene trapping agents,[17] under similar reaction conditions gave the corresponding 1,2-digermacyclohex-4-enes (22 and 29%), **3** (83 and 81%), **4a** (7 and 11%), and **6a** (36 and 10%) together with **8a** ($M_w = 1000$, $M_w/M_n = 1.1$ and $M_w = 700$, $M_w/M_n = 1.0$, respectively). The yields of 1,2-digermacyclohex-4-enes and **6a** are approximately independent of the butadiene concentration over the range of 10−20 times. The photolysate could be readily identified by NMR, GC, and GC−MS analyses by comparison with spectral data of authentic samples after ca. 80% conversion.



Similar photolysis of **1a** in benzene containing carbon tetrachloride (5−10 times) gave 1,1,2,2-tetramethyl-1,2-dichlorodigermane (71%), dimethyldichlorogermane (27%), **3** (95%), and hexachloroethane (38%). All photoproducts could be identified by their NMR, GC, and GC−MS analyses by comparison with those of authentic samples. The formation of 1,2-dichlorodigermane may have resulted from the stepwise abstraction of a chlorine atom from carbon tetrachloride with **2a** or with a 1,6-biradical generated by homolysis of the germanium−

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carbon bond of **1a** as stressed in the case of silylene and germylene formation from sila- and germanorbornadienes.[18]

$$\mathrm{Me_2Ge{=}GeMe_2} \xrightarrow{\mathrm{CCl_4}\ \ \mathrm{CCl_4}} \mathrm{ClMe_2GeGeMe_2Cl}$$

The formation of dimethyldichlorogermane may be a result of stepwise chlorine abstraction of dimethylgermylene.[19] Very recently, we discussed the generation of dimethylgermylene and the 1,5-biradical through the 1,6-biradical.[20] The material balance between chlorogermanes and hexachloroethane is consistent. Photolysis of a benzene solution of **1a** containing methanol (10−20 times) under similar reaction conditions yielded methoxydigermane (56%) and **3** (90%) as the main products. Small amounts of **4a** (7%) and **6a** (14%) were also detected in the photolysate. The methoxydigermane was characterized using ^{1}H NMR spectroscopy, showing a doublet at 0.28 ppm (J = 4.0 Hz, 6 H (Ge−Me)), a septet at 3.92 ppm (J = 4.0 Hz, 1 H (Ge−H)), and a singlet at 3.38 ppm (3 H) with the expected low-field shift for Ge−OMe.

On the other hand, in the photolysis of **1a** in benzene containing various concentrations of triethylsilane and 1-hexyne, no digermene trapped products were detected by GC−MS and NMR spectra in the photoproducts. A rearranged product **4a** (7 and 9%) and oligogermanes **7a** (51 and 13%) were still formed together with **3** (92 and 89%, respectively).

The photolysis of a benzene solution of **1a** in the absence and in the presence of trapping agents through a Pyrex tube with a high-pressure Hg arc lamp under argon at room temperature also gave similar results.

Transient UV absorption spectra were recorded by nanosecond laser flash photolysis techniques (λ = 266 nm, pulse width = 5 ns, power = 10 mJ/pulse)[21] in an attempt to obtain spectra of the reactive intermediates in the photochemistry of **1**.

Laser flash photolysis of **1a** (ca. 4.9 × 10^{-4} M) in cyclohexane at 293 K gave two transient absorption bands at 300 ns and at 3 μs after the laser pulse, as shown in Figure 1. As shown in Figure 1, after 3 μs the transient peak at 380 nm remains and that at 430 nm completely disappears. In Figure 2, the time dependence of absorbance $A(t)$ for both transient peaks observed under the conditions described in Figure 1 and their second-order plots are shown. The transient peak at the shorter wavelength (380 nm) appears very rapidly after laser pulsing and decays with a lifetime of ca. 80 μs. From the slope of the line, the second-order rate constant for the transient at 380 nm was evaluated to be $k/\epsilon = 6.5 \times 10^5$. Here k is the rate constant of the second-order decay, and ϵ is the molar extinction coefficient. On the other hand, the transient peak at longer wavelength (430 nm) arising from **1a** decays with second-order kinetics ($k/\epsilon = 4.0 \times 10^5$).

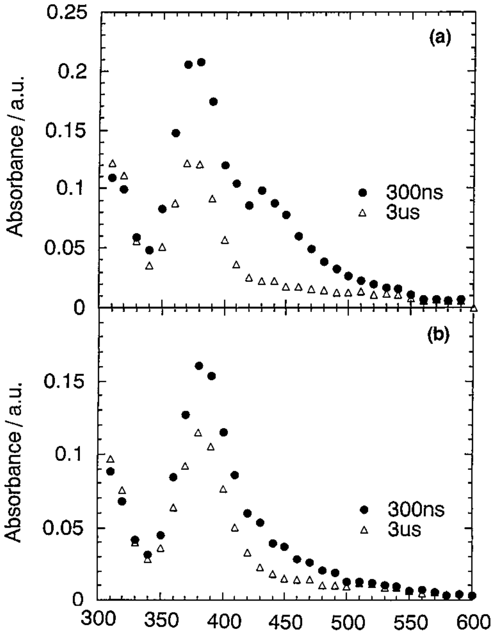

Figure 1. Transient absorption spectra of (a) 1,4-diphenyl-2,3-benzo-7,7,8,8-tetramethyl-7,8-digermabicyclo[2.2.2]-octadiene (**1a**) and (b) 1,4-diphenyl-2,3-benzo-7,7,8,8-tetraethyl-7,8-digermabicyclo[2.2.2]octadiene (**1b**) at 300 ns and 3 μs after laser pulsing at 293 K.

The peak at 380 nm is reasonably assigned to that of $\mathrm{Me_2Ge{=}GeMe_2}$ from comparison of its spectral characteristics with those formed by the previously reported dimerization of dimethylgermylene ($\mathrm{Me_2Ge:}$)[19] and by the matrix isolation method at 77 K described below. The assignment of the peak at 380 nm is further substantiated by quenching experiments with oxygen, 2,3-dimethylbuta-1,3-diene, polyhalomethanes (carbon tetrachloride, chloroform, and dichloromethane), alcohols, 1-hexyne, and triethylsilane. The addition of 2,3-dimethylbuta-1,3-diene, effective germanium double-bond scavenger,[17] quenched the transient peak at 380 nm in cyclohexane. The reaction rate constant was determined by the decay rate of the transient peak at 380 nm in the presence of 2,3-dimethylbuta-1,3-diene at a concentration greater 0.1 mM. The decay of the transient peak at 380 nm obeys the first-order kinetics, as shown in Figure 3. The slopes of the first-order plots yield the first-order rate constants (k_{obs}), which increase with the concentraion of the diene ($k_{\mathrm{obs}} = 1.2 \times 10^5$ s^{-1} at 100 mM, 1.9 × 10^5 s^{-1} at 200 mM, 2.7 × 10^5 s^{-1} at 300 mM, and 3.1 × 10^5 s^{-1} at 400 mM). The first-order plot of k_{obs} against [diene] is also shown in Figure 3, where a straight line can be obtained. From the slope of the line, the second-order rate constant for the quenching reaction of the transient peak at 380 nm with 2,3-dimethyl-1,3-butadiene was evaluated to be 5.3 × 10^5 M^{-1} s^{-1}, as listed in Table 1. On the other hand, the transient peak at 380 nm was very rapidly quenched with carbon tetrachloride. The rate constant for the quenching reaction of the transient peak at 380 nm with carbon tetrachloride was similarly analyzed and determined to be 1.2 × 10^7 M^{-1} s^{-1}. With the addition of chloroform and dichloromethane, the transient peak at 380 nm could not be quenched. This affords an estimate of <10^4 M^{-1} s^{-1} for the upper limit of the apparatus.

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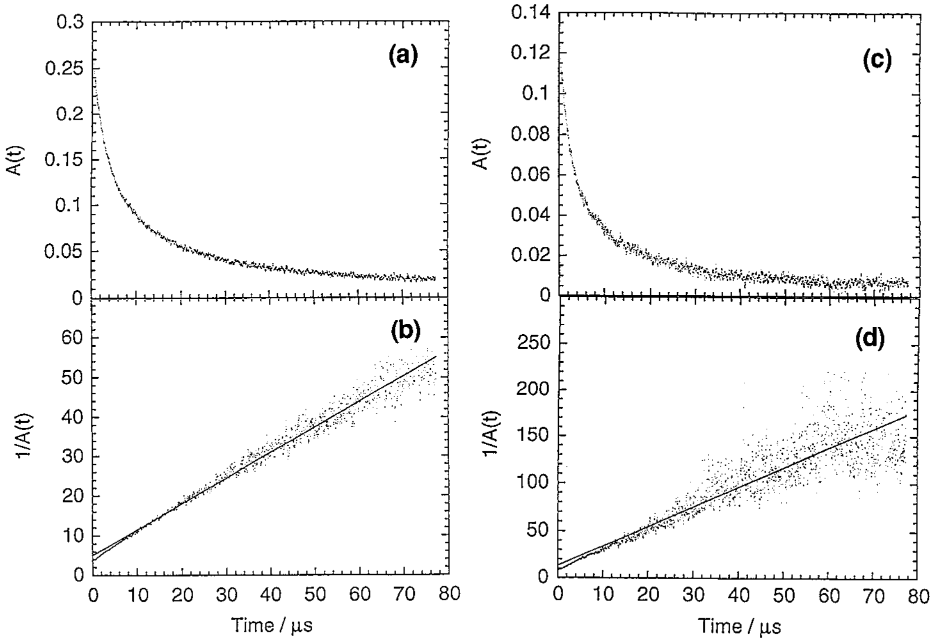

Figure 2. Absorption–time profiles obtained at 380 nm (a) and 430 nm (c) by laser flash photolysis of **1a**. Second-order plots for the decay of $Me_2Ge{=}GeMe_2$ at 380 nm (b) and 1,4-diphenylnaphthalene at 430 nm (d).

The rate constants for the reaction of tetramethyldigermene with polyhalomethanes reflect the C–Cl bond energies of polyhalomethanes.[22] The results are also included in Table 1.

The transient peak at 380 nm from **1a** (0.49 mM) in cyclohexane was rapidly quenched with ethanol at a concentration greater than ca. 10 mM and decayed with clean pseudo-first-order kinetics, as shown in Figure 4. Quenching reactions of the transient peak at 380 nm with several alcohols (ethanol-d_1, 2-propanol, and *tert*-butyl alcohol) were also carried out under similar conditions. Plots of k_{obs} against [alcohol] are linear in every case in Figure 4. The second-order rate constants for the quenching reaction of the transient peak at 380 nm with alcohols from the slope of the lines are determined and summarized in Table 2. Several interesting points are discussed. First, the quenching reaction of the digermene with alcohols is a rapid process. Second, the relative quenching rate decreases in the order EtOH > i-PrOH > t-BuOH, consistent with the steric bulkiness of the alcohols. Third, no significant deuterium isotope effect is found when ethanol-d_1 is used, suggesting that the nucleophilic attack of the alcoholic oxygen to the coordinately unsaturated germanium center is the rate-determining step of the addition reaction.

The transient peak at 380 nm was very rapidly quenched with oxygen ($k = 4.0 \times 10^8$ M^{-1} s^{-1}) owing to the large Ge–O bond energy.[23] However, this transient was not quenched by triethylsilane or 1-hexyne ($<10^4$ M^{-1} s^{-1}), and these results are in accord with the observed chemical properties. Products studies were not carried out.

The laser flash photolysis of 1,4-diphenyl-2,3-benzo-7,7,8,8-tetraethyl-7,8-digermabicyclo[2.2.2]octadiene (**1b**) was also carried out under the same conditions. The transient peaks at 380 nm with a shoulder at ca. 430 nm were observed at 300 ns after laser pulsing, as shown in Figure 1. The transient peaks at 380 and ca. 430 nm are assigned to the tetraethyldigermene, $Et_2Ge{=}GeEt_2$, and the T–T absorption of 1,4-diphenylnaphthalene. The rate constants for quenching of the digermene by several substrates are summarized in Table 1.

The transient peak at 430 nm observed during the photolyses of **1a** and **1b** is safely assigned to the T–T absorption band of 1,4-diphenylnaphthalene from comparison of its spectral characteristics with those of the authentic sample, as shown in Figure 5. The transient peak at 430 nm was very rapidly quenched with oxygen ($k = (3.5–4.0) \times 10^9$ M^{-1} s^{-1}). 1,2-Diphenylnaphthalene could be completely excluded during purification of **1a**,**b** with rapid chromatography with silica gel treated with triethylamine.

To ensure the assignment of the transient peak at 380 nm to the digermene, $R_2Ge{=}GeR_2$, irradiation of the 3-methylpentane (3-MP) of **1a**,**b** (ca. 10^{-3} M) with a low-pressure Hg arc lamp at 77 K was carried out. UV irradiation of **1a**,**b** immediately produced yellow glass with a broad band at 370–380 nm, as shown in Figure 6. The broad bands at $\lambda_{max} = 370–380$ nm obtained can be assigned to the corresponding digermene on the basis of chemical trapping experiments and transient UV data of $Me_2Ge{=}GeMe_2$ produced by the dimerization of dimethylgermylene.[19] The yellow species of tetraisopropyldigermene at $\lambda_{max} = 390$ nm generated by photolysis of octaisopropylcyclotetragermane at 77 K has been also reported.[24] No change in absorbance was observed over a 77–100 K temperature range. On prolonged UV irradiation, the peaks at 370–380 nm disappeared,

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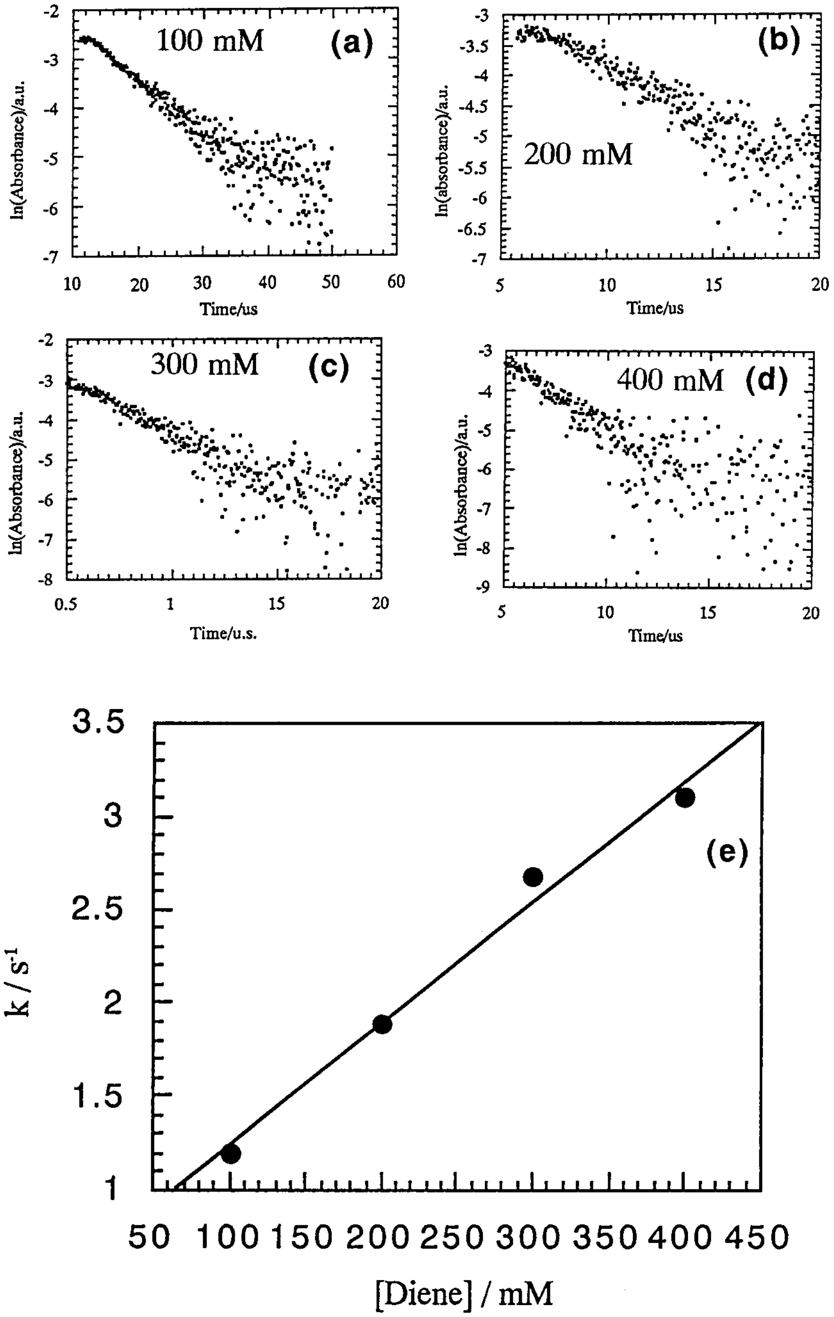

Figure 3. First-order plots for the decay of the transient peak at 380 nm in the presence of 2,3-dimethylbuta-1,3-diene in cyclohexane. 2,3-Dimethylbuta-1,3-diene concentration: (a) 100 mM; (b) 200 mM; (c) 300 mM; (d) 400 mM. (e) Dependence of the pseudo-first-order rate constant (*k*) for the decay of the transient peak at 380 nm on the concentration of 2,3-dimethylbuta-1,3-diene.

resulting in the buildup of broad peaks around 500 nm. We have no data to assign the broad peaks around 500 nm. The UV–vis absorption spectra of digermenes were not observed when the matrix was warmed to its softening points. The absorption bands of the digermenes, $R_2Ge{=}GeR_2$ (R=Me, Et), observed in this study are summarized in Table 2, together with those of other results. As shown in Table 2, a small red shift in the λ_{max} of the Ge=Ge absorption was observed in the order R = Me, Et < i-Pr[24] for $R_2Ge{=}GeR_2$. Furthermore, introduction of aryl groups onto the Ge=Ge double bond clearly causes a red shift in the λ_{max} of the Ge=Ge absorption.[25,26] Evidently, appreciable conjugation exists between the Ge=Ge chromophore and the aryl group.

From these results obtained by steady-state, laser flash photolysis, and matrix isolation techniques, photolysis of 7,8-digermabicyclo[2.2.2]octadienes (**1a**,**b**) leads to digermenes (**2a**,**b**) and 1,4-diphenylnaphthalene **3** as major products and to rearranged products **4a** as minor products in Scheme 1. The digermenes yield several oligogermanes.

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[26] Ando, W.; Tsumuraya, T. *J. Chem. Soc., Chem. Commun.* **1989**, 770.

Table 1. Rate Constants for Disappearance of Digermenes Produced by Photolysis of 7,8-Digermabicyclo[2.2.2]octadienes (1a,b)

	1a		1b	
reagent	380 nm	430 nm	380 nm	430 nm
k/ϵ[a]	6.5×10^5	4.0×10^5	4.2×10^5	4.0×10^5
O_2	4.0×10^8	3.5×10^9	3.3×10^8	4.0×10^9
2,3-dimethyl-1,3-butadiene	5.3×10^5	8.2×10^5	1.7×10^5	5.9×10^5
CCl_4	1.2×10^7	no	3.7×10^7	no
$CHCl_3$	$<10^4$	no	$<10^4$	no
CH_2Cl_2	$<10^4$	no	$<10^4$	no
EtOH	4.9×10^7	no	9.1×10^7	no
EtOD	4.8×10^7			
i-PrOH	2.0×10^7			
t-BuOH	2.4×10^6			
BuC≡CH	$<10^4$	no	$<10^4$	no
Et_3SiH	$<10^4$	no	$<10^4$	no

[a] k is the rate constant of second-order decay, and ϵ is the corresponding molar extinction coefficient.

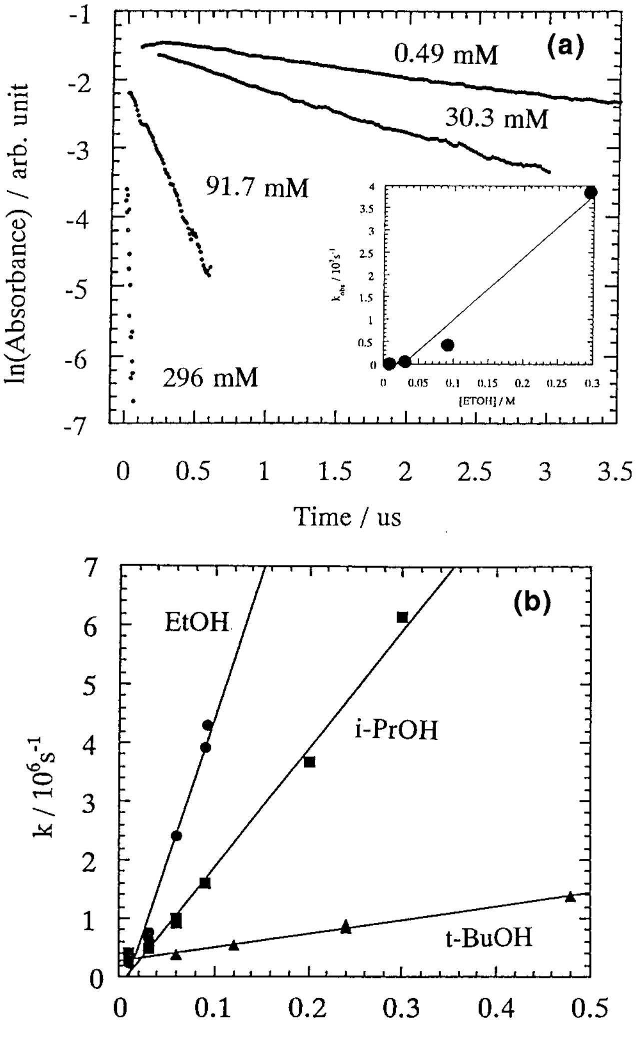


Figure 4. (a) First-order plots for the decay of the transient peak at 380 nm in the presence of ethanol (9.9, 30.3, 91.7, 296 mM) in cyclohexane. Inset: Dependence of the pseudo-first-order rate constant (k) for the decay of the transient peak at 380 nm on the concentration of ethanol. (b) Dependence of the pseudo-first-order rate constants (k) for the decay of the transient peak at 380 nm on the concentration of alcohols.

Table 2. Absorption Bands of Digermenes

digermene	temp/K	λ_{max}/nm	ref
$Me_2Ge{=}GeMe_2$	293	380[a]	this work
	293	380[a]	19
	77	370[b]	this work
$Et_2Ge{=}GeEt_2$	293	380[a]	this work
	77	380[b]	this work
${}^iPr_2Ge{=}Ge^iPr_2$	293	390[a]	24
	77	390[b]	24
$Mes_2Ge{=}GeMes_2$	293	405[c]	25
	77	410[a]	26

[a] In cyclohexane. [b] In 3-methylpentane. [c] In hexane.

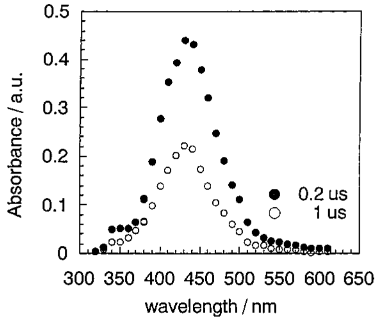


Figure 5. T−T absorption spectra of 1,4-diphenylnaphthalene in cyclohexane at 0.2 and 1 μs after laser pulsing.

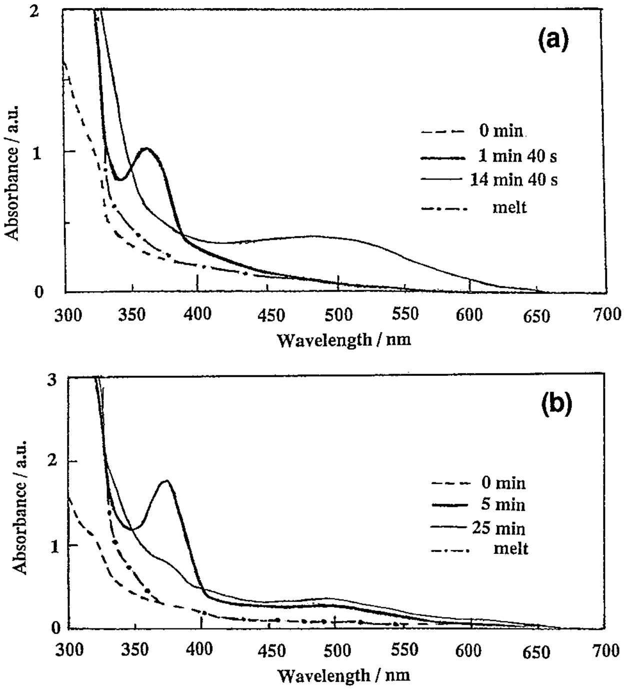
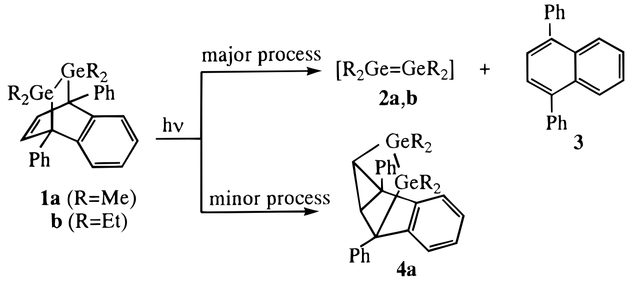


Figure 6. UV absorption spectra of **1a** and **b** in a 3-methylpentane glass at 77 K.

Scheme 1



Summary and Conclusions

Photolysis of 2,3-benzo-7,7,8,8-tetralkyl-7,8-digermabicyclo[2.2.2]octadienes in solutions gives tetraalkyldigermenes and naphthalene in the triplet excited state as a major process. The 1,2-germyl rearranged products, 2,3-benzo-6,6,7,7-tetraalkyl-6,7-digermatricyclo[3.3.0.0]octane, are formed as a minor process. The laser flash photolysis and matrix isolation studies show that the UV peaks of the digermenes are at ca. 380 nm. The digermenes react with 1,3-butadienes, a digermene trapping agent, to give 1,2-digermecyclohex-4-enes in good yields. The quenching reactions of digermenes with carbon teterachloride and ethanol and oxygen are 100 times and 1000 times, respectively, faster than those with 1,3-butadienes. Product analyses of the quenching reactions of digermenes with several substrates are carried out by steady-state methods.

Experimental Section

NMR spectra were obtained on a Varian Unity Inova 400 MHz NMR spectrometer. GC−MS spectra were measured on a JEOL JMS-DX 303 mass spectrometer. The infrared spectra were recorded with a Shimadzu FT IR 4200 spectrometer. The UV and UV−vis spectra were recorded on a Shimadzu UV 2200 spectrometer. Gas chromatography was performed on a Shimadzu GC 8A with a 1 m 20% SE30 column. Liquid chromatography was performed on a Twincle with an Asahipak GS 310 column.

Cyclohexane, cyclohexane-d_{12}, benzene, benzene-d_6, 2,3-dimethylbuta-1,3-diene, 2-methylbuta-1,3-diene, methanol, ethanol, ethanol-d_1, 2-propanol, *tert*-butyl alcohol, carbon tetrachloride, chloroform, dichloromethane, triethylsilane, 1-hexyne, and 3-methylpentane were distilled under argon after refluxing over calcium hydride, sodium, or magnesium for 1−2 days. 1,4-Diphenylnaphthalene, hexachloroethane, and 1-aminobenzotriazole were commercially available.

1,1,2,2-Tetramethyl-3,6-diphenyl-1,2-digermacyclohexa-3,5-diene,[3q] 1,4-diphenyl-2,3-benzo-7,7,8,8-tetramethyl-7,8-digermabicyclo[2.2.2]octadiene,[3q] dimethyldichlorogermane,[27] and 1,2-dichlorotetramethyldigermane[28] were prepared as reported in the literature.

Preparation of 1,1,2,2-Tetramethyl-3,6-diphenyl-1,2-digermacyclohexa-3,5-diene.[3q] To a suspension of 1,4-dibromo-1,4-diphenylbutadiene (5.26 g, 14.5 mmol) in 29 mL of ether, cooled in an ice-bath, was added 22.8 mL of 1.27 N *n*-butyllithium dropwise during a period of 20 min. The solution was allowed to come to room temperature. THF (48 mL) was added, and the solution was again cooled in an ice bath. During a period of 45 min, 1,2-dichloro-1,1,2,2-tetramethyldigermane (4.0 g, 14.5 mmol) in 19 mL of THF was added dropwise, and the mixture was stirred overnight at room temperature and then refluxed for 4 h. The mixture was then hydrolyzed, and the organic layer was separated and dried over anhydrous sodium sulfate. The solvent was removed in vacuo, and the residual brown oil was placed in a distilling flask. Fractional distillation gave 3.71 g (8.85 mmol, 61.0%) of pure 1,2-digermacyclohexa-3,5-diene: bp 152 °C/1.0 mmHg; ^{1}H NMR (δ in C_6D_6) 0.41 (s, 12 H), 6.81 (s, 2 H), 7.07−7.29 (m, 10 H); MS *m*/*z* M^+ 412.

Preparation of 1,1,2,2-Tetraethyl-3,6-diphenyl-1,2-digermacyclohexa-3,5-diene. 1,2-Dichloro-1,1,2,2-tetraethyldigermane[28] (3.85 g, 11.6 mmol) reacted with 1,4-dilithio-1,4-diphenylbutadiene to give 1,1,2,2-tetraethyl-3,6-diphenyl-1,2-digermacyclohexa-3,5-diene (1.15 g, 2.46 mmol, 21.2%) under the same reaction conditions for the case of 1,1,2,2-tetramethyl-3,6-diphenyl-1,2-digermacyclohexa-3,5-diene: bp 152 °C/0.5 mmHg; ^{1}H NMR (δ in C_6D_6) 0.84−1.17 (m, 20 H), 6.76 (s, 2 H), 7.06−7.23 (m, 10 H); ^{13}C NMR (δ in C_6D_6) 7.5, 10.7, 126.5, 126.8, 128.6, 139.3, 145.2, 146.8; MS *m*/*z* M^+ 466. Anal. Calcd for $C_{24}H_{32}Ge_2$: C, 61.90; H, 6.92. Found: C, 62.12; H, 7.02.

Preparation of 1,4-Diphenyl-2,3-benzo-7,7,8,8-tetramethyl-7,8-digermabicyclo[2.2.2]octadiene (1a).[3q] To a mixture of 1,1,2,2-tetramethyl-3,6-diphenyl-1,2-digermacyclohexa-3,5-diene (2.13 g, 5.2 mmol) and 1-aminobenzotriazole (1.05 g, 7.8 g) in dichloromethane (27 mL) was added lead tetraacetate (3.87 g, 8.0 mmol) in dichloromethane (30 mL) at −78 °C during a period of 40 min. As soon as the addition was completed, the reaction mixture was filtered through silica gel (Wako gel C 200) and washed with benzene, and the solvent was removed in vacuo. The residue was purified by rapid chromatography with silica gel treated with triethylamine and washed with hexane, and the solvent was removed in vacuo. The final product was pure solid 7,8-digermabicyclo[2.2.2]octadiene (0.79 g, 1.46 mmol, 28.0%): mp 150−153 °C; ^{1}H NMR (δ in C_6D_6) 0.24 (s, 6 H), 0.40 (s, 6 H), 6.04 (s, 2 H), 6.63−6.77 (m, 4 H), 7.17−7.54 (m, 10 H); ^{13}C NMR (δ in C_6D_6) −3.99, −2.22, 52.1, 125.0−132.6, 141.0, 146.1; MS *m*/*z* M^+ 486; UV (cyclohexane) $\lambda_{\max}$/nm (log ϵ) 213 (4.66), 235 (sh, 4.15), 285 (3.31). Anal. Calcd for $C_{26}H_{28}Ge_2$: C, 64.30; H, 5.81. Found: C, 64.55; H, 5.92.

Preparation of 1,4-Diphenyl-2,3-benzo-7,7,8,8-tetraethyl-7,8-digermabicyclo[2.2.2]octadiene (1b). 1,4-Diphenyl-2,3-benzo-7,7,8,8-tetraethyl-7,8-digermabicyclo[2.2.2]octadiene was similarly prepared by the reaction of 1,1,2,2-tetraethyl-3,6-diphenyl-1,2-digermacyclohexa-3,5-diene (1.15 g, 2.46 mmol), 1-aminobenzotriazole (0.60 g, 4.61 g), and lead tetraacetate (2.23 g, 4.61 mmol) in 54.0% yield: mp 119−123 °C; ^{1}H NMR (δ in C_6D_6) 0.88−1.21 (m, 20 H), 6.07 (s, 2 H), 6.68−6.75 (m, 4 H), 7.18−7.57 (m, 10 H); ^{13}C NMR (δ in C_6D_6) 8.0, 9.3, 10.5, 11.1, 53.0, 124.9, 125.5, 126.6, 128.9, 131.4, 131.5, 141.5, 146.5; MS *m*/*z* M^+ 542. UV(cyclohexane) $\lambda_{\max}$/nm (log ϵ) 213 (4.70), 235 (sh, 4.17), 285 (3.43). Anal. Calcd for $C_{30}H_{34}Ge_2$: C, 66.75; H, 6.35. Found: C, 67.01; H, 6.15.

Preparation of 1,1,2,2,4,5-Hexamethyl-1,2-digermacyclohex-4-ene. A mixture of 1,1,2,2-tetramethyl-1,2-dichlorodigermane (1.5 g, 5.4 mmol), 2,3-dimethylbuta-1,3-diene (0.56 g, 6.8 mmol), and lithium metal (56 mg, 8 mmol) in ether (45 mL)−THF (9 mL) was stirred at room temperature for 12 h. The mixture was then hydrolyzed, and the organic layer was separated and dried over anhydrous sodium sulfate. The solvent was removed in vacuo, and the residual brown oil was placed in a distilling flask. Fractional distillation gave 0.2 g (0.7 mmol, 13.0%) of pure 1,1,2,2,4,5-hexamethyl-1,2-digermacyclohex-4-ene: bp 160 °C/27 mmHg; NMR (δ in C_6D_6) 0.26 (s, 6 H), 1.59 (s, 4 H), 1.75 (s, 6 H); ^{13}C NMR (δ in C_6D_6) −4.2, 22.2, 24.2, 123.9; MS *m*/*z* M^+ 288. Anal. Calcd for $C_{10}H_{22}Ge_2$: C, 41.78; H, 7.71. Found: C, 41.84; H, 7.92.

Photolysis of 1,4-Diphenyl-2,3-benzo-7,7,8,8-tetramethyl-7,8-digermabicyclo[2.2.2]octadiene (1a). A degassed sealed Pyrex tube containing a benzene (1 mL) solution of 7,8-digermabicyclo[2.2.2]octadiene (**1a**) (20 mg, 0.04 mmol) was irradiated with a 120 W low-pressure Hg arc lamp (Sen Tokushu Kogen Co. Ltd.) for 3 h at room temperature. NMR, GC, and GC−MS analysis of the resulting mixture showed the presence of 1,4-diphenylnaphthalene (**3**, 81%), rearranged product (**4a**, 6%), 1-oxa-2,3,4,5-tetragermacyclopentane (**6a**, 29%), cyclotetragermane (**5a**, <0.1%), 1,4-dioxa-2,3,5,6- tetragermacyclohexane (**7a**, <0.1%), and oligo(tetramethyldigermenes)s (**8a**). **4a**: NMR (δ in C_6D_6) −0.34 (s, 3 H), 0.39 (s, 3 H), 0.46 (s, 3 H), 0.47 (s, 3 H), 1.63 (d, J = 8.6 Hz, 1 H), 2.69 (d, J = 8.6 Hz, 1 H), 6.90−7.55 (m, 14 H); MS *m*/*z* M^+ 486. The structures of oligogermanes **5a** and **7a** were very carefully assigned by comparing with their GC data reported previously.[15,16] The compound **5a** was very quickly oxidized to give

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6a in air. The structure of **6a** was very carefully assigned by comparing with the NMR and GC spectra of authentic and similar compounds previously reported.[15] **5a**: MS *m*/*z* M$^+$ 412 (20), 325 (25), 207 (75), 159 (10), 119 (100), 89 (20). **6a**: NMR (δ, CD_2Cl_2) 0.35 (s, 12 H), 0.55 (s, 12 H); MS *m*/*z* M$^+$ 427 (25), 411 (20), 323 (50), 207 (50), 177 (15), 119 (100), 89 (25). **7a**: MS *m*/*z* M$^+$ 442 (20), 426 (20), 323 (55), 207 (50), 177 (15), 119 (100), 89 (25). The molecular weight and its distributions of the oligogermanes **8a** were determined by gel-permeation chromatography (GPC) analysis using polystyrene samples for calibration (M_w= 1400, M_w/M_n = 1.1). **8a**: NMR (δ in C_6D_6) 0.2−0.6.

Photolysis of 1a in the Presence of 2,3-Dimethylbuta-1,3-diene. A degassed sealed Pyrex tube containing **1a** (5 mg, 0.01 mmol), 2,3-dimethylbuta-1,3-diene (8.4 mg, 0.1 mmol), and benzene (1 mL) was irradiated with a 120 W low-pressure Hg arc lamp for 3 h at room temperature. NMR, GC, and GC−MS analysis of the resulting mixture showed 1,2-digermacyclohex-4-ene (22%), **3** (83%), **4a** (7%), **6a** (36%), and oligo(tetramethylenedigermene)s (M_w = 1000, M_w/M_n = 1.1). With 2-methylbuta-1,3-diene, **1a** gave 1,2-digermacyclohex-4-ene (29%), **3** (81%), **4a** (11%), **6a** (10%), and oligo(tetramethyldigermene)s (M_w = 700, M_w/M_n = 1.0). 1,1,2,2,4-Pentamethyl-1,2-digermacyclohex-4-ene: NMR (δ in C_6D_6) 0.25 (s, 6 H), 0.26 (s, 6 H), 1.54 (d, J = 7.5 Hz, 2 H), 1.56 (s, 2 H), 1.78 (s, 3 H), 5.45 (t, J = 7.5 Hz, 1 H); ^{13}C NMR (δ in C_6D_6) −4.2, −3.8, 17.1, 22.0, 27.0, 118.2, 133.5; MS *m*/*z* M$^+$ 272.

Photolysis of 1a in the Presence of Carbon Tetrachloride. A degassed sealed Pyrex tube containing **1a** (5 mg, 0.01 mmol), carbon tetrachloride (15.4 mg, 0.1 mmol), and benzene (1 mL) was irradiated with a 120 W low-pressure Hg arc lamp for 3 h at room temperature. NMR, GC, and GC−MS analysis of the resulting mixture showed 1,1,2,2-tetramethyl-1,2-dichlorodigermane[26] (71%), dimethyldichlorogermane[27] (27%), **3** (95%), and hexachloroethane (38%).

Photolysis of 1a in the Presence of Methanol. A degassed sealed Pyrex tube containing **1a** (5 mg, 0.01 mmol), methanol (3.2 mg, 0.1 mmol), and benzene (1 mL) was irradiated with a 120 W low-pressure Hg arc lamp for 3 h at room temperature. NMR, GC, and GC−MS analysis of the resulting mixture showed 1,1,2,2-tetramethylmethoxydigermane (56%), **3** (90%), **4a** (7%), and **6a** (14%). 1,1,2,2-Tetramethylmethoxydigermane: NMR (δ in C_6D_6) 0.28 (d, J = 4.0 Hz, 6 H), 0.39 (s, 6 H), 3.38 (s, 3 H), 3.92 (sept., J = 4.2 Hz, 1H); MS *m*/*z* M$^+$ 236. With ethanol and 2-propanol, **1a** gave the corresponding trapped products. 1,1,2,2-Tetramethylethoxydigermane: NMR (δ in C_6D_6) 0.29 (d, J = 4.0 Hz, 6 H), 0.42 (s, 6 H), 1.20 (t, J = 7.0 Hz, 6H), 3.60 (q, J = 7.0 Hz, 2H), 3.93 (sept., J = 4.0 Hz, 1 H); MS *m*/*z* M$^+$ 252. 1,1,2,2-Tetramethylisopropoxydigermane: NMR (δ in C_6D_6) 0.61 (d, J = 4.2 Hz, 6 H), 0.45 (s, 6 H), 1.19 (d, J = 6.0 Hz, 6 H), 3.81 (sept., J = 4.2 Hz, 1 H), 3.95 (sept., J = 4.2 Hz, 1 H); MS *m*/*z* M$^+$ 266.

Time-Resolved Optical Absorption. Samples contained in quartz cells with an optical length of 1 cm were degassed by four freeze−pump−thaw cycles. The concentration of **1a** was ca. 0. 49 mmol. Transient absorption spectra were measured at room temperature with a laser photolysis system. The system was fully integrated to a Power Macintosh 8100/100 av microcomputer. Timings for laser pulsing, xenon lamp pulsing, and shutter control were set by a Stanford Research System DG535 delay generator. The digitizing oscilloscope, monochromator, delay generator, and power supply for a photomultiplier were interfaced to a GPIB bus. All settings on these units were controlled directly by the computer program written using VIEW (National Instruments).

The fourth harmonic (λ = 266 nm) of a Qunata-Ray GCR-11 Nd:YAG laser with a pulse width of 5 ns was used as the exciting light source. Time profiles of the transient absorption at fixed wavelengths were recorded by a LeCroy 9362 digitizing oscilloscope connected with a photomultiplier, and time-resolved spectra at several delay times were observed simultaneously by a Hamamatsu C2830 two-dimensional streak camera.

Matrix Isolation of 1a at 77 K. 1a (2.4 mg, 4.8 mmol) was dissolved in 3-MP (5 mL) and sealed in the vacuum of a quartz cell connected to a Pyrex tube. The cell was introduced into an Oxford cryostat. The sample was cooled to 77 K and then irradiated with a 120 W low-pressure Hg arc lamp. The UV spectra were recorded on a Shimadzu UV 2200 spectrometer.

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Supporting Information Available: Spectroscopic data for starting materials and products. This material is available free of charge via the Internet at http://pubs.acs.org.

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