



**Figure 1.** Relationship between ECL intensity and energy available from the chemiluminescent reaction involving the thianthrene cation and various anions. (Cf. Table I for relevant additional information; the TH<sup>+</sup>/TH<sup>-</sup> pair gives no singlet TH\* emission; [DPA] was 0.75 mM due to its low solubility in ACN-0.1 M TBAP; other anion parent and TH concentrations were 1 mM.)

**Table I.** Energy Data of Electrogenerated Chemiluminescence Systems with D = Thianthrene (TH).

$E^\circ(\text{TH}^+/\text{TH}^\cdot) = +1.22 \text{ V vs. sce}$ ;  $E_s(^1\text{TH}^*) = 2.84 \text{ eV}$

A	$E^\circ_{(A/A^\cdot-)^{a,b}}$ (V vs. sce) <sup>c</sup>	$-\Delta H_f^\circ$ , eV	Comment
9,10-Diphenylanthracene (DPA)	-1.85	2.97	d
2,5-Diphenyl-1,3,4-oxadiazole (PPD)	-2.14	3.26	e
2,5-Diphenyloxazole (PPO)	-2.25	3.37	e
Phenanthrene (PHEN)	-2.41	3.53	
Thianthrene (TH)	-2.54	3.66	f

<sup>a</sup> In dry, deaerated ACN-0.1 M TBAP containing 1 mM A (cf. d for DPA concentration). <sup>b</sup> Assuming the diffusion coefficients of A and A<sup>·-</sup> are equal. <sup>c</sup> Recalculated from V vs. Ag reference (cf. Experimental Section). <sup>d</sup> 0.75 mM due to low solubility of DPA in ACN-TBAP. <sup>e</sup> Cf. N. P. Shimanskaya and V. D. Bezuglyi, *Zh. Obshch. Khim.*, **33**, 1683 (1963), for reduction in 92% methanol-water, where the reduction product is not the monoanion. <sup>f</sup> Unstable TH<sup>·-</sup> makes  $E^\circ$  and  $\Delta H_f^\circ$  probably too small; an unstable anion can shift the reduction potential in the positive direction.

vibrational levels of it. In turn the probability of intersystem crossing to the triplet state decreases, and an increase in  $\Phi_f$  is predicted.

The ECL experiments were carried out under the same conditions and precautions reported earlier for the PPD-TH system;<sup>5</sup> the ECL cell has been described previously [Figure 1, ref 5], together with the electrochemical apparatus and Aminco-Bowman spectrofluorometer.<sup>5-8</sup> The ECL intensity ( $I_{\text{ECL}}$ ) for all systems was measured at 434 nm (the emission maximum of <sup>1</sup>TH\*) and an applied frequency of 50 Hz; this frequency is optimum for observing maximum  $I_{\text{ECL}}$  in these systems.<sup>8</sup> The relationship between <sup>1</sup>TH\* ECL emission and reduction potential of the various A species is shown in Figure 1. The very large changes in ECL efficiency are not explicable in terms of secondary effects such as differences in the quenching rate constants of the several A<sup>·-</sup> species but suggest that a true variation of  $\Phi_f$  is involved. For the most efficient system in Figure 1, a chemiluminescence efficiency

greater than  $\Phi_{f,\text{optio}}$  has been measured,<sup>8,9</sup> while all the systems remain subject to a substantially less than unit efficiency of excited-state production in eq 1.

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## High-Yield Syntheses of Monochloro Permethylated Polysilanes

Sir:

The reaction of 1,6-dichlorododecamethylhexasilane and an equimolar amount of methylmagnesium iodide in ethyl ether gave a 90% yield of 1-chloroterdecamethylhexasilane, a compound needed in our investigations of permethylated polysilanes. This yield is remarkable since the statistically predicted distribution of silicon-containing compounds is 50:25:25 for 1-chloroterdecamethylhexasilane, tetradecamethylhexasilane, and unreacted 1,6-dichlorohexasilane, respectively. The reactions for other  $\alpha,\omega$ -dichloropermethylpolysilanes with methylmagnesium iodide were studied to determine the yields of monochloropolysilanes as a function of chain length and to explore the nature of this high-yield reaction.

Halogenodemethylation with H<sub>2</sub>SO<sub>4</sub> and NH<sub>4</sub>Cl<sup>1</sup> or with either HCl or CH<sub>3</sub>COCl in the presence of AlCl<sub>3</sub><sup>2</sup> has been used to prepare chloropermethylpolysilanes. However, for higher polysilanes, side reactions decrease yields considerably.<sup>3,4</sup> Halogenodephenylations of phenylmethylpolysilanes,<sup>2</sup> halogenation of methylated polysilylhydrides,<sup>5</sup> and halogenodealkoxylations of methylalkoxypolysilanes<sup>6</sup> also have been used but these intermediates are not readily available.

The yields of monochloropolysilanes obtained from the reaction of equimolar amounts of  $\alpha,\omega$ -dichloropolysilanes and methylmagnesium iodide at 30° are given in Table I. The nmr chemical shifts, given in Table II, of the protons of the -Si(CH<sub>3</sub>)<sub>2</sub>Cl group<sup>7</sup> differ sufficiently for the mono- and dichloropolysilanes for the relative amounts of these compounds to be measurable from integrated intensities. Therefore, yields were determined and reported from the nmr spectra of the reaction mixtures. These yields agree well with values obtained by fractional distillation.

(1) (a) M. Kumada and M. Ishikawa, *J. Organometal. Chem.*, **1**, 153 (1963); (b) M. Kumada, M. Ishikawa, and S. Maeda, *ibid.*, **2**, 478 (1964).

(2) H. Sakurai, K. Tominaga, T. Watanabe, and M. Kumada, *Tetrahedron Lett.*, 5493 (1966).

(3) M. Kumada and K. Tamao, *Advan. Organometal. Chem.*, **6**, 19 (1968).

(4) D. V. Stynes, Ph.D. Thesis, Northwestern University, Evanston, Ill., 1972.

(5) U. G. Stolberg, *Chem. Ber.*, **96**, 2798 (1963).

(6) M. Kumada, M. Yamaguchi, Y. Yamamoto, J. Nakajima, and K. Shiina, *J. Org. Chem.*, **21**, 1264 (1956).

(7) Chlorodi- and -trisilanes were identified by nmr.<sup>8</sup> 1,4-Dichlorooctamethyltetrasilane and 1,6-dichlorododecamethylhexasilane were identified by nmr and boiling points (C<sub>12</sub>H<sub>30</sub>Si<sub>6</sub>Cl<sub>2</sub>, bp 161-164° (1 mm), lit. 160-162° (0.8 mm); C<sub>8</sub>H<sub>22</sub>Si<sub>4</sub>Cl<sub>2</sub>, bp 78-80° (1 mm), lit. 76-78° (1 mm); Me(SiMe<sub>2</sub>)<sub>6</sub>Cl and Me(SiMe<sub>2</sub>)<sub>4</sub>Cl apparently have not been reported previously. *Anal.* Calcd for C<sub>13</sub>H<sub>30</sub>Si<sub>3</sub>Cl: Cl, 8.88. Found: Cl, 8.90. Calcd for C<sub>9</sub>H<sub>22</sub>Si<sub>2</sub>Cl: Cl, 12.52. Found: Cl, 12.53.

(8) R. West, F. Kramer, E. Carberry, M. Kumada, and M. Ishikawa, *J. Organometal. Chem.*, **8**, 79 (1967).

**Table I.** Yields of Monochloropermethylpolysilanes

<i>n</i>	% Me(SiMe <sub>2</sub> ) <sub><i>n</i></sub> Cl	% Me(SiMe <sub>2</sub> ) <sub><i>n</i></sub> Me
2	58	19
3	67	16
4	82	8
6	90	5

**Table II.** Nmr Chemical Shifts<sup>a</sup>

Compound	-SiMe <sub>2</sub> Cl	-SiMe <sub>2</sub> -	-SiMe <sub>3</sub>
Me(SiMe <sub>2</sub> ) <sub>2</sub> Cl	0.432		0.147
Cl(SiMe <sub>2</sub> ) <sub>2</sub> Cl	0.532		
Me(SiMe <sub>2</sub> ) <sub>3</sub> Cl	0.478	0.163	0.129
Cl(SiMe <sub>2</sub> ) <sub>3</sub> Cl	0.520	0.258	
Me(SiMe <sub>2</sub> ) <sub>4</sub> Cl	0.447	0.138, 0.165	0.092
Cl(SiMe <sub>2</sub> ) <sub>4</sub> Cl	0.498	0.245	
Me(SiMe <sub>2</sub> ) <sub>6</sub> Cl	0.427	0.225, 0.204, 0.197, 0.123	0.070
Cl(SiMe <sub>2</sub> ) <sub>6</sub> Cl	0.484	0.243, 0.269	

<sup>a</sup> All shifts are expressed in ppm downfield from TMS and were obtained from 60-MHz spectra of dilute ethyl ether solutions at 30° with cyclohexane as the internal standard.

At least three conceivable explanations for the observed high yields must be considered. (1) The dichloropolysilane may form a chelate intermediate with magnesium in the Grignard reagent. (2) The monochloropolysilane and dichloropolysilane may differ significantly in reactivity toward methylmagnesium iodide. This would involve an electronic effect being transmitted through the silicon chain causing the dichloropolysilane to be more reactive toward the methylmagnesium iodide. (3) A catalytic redistribution of Cl(SiMe<sub>2</sub>)<sub>*n*</sub>Cl and Me(SiMe<sub>2</sub>)<sub>*n*</sub>Me to give Me(SiMe<sub>2</sub>)<sub>*n*</sub>Cl may take place in the presence of MgX<sub>2</sub> or MeMgX. A similar redistribution occurs for the disilanes in the presence of AlCl<sub>3</sub>.<sup>9</sup> Reid and Wilkins<sup>10</sup> and Corriu and Henner<sup>11</sup> have discussed the role of intermediates in the reaction of Grignard reagents with haloorganosilanes.

Successive portions of methylmagnesium iodide were added to a solution of 1,4-dichlorooctamethyltetrasilane at -20°. No methylmagnesium iodide was detected by nmr until a stoichiometric amount had been added. Further addition resulted in the methylmagnesium iodide remaining for several minutes indicating that the monochlorotetrasilane reacts much more slowly with methylmagnesium iodide than does the dichlorotetrasilane. Similar results were obtained with 1,6-dichloropermethyloctasilane, but the reaction was slower and as a result was studied at 10°. No spectral feature resulted which could be attributed to a long-lived intermediate species. These results tend to support the transmission of an electronic effect through the silicon chain but cannot rule out completely either of the other two possibilities.

A mixture of Me(SiMe<sub>2</sub>)<sub>6</sub>Me and Cl(SiMe<sub>2</sub>)<sub>6</sub>Cl in ethyl ether containing anhydrous MgCl<sub>2</sub>, MgI<sub>2</sub>, or MeMgI did not react during 2 days to form any Me(SiMe<sub>2</sub>)<sub>6</sub>Cl. Thus, the high yields are not due to catalytic redistributions.

For the determination of the relative importance of the transmission of electronic effects and the formation

(9) H. Sakurai, K. Tominaga, and M. Kumada, *Bull. Chem. Soc. Jap.*, **39**, 1820 (1966).

(10) A. F. Reid and C. J. Wilkins, *J. Chem. Soc.*, 4029 (1955).

(11) R. J. P. Corriu and B. J. L. Henner, *J. Chem. Soc., Chem. Commun.*, 116 (1973).

of a chelate intermediate, ClMe<sub>2</sub>Si(CH<sub>2</sub>)<sub>4</sub>SiMe<sub>2</sub>Cl<sup>12</sup> was treated with methylmagnesium iodide. The resulting yields were 26% for Me<sub>3</sub>Si(CH<sub>2</sub>)<sub>4</sub>SiMe<sub>3</sub><sup>14</sup> and 47% for Me<sub>3</sub>Si(CH<sub>2</sub>)<sub>4</sub>SiMe<sub>2</sub>Cl<sup>16</sup> and correspond approximately to a statistical distribution of products. Therefore, the dominating effect for the above reactions of polysilanes appears to be the transmission of electronic effects through the silicon chain.

The above results are consistent with the high yields of monochloropolysilanes being a consequence of a considerable difference in reactivity of the monochloro- and dichloropolysilanes toward methylmagnesium iodide. The trend in yields may be attributable to the chlorines being more strongly bound in the longer chains. This trend may reflect increased back-donation of electrons from the chlorine into a vacant polysilane orbital with increasing chain length. The greater reactivity of the dichloropolysilanes can be explained by the transmission of the effect of the second chlorine through the silicon chain *via* molecular orbitals.

The nmr data in Table II, as well as the above chemical evidence, are consistent with the transmission of electronic effects through silicon chains. In each case, the proton resonance of the -SiMe<sub>2</sub>Cl group occurs at a higher field for Me(SiMe<sub>2</sub>)<sub>*n*</sub>Cl than for the corresponding Cl(SiMe<sub>2</sub>)<sub>*n*</sub>Cl. No variation of δ<sub>-SiMe<sub>2</sub>Cl</sub> was observed in the Me<sub>3</sub>Si(CH<sub>2</sub>)<sub>4</sub>SiMe<sub>3</sub>, Me<sub>3</sub>Si(CH<sub>2</sub>)<sub>4</sub>SiMe<sub>2</sub>Cl, ClMe<sub>2</sub>Si(CH<sub>2</sub>)<sub>4</sub>SiMe<sub>2</sub>Cl series (δ<sub>-SiMe<sub>3</sub></sub> 0.025, δ<sub>-SiMe<sub>2</sub>Cl</sub> 0.390).

This study has shown that the Grignard method can be readily used to prepare 1-chloro permethylated polysilanes as a result of the transmission of electronic effects through silicon chains. For the tetra- and hexasilanes, the Grignard reaction is particularly advantageous since other convenient methods give side reactions.

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(12) Prepared by addition of BrMg(CH<sub>2</sub>)<sub>4</sub>MgBr in tetrahydrofuran to excess Me<sub>2</sub>SiCl<sub>2</sub> at 0°: bp 50-52° (1 mm) (lit.<sup>13</sup> 70-72° (4 mm)); yield 61%. *Anal.* Calcd for C<sub>8</sub>H<sub>20</sub>Si<sub>2</sub>Cl<sub>2</sub>: Cl, 29.14. Found: Cl, 29.08.

(13) M. Ishikawa, M. Kumada, and H. Sakurai, *J. Organometal. Chem.*, **23**, 63 (1970).

(14) Bp 30° (1 mm) (lit. 193° (732 mm)); n<sub>D</sub><sup>20</sup> 1.4259 (lit.<sup>15</sup> 1.4260).

(15) L. H. Sommer and G. R. Ansul, *J. Amer. Chem. Soc.*, **77**, 2482 (1955).

(16) *Anal.* Calcd for C<sub>9</sub>H<sub>22</sub>Si<sub>2</sub>Cl: Cl, 15.90. Found: Cl, 15.91.

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## A Novel Cyclization of Diallenic Sulfones

Sir:

In view of the vast amount of interesting work performed so far on intermolecular reactions of monoallenic systems,<sup>1</sup> it is quite surprising that the study of intramolecular reactions of diallenic systems has received relatively little attention in the past. The Cope-type

(1) For reviews on this subject see (a) J. D. Roberts and C. M. Sharts, *Org. React.*, **12**, 1 (1962); (b) K. Griesbaum, *Angew. Chem., Int. Ed. Engl.*, **5**, 933 (1966); (c) D. R. Taylor, *Chem. Rev.*, **67**, 317 (1967); (d) J. E. Baldwin and R. H. Fleming, *Fortschr. Chem. Forsch.*, **15**, 281 (1970); (e) T. Okamoto, *Bull. Inst. Chem. Res., Kyoto Univ.*, **50**, 450 (1972).