Photoisomerization of Dimethylsilylene to 2-Silapropene and Thermal Reversion to Dimethylsilylene[1]

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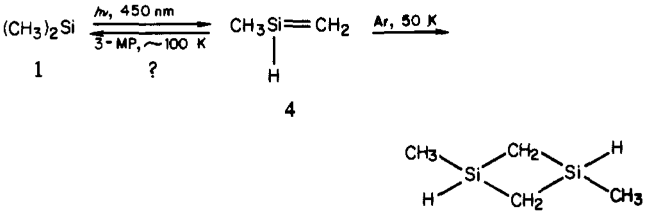
In a recent communication we reported the isolation of the bright-yellow species dimethylsilylene (1) from photolysis of dodecamethylcyclohexasilane (2), in both argon matrices at 10 K and hydrocarbon matrices at 77 K.[2]

$$\underset{\mathbf{2}}{[(CH_3)_2Si]_6} \xrightarrow[254\ \text{nm}]{h\nu} \underset{\mathbf{3}}{[(CH_3)_2Si]_5} + \underset{\mathbf{1}}{(CH_3)_2Si}$$

In this communication reference was also made to the bleaching of matrices containing 1 with visible light and the possible photochemical conversion of 1 to 2-silapropene (4). We now confirm that this photoconversion takes place. Annealing of argon matrices after photoisomerization, containing 4 but no 1, produces 1,3-dimethyl-1,3-disilacyclobutane (5), the product expected to form upon cyclodimerization of 4.[3] However, annealing of hydrocarbon matrices containing 4 at higher temperatures appears to lead to rapid reversion to 1. The infrared spectra in Figure 1, all taken in argon matrices, show the conversion of 1 to 4 and 5. The top spectrum is of a matrix originally containing 2, irradiated to produce 1 and 3 in approximately 30% conversion. Bands marked "x" are due to 2 and 3; those assigned to the five- and six-membered rings individually are indexed (5) and (6), respectively. Dark arrows indicate the bands due to 1, at 1438 and 1220 cm^{-1}. (Other bands in the spectrum, marked "O", were shown in separate experiments to be due to products produced by overirradiation of 2.) The middle spectrum shows a similar sample after bleaching by irradiation at 450 nm for 16.5 h. The bands assigned to 1 are nearly gone, and in their place a number of sharp bands appear which we assigned to 4. As shown in Table I, most of the frequencies correspond rather well to those previously reported for the structurally related 2-methyl-2-silabutene.[4] In addition, for 4 a strong doublet appears near 2195 cm^{-1} in the right region for a Si–H stretching mode.[5]



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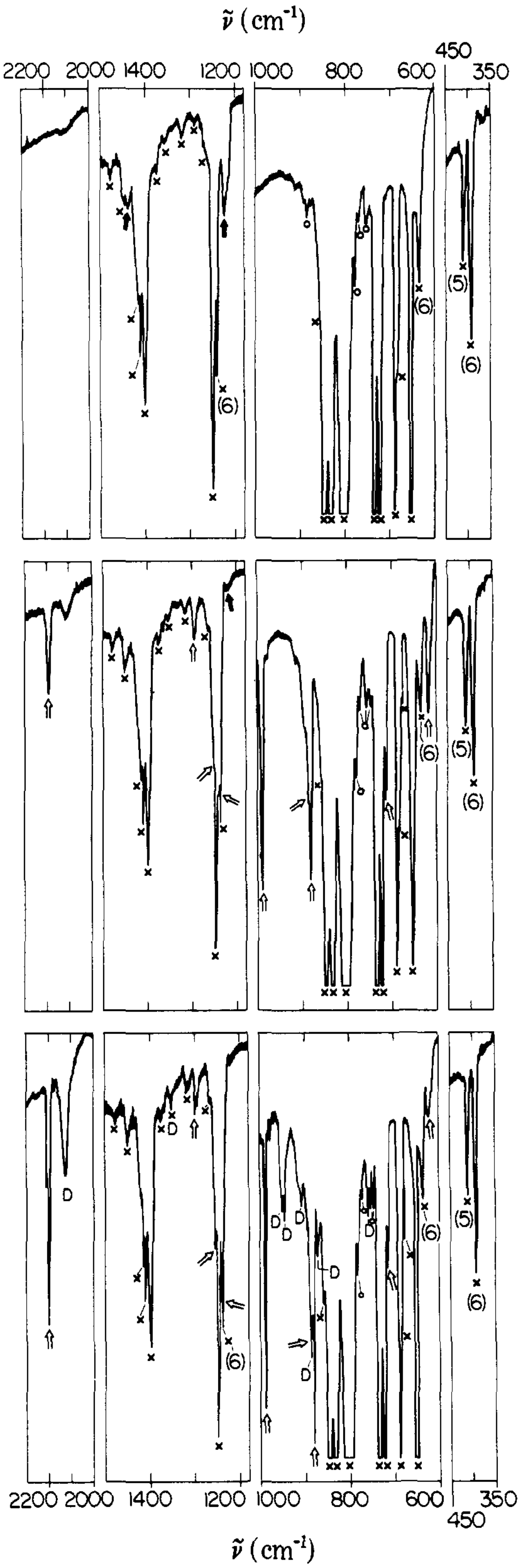

Figure 1. Infrared spectra in argon matrices at 10 K. Top, dimethylsilylene (dark arrows); center, 2-silapropene (light arrows); bottom, 1,3-dimethyl-1,3-disilacyclobutane (D). For full explanation see text.

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(1) Presented at the XIV Organosilicon Symposium, Fort Worth, TX, April 1980.

(2) Drahnak, T. J.; Michl, J.; West, R. *J. Am. Chem. Soc.* **1979**, *101*, 5427. Additional support for this structure assignment is now available: The same yellow species is formed upon photolysis of bis(trimethylstannyl)dimethylsilane in a hydrocarbon glass, and similar colored species have been obtained from a series of polysilane precursors for silylenes with dialkyl, alkylaryl, and diaryl substitution: Fink, M. J.; West, R.; Michl, J., unpublished results.

(3) Gusel'nikov, L. E.; Nametkin, N. S. *Chem. Rev.* **1979**, *79*, 529. The spectra obtained so far do not permit us to safely exclude the presence of 1,1-dimethyl-1,3-disilacyclobutane (5a). As a referee pointed out, it is therefore conceivable that the disappearance of 4 is actually due to a more complex process, 4 → 1 → tetramethyldisilene → 5 + 5a.

(4) Chapman, O. L.; Chang, C. C.; Kolc, J.; Jung, M. E.; Lowe, J. A.; Barton, T. J.; Tuney, M. L. *J. Am. Chem. Soc.* **1976**, *98*, 7844. Chedekel, M. R.; Skogland, M.; Kreeger, R. L.; Schechter, H. *Ibid.* **1976**, *98*, 7846.

(5) The frequency of 2195 cm^{-1} is slightly higher than normal for Si–H and is consistent with the silene structure for 4. The vinylic SiH in 4 should show a higher IR frequency than normal SiH vibrations. The value 2195 cm^{-1} is the average of the positions of the two sharp peaks at 2191 and 2198 cm^{-1} observed after careful annealing of the matrix. The presence of the doublet is most likely due to site effects. Before annealing, a broader peak at 2186 cm^{-1} is observed.

Table I. Infrared Frequencies for Matrix-Isolated Species and Corresponding Known Compounds[a]

4	$Me_2Si=CHMe$[b]	5	$(MeSiHCH_2)_2$[c]
615 m	608	721 w	715 m
619 m			
	645	*d*	815 m
	708		
715 m	712	869 m	
			875 s
795 m	795	886 s	
			892 s
800 m		906 s	
812 m	808	945 s	
880 s		951 s	955 s
883 s	883	*d*	1260 m
888 s		1353 w	1355 w
986 s	978	2113 s	
1242 m		2116 s	
1254 m	1255	2134 s	2140 s
1295 w			
1298 w			
1315 w	1315		
	1370		
d	1410		
d	1450		
2191 s			
2198 s			

[a] In cm^{-1}. [b] Reference 4. [c] Room temperature spectrum.[6] [d] Bands in this region are masked by strong absorptions of **2** and **3**.

The lower spectrum shows a sample which has been photolyzed at 254 nm, bleached at 450 nm, and then annealed at 50 K for 15 min. The annealing sharpens the bands considerably and leads to the formation of new bands marked D, attributed to **5**, the cyclodimer of **4**. The observed bands agree fairly well with the room temperature infrared spectrum of authentic **5** (Table I).[6] Upon further annealing the bands due to **5** become strong while those of **4** completely disappear. Identification of **5** was confirmed by mass spectrometry which gave a parent peak at $M = 116$.

Similar bleaching of **1** upon irradiation with 450-nm light takes place in 3-methylpentane matrix at 77 K. Attempts were made to trap **4** with various reagents present in the matrix (methanol, 2,3-dimethyl-1,3-butadiene, and bis(trimethylsilyl)acetylene). However, complete photodestruction of **1** followed by annealing of the matrix at ~100 K led to the same products obtained for trapping of **1** under otherwise similar conditions, although in slightly lower yield.[7] A likely explanation is that thermal reversion of **4** to **1** is rapid at 100 K, and the latter is then trapped. At lower temperatures (50 K) thermal reversion is slowed and self-trapping of **4** takes place to form **5**. These experiments complement studies which show that thermolysis of **4** to **1** also takes place at high temperatures.[8]

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[6] Conlin, R. T. Ph.D. Thesis, Washington University, St. Louis, MO, 1976, p 96. Compound **5** is probably formed as a mixture of cis and trans isomers.

[7] At high trap concentrations, a significant amount of trapping occurs even during the initial photolysis, as indicated by the observation that the initially produced visible optical density due to **1** is lower. However it is impossible to account for the results by this mechanism alone. For instance, with 1% (v/v) v of triethylsilane in 3-methylpentane glass, the initial optical density due to **1** is 86% of that observed in pure 3-methylpentane. Under these conditions, (70 ± 5)% of **1** is trapped as 1,1-dimethyl-2,2,2-triethylsilane with or without bleaching by irradiation at 450 nm. With 10% (v/v) triethylsilane, the initial optical density due to **1** is only 36% of that observed in the pure solvent, and under these conditions, (80 ± 5)% of **1** is trapped with or without bleaching.

[8] Conlin, R. T.; Wood, D. L. *J. Am. Chem. Soc.* **1981**, *103*, preceding paper in this issue.

[9] Note **Added in Proof**: A recent calculation (Goddard, J. D.; Yoshioka, Y.; Schaefer, H. F., III *J. Am. Chem. Soc.* **1980**, *102*, 7644) predicts that the hydrogen shift $H_2Si{=}CH_2 \rightarrow HSiCH_3$ is approximately thermoneutral but that the activation energy is about 40 kcal/mol. Unless the additional methyl in **1** and **4** has a dramatic effect, this result is not compatible with our interpretation. No simple alternatives have occurred to us.

Stereochemical Aspects of the Nickel-Catalyzed Alkylation of Allylic Alcohols[1]

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It has recently been shown that Grignard reagents are able to alkylate allylic alcohols when nickel–phosphine complexes are used as the catalyst precursors.[2,3] Even though some stereochemical characteristics of the reaction have been investigated in relation to the synthesis of particular terpene derivatives,[4] the stereochemistry of the reaction is still unknown.

We have found that nickel–diphosphine complexes also are able to catalyze the alkylation of cyclic allylic alcohols such as 2-cyclohexen-1-ol.[5] We wish to report on the stereochemistry of the alkylation of *cis*- (**1a**) and *trans*-4-methyl-2-cyclohexen-1-ol (**1b**) by methylmagnesium iodide in the presence of [1,2-bis(diphenylphosphino)ethane]nickel(II) chloride.

cis-**1a** and *trans*-**1b** have been prepared, as has been previously reported,[6] through reduction of 4-methyl-2-cyclohexen-1-one with lithium aluminum hydride and separated on a highly efficient rectification column (auto annular still, Perkin Elmer 251). The alkylation reactions were carried out as we have previously reported.[5] The configurations of the olefins formed were established by hydrogenation in ethanol on Pt Adams catalyst at room temperature and atmospheric pressure to be those of the corresponding dimethylcyclohexanes (Scheme I). The isomeric composition of the alkylation products and the corresponding hydrogenated products was determined by capillary gas chromatography (100 M Squalane), which gave base line separation. The data obtained in the alkylation reactions are reported in Table I. They were reproducible within 1%.

These data show that the alkylation of allylic alcohols by Grignard reagent in the presence of nickel–diphosphine catalysts is stereospecific and takes place on the side of the ring opposite to that of the replaced hydroxyl group (anti attack).[7] The minor amount of the alternative diastereomeric alkylation product corresponds indeed to the diastereomeric purity of the starting material.

The regioselectivity for alkylation at the α or γ position (position 1 or 3, respectively, in the starting material) for the two diastereomeric 4-methyl-2-cyclohexen-1-ols is remarkably different. As

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[1] Dedicated to Professor Dr. P. Pino on the occasion of his 60th birthday.

[2] C. Chuit, H. Felkin, C. Frajerman, G. Roussi, and G. Swierczewski, *J. Organomet. Chem.*, **127**, 371 (1977).

[3] H. Felkin, E. Jampel-Costa, and G. Swierczewski, *J. Organomet. Chem.*, **134**, 265 (1977).

[4] B. L. Buckwalter, I. R. Burfitt, H. Felkin, M. Joly-Goudket, K. Naemura, M. F. Salomon, E. Wenkert, and P. M. Wovkulich, *J. Am. Chem. Soc.*, **100**, 6445 (1978).

[5] G. Consiglio, F. Morandini, and O. Piccolo, *Helv. Chim. Acta*, **63**, 987 (1980).

[6] A. L. J. Beckwith and G. Phillipou, *Aust. J. Chem.*, **29**, 1277 (1976).

[7] A referee called our attention to the fact that predominant inversion of configuration has been found in the alkylation of (+)-1-buten-3-ol by C_6H_5MgBr in the presence of $(Ph_3P)_2NiCl_2$ (M. Joly-Goudket, Thesis, Université de Paris-Sud, Orsay, France, 1972, cited in a footnote, p 379 of ref 2).

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