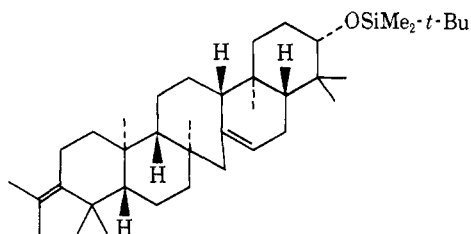


was reduced and oxidized as described for ester **12** to give a new aldehyde **14** in 58% overall yield from **13**. Reaction of **14** with isopropenylmagnesium bromide gave an allylic alcohol which was transformed *via* the chloro ketal Claisen sequence (see above) into the tetraenic alcohol **2** in 48% overall yield from **14**. This polyolefinic precursor to the serratene skeleton was thus obtained in an overall yield of 3.1% from *m*-methoxycinnamic acid.

Cyclization of **2** with trifluoroacetic acid (TFA) in dichloromethane at  $-78^\circ$  gave the pentacyclic substance **15** (methyl resonances:  $\delta$  0.02 (6 H), 0.65 (3 H), 0.73 (3 H), 0.80 (6 H), 0.87 (12 H), 1.07 (3 H), 1.18 (3 H), 1.64 (3 H), 1.77 (3 H); vinyl proton,  $\delta$  5.32), in 20% yield. This product contained an isomeric substance (*ca.* 14% yield) which could be separated by chromatography. Based on its nearly identical mass spectrum and similar nmr spectrum, we tentatively regard it as having the constitution shown in formula **17**, which



17

could arise by an alternative cyclization pathway in which ring C assumes a quasi-boat conformation.<sup>16</sup>

Selective ozonolysis of the isopropylidene group of **15** was unsuccessful, but the use of ruthenium tetroxide<sup>17</sup> effected the conversion to **16**, mp 208.5–210.5°, in 39% yield after purification by preparative tlc. The ketone was then reduced to the C-3 equatorial alcohol, mp 182–191°, and the C-21 hydroxyl protecting group was removed to give *dl*-serratenediol (**1**), mp 258.5–264.5° (reported for natural serratenediol,<sup>2b</sup> 282–284°) in 85% yield. The ir (CHCl<sub>3</sub>), 100-MHz nmr, and mass spectrum of **1** were identical within experimental limits to the corresponding spectra of the naturally occurring material.<sup>2,3</sup> Moreover, the natural and synthetic materials had identical retention times on glc and identical *R<sub>f</sub>* values on tlc. In addition, synthetic **1** was converted by oxidation and Wolff-Kishner reduction<sup>2b</sup> to the parent hydrocarbon, serratene. Acid isomerization gave a 3:1 equilibrium mixture of isoserratene (double bond at 13, 14) and serratene. These were identified by coinjection glc experiments with naturally derived materials. Thus, for the first time, totally synthetic serratenediol has been produced.<sup>18</sup>

**Acknowledgments.** This work was carried out in the laboratories of Professor William S. Johnson, to whom we are deeply indebted for encouragement and for his assistance in the preparation of this manuscript. We wish to thank the National Institutes of Health and National Science Foundation for grants (to W. S. J.) in support of this research. Finally, we are also grate-

(16) Cf. E. E. van Tamelen and R. J. Anderson, *J. Amer. Chem. Soc.*, **94**, 8225 (1972).

(17) H. Nakata, *Tetrahedron*, **19**, 1959 (1963).

(18) The reported conversion<sup>2a</sup> of naturally occurring  $\alpha$ -onocerin, which has been totally synthesized,<sup>4</sup> into serratenediol, constitutes a formal total synthesis.

ful to Dr. John W. Rowe and Professor Yasuo Inubushi for generous gifts of natural serratenediol, serratene, and isoserratene, and to Professor Gilbert Stork for supplying a specimen of ketone **8**.

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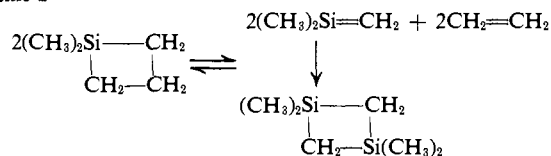
Received July 1, 1974

### Silicon–Carbon Multiple-Bonded ( $p_\pi$ – $p_\pi$ ) Intermediates. Evidence for Dipolar Character in Reactions with Trichlorosilane and Other Silicon Halides

Sir:

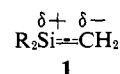
Pioneering studies concerning the generation and reactions of an unsaturated silicon–carbon reaction intermediate,  $(\text{CH}_3)_2\text{Si}=\text{CH}_2$ , led Gusel'nikov and Flowers to conclude that this reactive intermediate does not behave as a diradical (odd electron spins unpaired).<sup>1</sup> All of their evidence, quantitative and qualitative, was consistent with thermolytic generation of this intermediate as a  $p_\pi$ – $p_\pi$  bonded species. In the absence of a suitable trapping agent, generation and reaction (in the gas phase) proceeds according to Scheme I.

Scheme I



Absence of involatile products, an exact product ratio of 2:1 for ethylene:cyclodimer, and too high a pre-exponential factor, *A*, all disfavor a diradical structure (which would require electron spin unpairing during generation of  $(\text{CH}_3)_2\text{Si}-\dot{\text{C}}\text{H}_2$ ) and favor a  $p_\pi$ – $p_\pi$  bonding formulation,  $(\text{CH}_3)_2\text{Si}=\text{CH}_2$ .

During previous studies we formed and recorded the (largely unproven) conviction that silicon–carbon double bonds, generated thermolytically according to Scheme I, possessed considerable dipolar character.<sup>2</sup>



In the present work, bonding postulate **1** led us to undertake the first studies of the reactions of silicon–carbon double bonds with silicon chlorides and fluorides. Especially for the latter, the extremely high bond energy of the silicon–fluorine bond ( $\sim 135$  kcal/mol)<sup>3</sup>

(1) M. C. Flowers and L. E. Gusel'nikov, *J. Chem. Soc. B*, 419 (1968).

(2) (a) D. N. Roark and L. H. Sommer, *J. Chem. Soc., Chem. Commun.*, 167 (1973); (b) R. D. Bush, C. M. Golino, D. N. Roark, and L. H. Sommer, *J. Organometal. Chem.*, **59**, C17 (1973); (c) C. M. Golino, R. D. Bush, D. N. Roark, and L. H. Sommer, *J. Organometal. Chem.*, **66**, 29 (1974); (d) C. M. Golino, R. D. Bush, and L. H. Sommer, *J. Amer. Chem. Soc.*, **96**, 614 (1974); (e) R. D. Bush, C. M. Golino, G. D. Homer, and L. H. Sommer in press.

(3) T. Cottrell, "The Strength of Chemical Bonds," 2nd ed, Butterworths, London, 1958, pp 270–280.

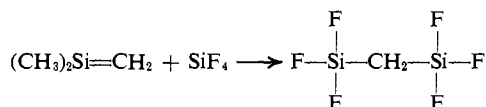
**Table I.** Reactions of 1,1-Dimethyl-1-silaethene,  $(\text{CH}_3)_2\text{Si}=\text{CH}_2$  (**2**), with Silicon Halides at  $611^\circ$  <sup>a</sup>

Reaction no.	[SiMe <sub>2</sub> ] <sup>b</sup> (mmol)	Substrate	(mmol)	Products (% yield) <sup>c</sup>		
				1:1 Adduct		Me <sub>2</sub> Si-SiMe <sub>2</sub>
1	18.4	SiF <sub>4</sub>	(~124)	F <sub>3</sub> SiCH <sub>2</sub> SiMe <sub>2</sub> F	(44)	Trace
2	13.9	HSiCl <sub>3</sub>	(49.8)	HCl <sub>2</sub> SiCH <sub>2</sub> SiMe <sub>2</sub> Cl	(22)	Trace
3	13.3	SiCl <sub>4</sub>	(20.5)	Cl <sub>3</sub> SiCH <sub>2</sub> SiMe <sub>2</sub> Cl	(20)	3
4	14.3	MeSiCl <sub>3</sub>	(38.0)	Cl <sub>2</sub> MeSiCH <sub>2</sub> SiMe <sub>2</sub> Cl	(16)	16
5	9.76	Me <sub>2</sub> SiCl <sub>2</sub>	(26.4)	ClMe <sub>2</sub> SiCH <sub>2</sub> SiMe <sub>2</sub> Cl	(13)	25
6	10.1	Me <sub>3</sub> SiCl	(27.2)	Me <sub>3</sub> SiCH <sub>2</sub> SiMe <sub>2</sub> Cl	(<~2) <sup>d</sup>	40
7	15.3	CF <sub>4</sub>	(112)			46

<sup>a</sup> All experiments except for the SiF<sub>4</sub> and CF<sub>4</sub> experiments used nitrogen carrier gas. Full experimental details are given in ref 2b. <sup>b</sup> Precursor to 1,1-dimethyl-1-silaethene, see text. <sup>c</sup> All reported yields are based on amounts of material actually isolated by preparative glpc. All new compounds reported were unambiguously identified on the basis of their nmr, ir, and mass spectra. Determination of the exact mass was done on either the parent or parent minus methyl ion. The less than quantitative yields are due to: ca. 20–40% wt loss during preparative glpc as verified by control experiments, a number of minor (<5%) products present in each of the reactions studied, and mechanical losses due to the small scale reactions. <sup>d</sup> Estimated yield is an upper limit for 1:1 adduct. Material could not be isolated in sufficient quantity for identification.

would be expected to disfavor such addition reactions in the absence of dipolar character as shown in **1**. Indeed, addition reactions of silicon fluorides with ordinary carbon-carbon double bonds are, to our knowledge, completely unknown.<sup>4</sup> In contrast, strong nucleophiles attack the silicon-fluorine bond quite readily.<sup>5</sup>

In the present study, the nucleophilic potential of the carbon component of the silicon-carbon double bond, and hence the validity of formulation **1**, was strongly indicated by the following reaction of  $(\text{CH}_3)_2\text{Si}=\text{CH}_2$  with silicon tetrafluoride to give a 44% yield of adduct.



As in our previous studies,  $(\text{CH}_3)_2\text{Si}=\text{CH}_2$ , 1,1-dimethyl-1-silaethene (**2**), was generated by gas-phase pyrolysis of the silacyclobutane at  $611^\circ$ . The details of this addition reaction, others with silicon chlorides, and the failure of CF<sub>4</sub> to react with **2** are summarized in Table I.

Reaction 2 in Table I provides further strong evidence for the dipolar nature of **2** and additional evidence against diradical character for this intermediate. In sharp contrast to silicon-fluorine and silicon-chlorine bonds, the silicon-hydrogen bond is well known to react *via* a radical mechanism.<sup>4,6</sup> Thus, diradical character of **2** should lead to addition of the silicon-hydrogen bond to **2** when the latter is generated in the presence of SiHCl<sub>3</sub>. Instead, exclusive addition of the silicon-chlorine bond is found.

The structure-reactivity pattern shown by reactions 3–6, diminishing reactivity with replacement of Cl in SiCl<sub>4</sub> by methyl, is not an unexpected pattern for nucleophilic reaction at silicon.

Also, in view of the high bond energy of the silicon-fluorine bond and the lower value for the carbon-fluorine bond (116 kcal/mol),<sup>3</sup> it would be reasonable to expect that diradical character of **2** should lead to

(4) E. Y. Lukevits and M. G. Voronkov, "Organic Insertion Reactions of Group IV Elements," Plenum Press, New York, N. Y., 1966.

(5) C. Eaborn, "Organosilicon Compounds," Butterworths, London, 1960.

(6) A. G. MacDiarmid, "The Bond to Carbon," Marcel Dekker, New York, N. Y., p 213.

addition of CF<sub>4</sub>. As reaction 7 in Table I shows, no adduct was formed. This is in accord with lower susceptibility to nucleophilic attack of CF<sub>4</sub> compared to SiF<sub>4</sub>.<sup>5</sup>

In addition to providing evidence for the dipolar nature of the silicon-carbon double bond, and additional evidence against a diradical structure for such intermediates, the present study also furnishes a new synthetic route to fairly inaccessible silylmethylene compounds.

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### Substituent Effects in the $n \rightarrow \pi^*$ Transition of Ketones

Sir:

Cd and ord spectroscopy of chiral ketones yields information not only about the energetics of the  $n \rightarrow \pi^*$  transition but also about the variation in the transition probability for the differential absorption of left and right circularly polarized light. The latter property was utilized in the derivation of the octant rule.<sup>1</sup> This topic has been well documented;<sup>2</sup> however, it is a subject of our current work on account of some serious breakdowns of the rule when the ketone is perturbed by some substituents in certain orientations.<sup>3</sup> In comparison, relatively little use has been made of the  $\lambda_{\text{max}}$  of the  $n \rightarrow \pi^*$  transition, except in the case of  $\alpha$ -axial

(1) W. Moffitt, R. B. Woodward, A. Moscowitz, W. Klyne, and C. Djerassi, *J. Amer. Chem. Soc.*, **83**, 4013 (1961).

(2) C. Djerassi in "Optical Rotatory Dispersion: Applications to Organic Chemistry," McGraw-Hill, New York, N. Y., 1960; P. Crabbe, "Optical Rotatory Dispersion and Circular Dichroism in Organic Chemistry," Holden-Day, San Francisco, Calif., 1965; W. Klyne, *Advan. Org. Chem.*, **1**, 239 (1960); L. Velluz, M. Legrand, and M. Grosjean, "Optical Circular Dichroism," Academic Press, New York, N. Y., 1965; G. Sneath, Ed., "Optical Rotatory Dispersion and Circular Dichroism in Organic Chemistry," Heyden and Son, London, 1967; P. Crabbe, "Optical Rotatory Dispersion and Circular Dichroism in Organic Chemistry," Gauthier-Villars, Paris, 1968; P. Crabbe, "An Introduction to the Chiroptical Methods in Chemistry," Syntex S. A., Mexico, 1971.

(3) J. Hudec, *Chem. Commun.*, 829 (1970).

(4) R. C. Cookson, *J. Chem. Soc.*, 282 (1954).