

modulation techniques were carried out on an SLM-4800 spectrofluorimeter following the method described by the manufacturer (SLM Instruments, U.S.A.). Solutions (10^{-4} M) were prepared in quartz tubes and purged with argon for single-photon counting analysis. Samples for the SLM-4800 were prepared in 1.00-cm quartz cuvettes. The excitation wavelength for both methods was 260 nm and emission was viewed through a 290-nm cut-off filter.

Preparative Photolysis. Preparative photolyses were carried out in 10-mL quartz tubes by using a Hanovia 450-W Hg lamp (Vycor filter). A solution of 2-5 mg of the substrate dissolved in 4 mL of MeOH (or HOAc) and 6 mL of pH 0.2 (measured pH; aqueous H_2SO_4) was photolyzed for 30 min-2 h, depending on the substrate. The meta isomers required ca. 30 min of irradiation for measurable conversion, while the para isomers required much longer photolysis times (>1 h). Conversions were kept below 20%. After workup (CH_2Cl_2 extraction), the product mixtures were analyzed on a Varian Aerograph Model 3700 gas chromatograph (SE-30 capillary column) and on a Finnigan 3300 GC/MS system operating in CI/methane. The products were identified by comparison with the authentic samples.

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Registry No. 1, 459-56-3; 2, 456-47-3; 3, 589-18-4; 4, 587-03-1.

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Insertion of an Alkylidenecarbene into the Silicon-Hydrogen Bond. Isotope Effect for the Reaction

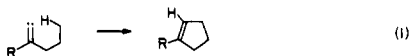
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Introduction

We recently described the use of the temperature dependence of the kinetic isotope effects² as a means of defining the reaction trajectory for intramolecular C-H insertion of alkylidenecarbenes to give cyclopentenes (eq 1).³ This Note describes extension of this mechanistic probe to an intermolecular insertion reaction of this type of carbene.



There is a paucity of examples in which alkylidenecarbenes are claimed to undergo intermolecular insertion into carbon-hydrogen bonds. In fact, a search of the literature revealed only two examples, and both of these were in low yields.^{4,5} Consequently, we elected to determine

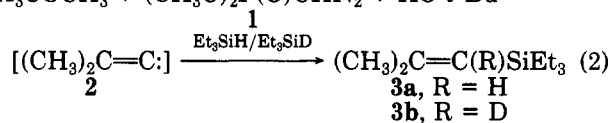
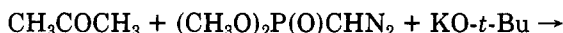
Table I. GC-MS Data for Determination of Kinetic Isotope Effect

run	temp, °C	ratio of m/e^a	k_H/k_D^b
1	ambient	69.2:91.9	
2	ambient	69.2:91.9	
3	21	98.1:90.7	1.43 (8), 1.43 (7)
4	21	97.7:90.7	1.43 (2), 1.43 (1)
5	-78	99.2:90.6	1.45 (5), 1.45 (4)
6	-78	98.3:90.7	1.44 (1), 1.44 (0)

^aThe ratios given in runs 1 and 2 are for the molecular ions of Et_3SiH and Et_3SiD at m/e 116 and 117, respectively. The value for m/e 117 has been corrected for the contribution to it of the $M + 1$ peak arising from the protio material; this correction corresponds to 11.7% of the area of the peak at m/e 116. In the remaining runs, the ratios are for the $M - ethyl$ peaks of **3a** and **3b** at m/e 141 and 142, respectively; the area of the latter peak was again corrected for the presence of the $M + 1$ peak from protio compound **3a**, the factor being 9.5% in this case. ^bThe two values of k_H/k_D for each run are derived by use of the ratios of protio- and deuteriotriethylsilane determined in runs 1 and 2.

the isotope effect associated with insertion of an alkylidenecarbene into a silicon-hydrogen bond, a reaction known to occur in acceptable yields.⁶⁻⁸

A mixture of triethylsilane and triethylsilane- d_1 was allowed to react with 2-methyl-1-propenylidene (isopropylidenecarbene, **2**), which was generated by reaction of acetone and dimethyl (diazoethyl)phosphonate (eq 2). The ratio of the two starting silanes as well as that of **3a**:**3b** was determined by GC-MS analyses; the data that resulted are collected in Table I. The relative proportion of the two insertion products, **3**, was determined by integration of the peak areas of the molecular ions minus ethyl. Important to the success of this analysis was the complete absence of ions representing the loss of ethane from the molecular ion as this simplified the procedure needed to correct the peak areas for contributions from ¹³C and ²⁹Si. The ratio of the two substrate silanes was determined similarly; the correction of peak areas for isotope effects was again made convenient by virtue of the fact that the only fragmentation process that occurs for the molecular ion, but does not involve cleavage of a carbon-silicon bond, is the loss of the hydrogen (or deuterium) atom bound to silicon. The kinetic deuterium isotope effect was calculated by use of eq 3, which is analogous to the expression developed by Skell for evaluation of relative reactivities of alkenes toward carbenes.⁹



$$k_H/k_D = [Et_3SiD/Et_3SiH][\mathbf{3a}/\mathbf{3b}] \quad (3)$$

As shown by the data in Table I, the insertion reaction was performed in duplicate at both -78 and 21 °C, and values of k_H/k_D of 1.44 (7) (standard deviation of 0.008) and 1.43 (5) (standard deviation of 0.004), respectively, were obtained. Within experimental error, the isotope effect is independent of temperature. This implies that the transition state for the insertion reaction is nonlinear, just as in the case of the intramolecular process.³ Although theoreticians have not undertaken a calculation of the

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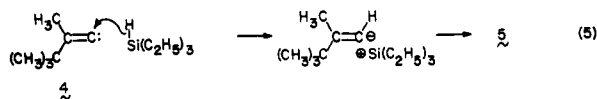
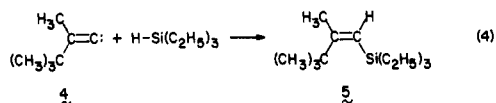
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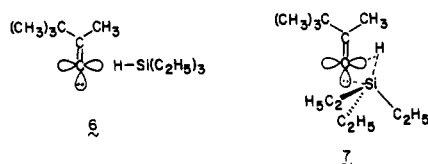
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reaction trajectory of the reaction of a carbene with a silicon-hydrogen bond, our experimental results are consistent with the most recent theoretical efforts involving attack of carbenes on the carbon-hydrogen bond.¹⁰

Both Newman^{6,7} and Stang⁸ have reported that 2,3,3-trimethyl-1-butenylidene (**4**) reacts with triethylsilane to afford predominantly the *Z* isomer **5**, the thermodynamically less stable product of Si-H insertion (eq 4). Newman⁶ rationalized this result by proposing that the reaction proceeded by way of initial hydride abstraction on the sterically less hindered face of the carbene, followed by trapping of the vinyl anion, which is presumed to retain its initial conformation, by the triethylsilylenium ion (eq 5).⁶ In the context of the present work, such a mechanism is rendered unlikely since, in our opinion, a colinear arrangement of the Si-H bond and the carbenic carbon atom might be expected, as shown by **6**, and such a geometry at the rate-determining transition state for the reaction should produce a temperature-dependent isotope effect, according to Kwart's hypothesis.²



A more conventional mechanism for the insertion that accounts for the stereochemical outcome of eq 4 and for the temperature independence of the isotope effect involves a nonlinear transition state such as **7**, in which the



substituents on the α -carbon atom of the carbene are oriented so as to minimize steric interactions. The plane defined by the carbon skeleton of the alkylidenecarbene can be at various angles relative to that defined by Et, Si, and H (the plane of the paper as shown for **7**), but electronic considerations suggest an orientation that allows development of interaction between the electropositive silicon atom and the filled "sp"-hybrid orbital of the carbene at the transition state of the reaction. This same type of transition state has previously been proposed for the insertion of dichlorocarbene in the silicon-hydrogen bond.¹¹

It is to be noted that the magnitude of the isotope effect measured in this work is in line with the values of 1.23 and 1.26 associated with the insertion of dichlorocarbene into the silicon-hydrogen bond of tri-*n*-butylsilane^{12a} and methylphenylsilane,^{12b} respectively. As reported earlier,³ similarity in magnitudes also exists between the kinetic deuterium isotope effects for insertion of dichlorocarbene and of alkylidenecarbenes into carbon-hydrogen bonds.

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Experimental Section

IR spectra were recorded on a Beckman AccuLab 8 spectrophotometer, and the polystyrene absorption at 1601 cm^{-1} was used as reference. Samples were run as liquid films between salt plates. ¹H NMR spectra were measured with a Varian Associates EM-390 spectrometer; chloroform-*d* was used as the solvent and Me₄Si served as the internal standard. GC-MS data were obtained with a Finnegan 4023 instrument having an INCOS data system; the ionizing voltage was 60 eV.

Triethylsilane-*d*₁ (3b). Chlorotriethylsilane was reduced in 62% yield by LiAlD₄, using a procedure modeled after that of Finholt et al.¹³ The IR and ¹H NMR spectra were identical with those of a commercial sample of triethylsilane¹⁴ except that the deuterated silane had a ¹H NMR spectrum devoid of the peak at the chemical shift for the proton bound to silicon and gave an IR spectrum containing an Si-D stretching band at 1120 cm^{-1} in lieu of the corresponding absorption at 2100 cm^{-1} in protio material: MS, *m/e* (relative intensity) 119 (*M* + 2, 3.3%), 118 (*m* + 1, 8.7%), 117 (*M*⁺, 60.8%), 88 (*M* - C₂H₅, 99.5%); 60 (*M* - C₄H₁₀, 100%).

Reaction between Triethylsilane-*d*₁ and 2-Methyl-1-propenylidene (2). Potassium *tert*-butoxide (0.273 g, 2.44 mmol) and anhydrous THF (2.5 mL) were combined in a round-bottomed flask equipped for magnetic stirring. The flask was purged with dry nitrogen and sealed with a rubber septum, and a solution of **3a** and **3b** (1.1 mL, 0.82 g, 6.9 mmol) was added. After the flask was placed in a bath held at either -78 or 21 °C, a solution of acetone (0.10 g, 1.7 mmol), dimethyl (diazomethyl)phosphonate (0.28 g, 1.9 mmol), and THF (1.0 mL) was added dropwise over 2 min. The resulting mixture was stirred for 3 h, with venting as needed to relieve pressure. Pentane (3 mL) was added, and the solution was washed with water (3 × 5 mL) and dried (Na₂SO₄). After concentration by rotary evaporation, the residue (ca. 1 mL) was analyzed by GC-MS.

The IR and ¹H NMR spectra of **3a**, prepared from triethylsilane by the above procedure and purified by gas chromatography (Varian A-90-P, 3 m × 0.25 in. column packed with 10% SE-30 on 30/60 mesh Chromosorb W, 110 °C, 55 mL/min helium), were identical with those reported.⁷

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Registry No. 1, 27491-70-9; 2, 26265-75-8; **3a**, 18081-24-8; **3b**, 96617-49-1; CH₃COCH₃, 67-64-1; Et₃SiH, 617-86-7; Et₃SiD, 1631-33-0; D₂, 7782-39-0; chlorotriethylsilane, 994-30-9.

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A Convenient Preparation of Dicarboxyl(η⁵-cycloheptadienyl)(triphenyl phosphonyl)iron Tetrafluoroborate, a Potential Macrolide Antibiotic Precursor

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(Dienyl)Fe(CO)₃ cations occupy a prominent place as emerging synthetic intermediates,² largely due to their ready availability, low cost, and reactivity toward nucleo-

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