species boron triformate can N^5-formylate at a temperature which is low enough to preclude cyclization to an N^5,N^{10}- or N^5,N^{11}-methenyl derivative.

Experimental Section

IR spectra were obtained on a Perkin-Elmer Model 781 double-beam recording spectrophotometer, UV spectra were obtained on a Varian Model 210 UV/visible instrument, and NMR spectra were obtained on a Varian Model T60A instrument with chemical shifts (δ) reported relative to Me_4Si. TLC was performed on Eastman 13181 silica gel or Eastman 13254 cellulose sheets containing a fluorescent indicator. Spots were visualized under 254-nm illumination. Microanalyses were performed by Galbraith Laboratories, Knoxville, TN, and MCL Laboratories, Lowell, MA. Folic acid was purchased from Sigma Chemical Company, St. Louis, MO. Homofolic acid was provided by Dr. J. A. R. Mead, Division of Cancer Treatment, National Cancer Institute, Bethesda, MD.

Leucovorin, Calcium Salt (1, Ca Salt). A solution of folic acid (477 mg, 1 mmol) in 97–100% formic acid (10 mL) was cooled in an ice bath and treated with $BH_3{\cdot}HNMe_2$ (858 mg, 15 mmol) in small portions over 1 h with vigorous stirring. When addition was complete the light-orange solution was left to stand in the refrigerator at 4 °C for 24 h. The solution was then poured with stirring into ether (50 mL), the ether was decanted, and the residue was triturated with fresh ether until a powder was obtained. After decantation of the ether, water (10 mL) was added and calcium hydroxide was added to the suspension, in small portions with stirring, until the pH was strongly alkaline. Final solubilization was achieved with the aid of an ultrasonic bath. The pH was adjusted to 7.5 with dilute formic acid, a small amount of fine insoluble material was filtered off, and the filtrate was diluted with EtOH (120 mL). After several hours of refrigeration the crude product was collected, reprecipitated once more from aqueous EtOH, and dried in vacuo at 65 °C over P_2O_5 to obtain a white solid (396 mg, 64% yield); R_f 0.7 (cellulose, 3% NH_4Cl); IR ν (KBr) 3400, 1610–1640 cm^{-1}; NMR δ (D_2O) 1.5–3.4 (m, alkyl), 6.60 (d, J = 8 Hz, aryl protons ortho to N^{10}), 7.57 (d, J = 8 Hz, aryl protons ortho to CONH); UV λ_{max} (H_2O) 285 nm (ϵ 25 700). Anal. Calcd for $C_{20}H_{21}N_7O_7Ca{\cdot}0.25Ca(OOCH)_2{\cdot}4.5H_2O$: C, 39.39; H, 4.92; N, 15.68; Ca, 8.01. Found: C, 39.52; H, 5.26; N, 15.78; Ca, 8.01.

5-Formyl-5,6,7,8-tetrahydrohomofolic Acid, Calcium Salt (2, Ca Salt). A solution of homofolic acid (491 mg, 1 mmol) in 97–100% formic acid was cooled in an ice bath. Then $BH_3{\cdot}HNMe_2$ (118 mg, 2 mmol) was added all at once with vigorous stirring at 15-min intervals for a total of 8 times (16 mmol). When all additions were complete, the solution was placed in the refrigerator (4 °C) overnight before being poured into ether (100 mL) with stirring. The ether was decanted and the residue was washed repeatedly with ether and dissolved in water (5 mL). A minimum amount of NH_4OH was added to dissolve the compound, and $CaCl_2{\cdot}2H_2O$ (1 g) was added, followed by EtOH (100 mL). After overnight refrigeration, the collected product was dissolved in water (15 mL) with the help of a sonicating bath. A small amount of insoluble material was removed by filtration, the filtrate was decolorized with charcoal, and the product was reprecipitated with EtOH (100 mL), collected, and dried in vacuo at 60–65 °C over P_2O_5 to give a colorless powder (375 mg, 60% yield); R_f 0.7 (cellulose, 3% NH_4Cl); IR (KBr) ν 3390, 1610–1640, 1560 cm^{-1}; NMR δ (D_2O) 1.5–2.7 and 2.9–3.7 (m, alkyl), 6.87 (d, J = 8 Hz, aryl protons ortho to N^{10}), 7.87 (d, J = 8 Hz, aryl protons ortho to CONH); UV λ_{max} (H_2O) 285 nm (ϵ 26 000). Anal. Calcd for $C_{21}H_{23}N_7O_7Ca{\cdot}5.5H_2O$: C, 40.38; H, 5.49; N, 15.70; Ca, 6.42. Found: C, 40.38; H, 5.38; N, 15.45; Ca, 6.44.

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Registry No. 1, 58-05-9; 1·Ca, 1492-18-8; 2, 96482-98-3; 2·Ca, 96482-99-4; $BH_3{\cdot}NHMe_2$, 74-94-2; HCO_2H, 64-18-6; folic acid, 59-30-3; homofolic acid, 3566-25-4.

Acid-Catalyzed Photochemical Generation of Benzyl Cations as a Probe of the Electron-Donating Abilities of Benzene Substituents in the Singlet Excited State

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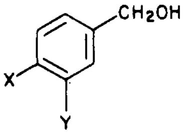
In a recent study[1] we showed that certain methoxybenzyl alcohols undergo efficient photochemical dehydroxylation (solvolysis) in aqueous solution to give the corresponding benzyl cations, which could be subsequently trapped by external nucleophiles (eq 1). *o*- and *m*-methoxy-substituted benzyl alcohols showed this reactivity; the para isomer was unreactive under similar conditions. This study was the first, to our knowledge, which characterized in quantitative terms the long-postulated paradigm of different relative reactivities of methoxy-substituted benzenes in organic photochemistry,[2] initially postulated by Zimmerman and Sandel.[3] Additionally, we showed that novel catalytic effects[4] due to the hydronium ion was observable at sufficiently low pH's, the overall effect being to increase the rate of photochemical dehydroxylation.

$$ArCH_2OH \underset{H_2O}{\overset{h\nu}{\rightleftarrows}} [ArCH_2{}^+] \xrightarrow{ROH} ArCH_2OR \qquad (1)$$

An important application of the above results is in the use of the reaction as a probe of the relative electron-donating abilities of substituents other than methoxy, assuming that photochemical dehydroxylation occurs to measurable extent for other substituted benzyl alcohols. We report here such an application to the fluoro and methyl substituents and provide evidence to suggest that *m*-fluoro *m*-methyl groups have significantly better electron-donating effects compared to their para analogues in S_1.

Substituted benzyl alcohols 1–4 were chosen for study because they showed relatively strong fluorescence ($\phi_f \sim 0.1$), thus enabling emission spectroscopy to be used to probe their excited-state behavior. Fluorescence emission from these alcohols was quenched on going from pH 7 to lower pH, as shown in Figure 1 for *m*-fluorobenzyl alcohol (**2**). The proportion of fluorescence quenching, as measured by $\phi_f/\phi_f{}^0$, where $\phi_f{}^0$ represents the fluorescence yield in pH 7, plotted against pH (or H_0) is shown in Figure 2 for all these compounds. Both of the meta isomers are quenched more efficiently with increasing acidity than



1, X = F; Y = H
2, X = H; Y = F
3, X = CH_3; Y = H
4 X = H; Y = CH_3

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[1] Turro, N. J.; Wan, P. *J. Photochem.* **1985**, *28*, 93.

[2] (a) Cristol, S.; Bindel, T. H. *Org. Photochem.* **1983**, *6*, 327. (b) Turro, N. J. "Modern Molecular Photochemistry"; Benjamin/Cummings: Menlo Park; 1978; pp 404–406. (c) Barltrop, J. A.; Coyle, J. D. "Excited States in Organic Chemistry"; Wiley: London; 1975; p 288. (d) Cowan, D. O.; Drisko, R. L. "Elements of Organic Photochemistry"; Plenum Press: 1976; p 534.

[3] Zimmerman, H. E.; Sandel, V. R. *J. Am. Chem. Soc.* **1963**, *85*, 915.

[4] The reader is directed to a recent review by Wubbels on catalysis of photochemical reactions.

0022-3263/85/1950-2583$01.50/0

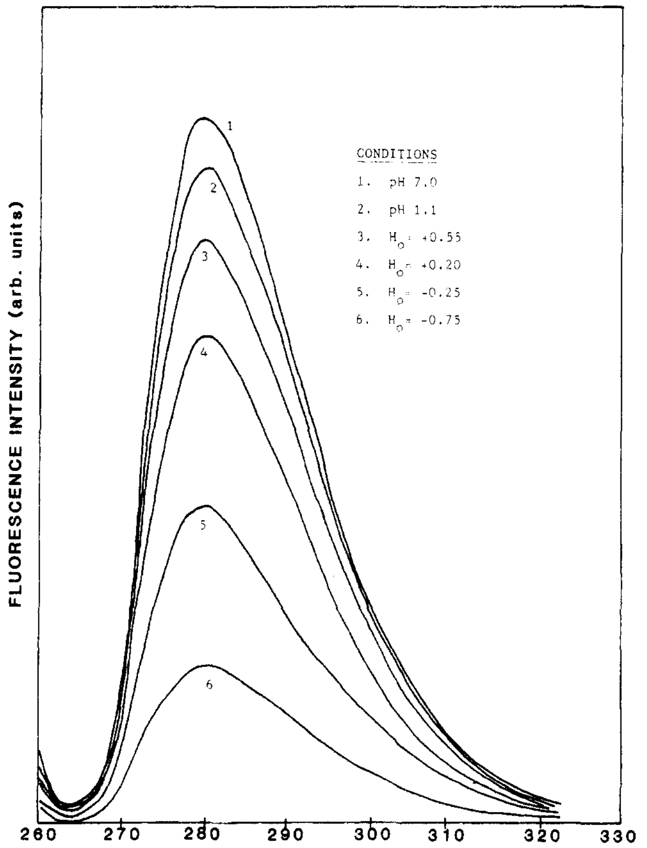


Figure 1. Fluorescence quenching of *m*-fluorobenzyl alcohol (2) by added acid (λ_{excit} = 260 nm).

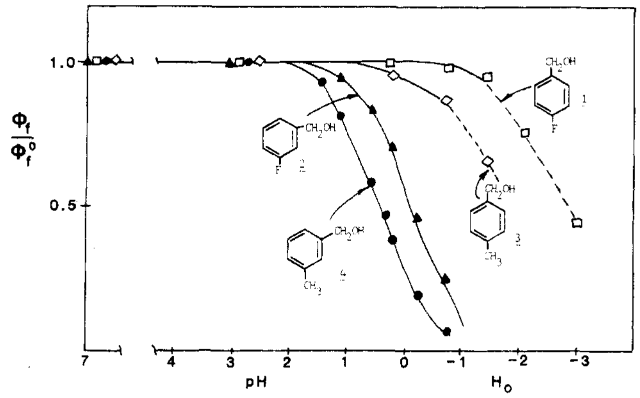
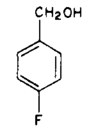
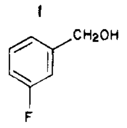
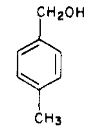
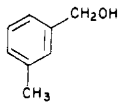


Figure 2. Fluorescence quenching (ϕ_f/ϕ_f^0) by added acid for benzyl alcohols 1–4. Dashed lines shown for the para isomers (1 and 3) indicate the possibility of thermal reaction contributing to the observed quenching, the exact extent of which was not estimated in the present study.

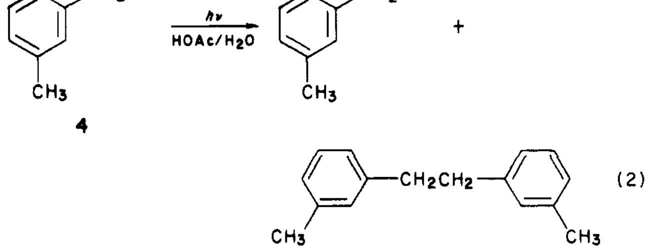
their para analogues. However, such an observation from steady-state fluorescence studies does not necessarily imply a difference in intrinsic relative reactivity since such a quenching phenomenon can be ascribed to differences in singlet excited-state lifetimes of the molecules. To further assess the implication of these observations, fluorescence lifetimes of these compounds were measured by using the single-photon counting technique and via the phase-shift and relative modulation techniques. The results are shown in Table I. These additional results indicate that the observed quenching due to hydronium ion is a dynamic phenomenon and that the difference in quenching efficiencies of the isomers indeed reflects a difference in relative reactivity of the photoexcited molecules. Assuming that hydronium ion is the quenching species, Stern–Volmer plots for the meta isomers were linear and gave $k_q(2) = 1.6\ (\pm 0.3) \times 10^8\ M^{-1}\ s^{-1}$ and $k_q(4) = 3.5\ (\pm 0.5) \times 10^8\ M^{-1}\ s^{-1}$. For the para isomers, however, Stern–Volmer plots could not be obtained since rather high acidities were required to effect significant quenching. At these high acidities, the concentration (or activity) of the hydronium ion to be used for Stern–Volmer analysis is difficult to assess. In addition, thermal acid-catalyzed dehydroxylation (i.e., thermal solvolysis) cannot be avoided at acidities greater than $H_0 \sim -1$ for these para isomers under the experimental conditions.

Table I. Fluorescence Lifetimes

compound	lifetime (ns)[a] pH 7	lifetime (ns)[a] $H_0 = -0.22$
 1	6.5	6.0[b]
 2	6.6	4.8
 3	9.8	9.4[b]
 4	6.6	~2

[a] All decays were first order. Estimated error ±0.5 ns. [b] Change in lifetime within experimental error. Higher acidities were not employed due to the possibility of thermal acid-catalyzed dehydroxylation.

Preparative photolyses in aqueous methanol and aqueous acetic acid provided the necessary additional information for an interpretation of the above-observed fluorescence quenching data. Photolysis of *m*-methylbenzyl alcohol (4) in aqueous acetic acid (40% pH 0.2 H_2SO_4/60% HOAc) gave 92% of the acetate of 4 and 8% of *m*,*m*′-dimethylbibenzyl (eq 2) in low conversion (<20%)



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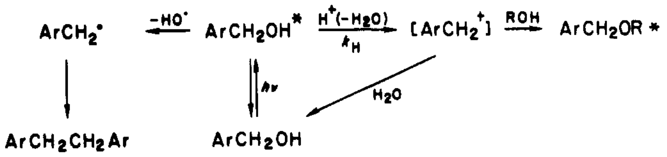
(2)

experiments. When MeOH was used in place of HOAc, the major product was *m*-methylbenzyl methyl ether. Additionally, when the aqueous portion of the solvent mixture was changed to pH 7 (neutral water), much longer photolysis times were required to effect observable reaction. This indicates that proton transfer from water or hydronium ion is required for photodehydroxylation, which is consistent with the observed acid quenching of fluorescence (Figure 1) for this compound. Moreover, hydronium ion is a much better catalyst than water in the reaction. In contrast, photolysis of *p*-methylbenzyl alcohol

Scheme I



(3) under similar photolysis conditions resulted in nearly complete recovery of starting material. However, under exhaustive photolysis (photolysis time ca. 5 times longer than that for the meta isomer), about 70% of the bibenzyl product (*p,p'*-dimethylbibenzyl) and 30% of the solvolysis product was observed. A significant amount of polymeric material was also observed under these conditions. Preparative photolysis of fluorobenzyl alcohols 1 and 2 in aqueous MeOH and HOAc gave very similar results. However, photolysis of benzyl alcohol (the parent substrate) under the above conditions failed to give detectable amounts of solvolysis product; >90% of the material was recoverable after photolysis.

These observations are best interpreted as reflecting the different abilities of the benzene substituents to stabilize a developing positive charge at the benzylic position in S_1. Those substituents with a greater ability to stabilize the positive charge will result in a higher proportion of heterolytic (solvolysis) product on photolysis of the molecule. The fact that added hydronium ions can catalyze the rate of photochemical dehydroxylation supports a scheme where dehydroxylation is competitive with homolytic cleavage from S_1 (Scheme I). Thus in the presence of hydrogen ion donating solvents such as aqueous acid solutions, dehydroxylation becomes competitive with homolytic cleavage (which in itself is a high-energy process that does not appear to be subject to catalysis under the conditions employed). An alternative scheme in which the initial primary step is homolytic cleavage to give a radical pair, which then can undergo electron transfer to give an ion pair, is inconsistent with the following observations: (1) fluorescence quenching by added hydronium ions; (2) acid-catalysis of photodehydroxylation; (3) requirement of water in the reaction medium for photosolvolysis to occur.

Since the evidence indicates that k_q (the fluorescence quenching rate constant) is equivalent to k_H, the acid-catalyzed rate constant for photodehydroxylation from S_1 (Scheme I), we can rank the relative reactivities of several substituted benzyl alcohols studied in this and previous work,[1] based on their absolute k_q values, as follows: *m,-m'*-$(CH_3O)_2$ (1.4×10^{10} M^{-1} s^{-1}) > *o*-CH_3O (1.2×10^{10}), > *m*-CH_3O (3.7×10^9) > *m*-CH_3 (3.5×10^8) > *m*-F (1.6×10^8), all of which are significantly more reactive than the para-substituted compounds studied and the parent benzyl alcohol.

It is interesting to note that although the fluoro substituent at the meta position is an electron-withdrawing group (σ(*m*-F) = +0.34)[6] in the ground-state, it becomes effectively an electron-donating group in S_1 (relative to the parent benzyl alcohol). The *p*-fluoro group does not appear to exhibit such a drastic change in electron-donating power, although it is clearly less electron-donating than *m*-fluoro in S_1, which is reversed from the situation in the ground state (σ(*p*-F) = +0.06; σ^+(*p*-F) = −0.25).[6] Studies of the photohydration of substituted styrenes[10b] corroborate this finding. Both *m*- and *p*-methyl groups have somewhat similar σ values (σ(*m*-CH_3) = −0.07; σ(*p*-CH_3) = 0.17)[6] in the ground state, with the *p*-methyl being a slightly better electron donor. However, the results of this study would suggest that *m*-methyl becomes a much better electron donor than *p*-methyl in S_1. Although the mechanism by which the electron-donating effect operates in S_1 is unclear—especially for simple alkyl groups such as methyl, which lack a readily available lone pair of electrons—these results suggest that the meta-selectivity principle,[2] as postulated by Zimmerman and Sandel[3] for the methoxy group, is applicable to many other other substituents.[7] These results are important in the continuing quest for a better understanding of structure–reactivity relationships for photochemical reactions, along the lines well-established for ground-state reactions of substituted benzenes.

Experimental Section

Materials. Methanol, acetonitrile, and acetic acid were reagent grade and used without further treatment. Aqueous H_2SO_4 was used for all the acid-catalysis experiments. Aqueous HCl was avoided due to the possibility of chloride ion quenching or reaction with the photogenerated benzyl cations. For lifetime and fluorescence measurements, the aqueous H_2SO_4 used was purchased prestandardized from Fisher Chemicals. For preparative experiments, aqueous H_2SO_4 was prepared by dilution from concentrated H_2SO_4. Benzyl alcohols 1–4 were purchased from Aldrich and used without further treatment. GC analysis showed these materials to be >98% pure. Authentic samples of the acetate esters of 1–4 were prepared by treatment of the corresponding benzyl alcohols with acetyl chloride in CH_2Cl_2/pyridine. Authentic samples of the methyl ethers of 1-4 were prepared by thermal solvolysis of the corresponding alcohols in MeOH/concentrated H_2SO_4. Typical yields were 30–40%. Authentic samples of the disubstituted bibenzyl products were obtained by photolysis of the corresponding benzyl acetates in CH_3CN (eq 3). Photolysis in aqueous CH_3CN gave, in addition to the disubstituted bibenzyl products, variable amounts of the parent alcohol via photosolvolysis.

$$\mathrm{ArCH_2OAc} \xrightarrow[\mathrm{CH_3CN}]{h\nu} \mathrm{ArCH_2CH_2Ar} \qquad (3)$$

Fluorescence Spectra. Fluorescence emission spectra were recorded on either a Perkin-Elmer MPF 44B or LS-5 instrument. The MPF 44B instrument was coupled to a Houston Instruments flatbed *X–Y* recorder, while the LS-5 was equipped with microcomputer drive. All fluorescence spectra are uncorrected and were taken at ambient temperature (20 ± 2 °C). Solutions (ca. 10^{-4} M) were prepared by injecting a known volume (ca. 50 μL) of the substrate dissolved in pure CH_3CN (via a microlitre syringe) into 3.0-mL solutions of known acidity contained in a 1.00-cm path-length quartz cuvette. After vigorous shaking, the fluorescence spectrum was recorded. No difference in fluorescence efficiency was observed between argon-purged and oxygen-purged solutions of the same acidity. The quantum yields of fluorescence of 1–4 were in the range of 0.05–0.15, using *m*-methoxybenzyl alcohol as reference.[1]

Lifetime Measurements. Fluorescence lifetimes were measured via the method of single-photon counting and via the phase-shift and relative modulation techniques. The method and instrumentation for single-photon counting are identical with those described by us previously.[10] The phase-shift and relative

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(5) Wubbels, G. G. *Acc. Chem. Res.* **1983**, *16*, 285.

(6) Murov, S. "Handbook of Photochemistry"; Marcel Dekker: New York, 1973; p 203.

(7) The nitro group, as an electron-withdrawing group in the excited-state, also appears to possess this "meta-selectivity" (see ref 2 and 8). As for other types of substituents, we have carried out exploratory studies with a number of other substituted benzyl alcohols. With nitrobenzyl alcohols, we discovered some novel photochemistry,[9] which was totally unexpected, but not a "photodehydroxylation". Preliminary studies with chlorobenzyl alcohols are problematic since it appears that aryl–chloro bond cleavage can compete to some extent with photodehydroxylation, at least for the para isomer. Promising results have been obtained for hydroxybenzyl alcohols, as well as the ortho isomers of the compounds studied in this work. These results will be reported in due course.

(8) Cornelisse, J.; Havinga, E. *Chem. Rev.* **1975**, *75*, 353.

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.

Acknowledgment. I thank Professors Keith Yates and Nicholas J. Turro for the use of their respective laboratories, where part of this work as conceived and carried out. Additional thanks are due to Professor Mitchell Winnik for the use of the single-photon counting apparatus. Support of this research by the Natural Sciences and Engineering Research Council of Canada (NSERC) and the University of Victoria is gratefully acknowledged.

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

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(9) Wan, P.; Yates, K. *J. Org. Chem.* **1983**, *48*, 136.

(10) (a) Wan, P.; Culshaw, S.; Yates, K. *J. Am. Chem. Soc.* **1982**, *104*, 2509. (b) Wan, P.; Yates, K. *J. Org. Chem. 1983*, *48*, 869.

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 effects[2] 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.

(1)

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

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)

[a] The 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. [b] The 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.

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 ^{13}C and ^{29}Si. 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]

$$CH_3COCH_3 + \underset{\mathbf{1}}{(CH_3O)_2P(O)CHN_2} + KO\text{-}t\text{-}Bu \rightarrow$$

$$\underset{\mathbf{2}}{[(CH_3)_2C{=}C{:}]} \xrightarrow{Et_3SiH/Et_3SiD} \underset{\substack{\mathbf{3a},\ R\,=\,H \\ \mathbf{3b},\ R\,=\,D}}{(CH_3)_2C{=}C(R)SiEt_3} \quad (2)$$

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

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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(1) Taken in part from the dissertation D.H.G., submitted in partial fulfillment of requirements for the Ph.D. degree.

(2) Kwart, H. *Acc. Chem. Res.* **1982**, *15*, 401.

(3) Gilbert, J. C.; Giamalva, D. H.; Baze, M. E. *J. Org. Chem.*, in press.

(4) Gilbert, J. C.; Butler, J. R. *J. Am. Chem. Soc.* **1970**, *92*, 7493.

(5) Sakakibara, T.; Odaira, Y.; Tsutsumi, S. *Tetrahedron Lett.* **1968**, *4*, 503.

(6) Newman, M. S.; Patrick, T. B. *J. Am. Chem. Soc.* **1970**, *92*, 4312.

(7) Newman, M. S.; Beard, C. D. *J. Am. Chem. Soc.* **1970**, *92*, 4309.

(8) Stang, P. J.; Mangum, M. G.; Fox, D. P.; Haak, P. *J. Am. Chem. Soc.* **1974**, *96*, 4562.

(9) Skell, P. S.; Garner, A. Y. *J. Am. Chem. Soc.* **1956**, *78*, 5430.