

shift is the highest so far known for a neutral organic compound. The general correspondence with the cyclopropane carbon shift, which has been interpreted in terms of ring current induced diamagnetic shielding,<sup>30c</sup>

suggests a similar explanation for nitrogen resonance as well. Whether this is correct or not, the <sup>15</sup>N shifts correspond to the substantial diamagnetic shieldings observed for the <sup>13</sup>C resonances of aziridine.

## Catalytic Mode, Solvent Isotope Effects, and Transition-State Structure in Hydride Expulsion from Silicon<sup>1,2</sup>

Kathleen O'Donnell, Rhonda Bacon, K. L. Chellappa,  
Richard L. Schowen,<sup>\*3</sup> and J. K. Lee

Contribution from the Department of Chemistry, University of Kansas,  
Lawrence, Kansas 66044. Received May 12, 1971

**Abstract:** Triphenylsilane, tribenzylsilane, and tributylsilane are methanolized to hydrogen and the methoxysilanes in a specific methoxide catalyzed reaction ( $\beta > 0.8$  for triphenylsilane,  $> 0.5$  for tribenzylsilane,  $> 0.7$  for tributylsilane in phenol-phenoxide buffers). Deuterated silanes react more slowly by factors of  $1.20 \pm 0.08$ ,  $1.35 \pm 0.09$ , and  $1.40 \pm 0.10$ , respectively. The protiated compounds have  $\Delta G^*_{298} = 18.17 \pm 0.02$ ,  $20.33 \pm 0.02$ ,  $21.89 \pm 0.02$  kcal/mol,  $\Delta H^* = 9.4 \pm 0.3$ ,  $11.4 \pm 0.3$ ,  $12.3 \pm 0.5$  kcal/mol, and  $\Delta S^* = -29.5 \pm 1.8$ ,  $-30.0 \pm 1.8$ ,  $-32.1 \pm 3.2$  gibbs/mol, respectively. For triphenylsilane, the second-order rate constants  $k_n$  in mixtures of  $\text{CH}_3\text{OH}$  and  $\text{CH}_3\text{OD}$  (mole fraction  $n$ ) are given by  $k_n = k_0(1 - n + 0.22n)/(1 - n + 0.76n)^3$ . The transition state strongly resembles a quinquivalent-silicon compound, the Si-H bond being strong and the H-H bond of the product still weak. The absence of a nonbonded electron pair on the leaving group prevents electrophilic assistance by prior-protonation or solvation-catalysis mechanisms, forcing concerted donation of a solvent proton to the hydride in the course of its departure. Proton transfer to this very basic species is little advanced in the transition state so that the reaction is unselective and general acids do not compete with solvent.

Understanding the catalysis of very unfavorable processes is central to development of a comprehensive theory of catalytic action. The hydride ion,  $\text{H}^-$ , is a very poor leaving group because it is extremely basic and because, when bonded, it has no lone pair of electrons for attachment of an acid catalyst to aid its departure. Nevertheless, it is displaced by nucleophiles from silicon centers with simultaneous bonding to a solvent proton to form a hydrogen molecule.<sup>4</sup> The nucleophile must bind tightly to the silicon in order to effect this displacement, as shown by the strong acceleration produced by electron withdrawal at silicon (Hammett  $\rho$  values of  $+2$  to  $+5$ ).<sup>5</sup> Since donation of nucleophile lone-pair electrons into silicon d orbitals could give relative negative charge at silicon even if the leaving group bond is broken considerably, the degree to which the

Si-H bond has been broken and the H-H bond formed in the transition state is not known. The hydride isotope effects,<sup>6</sup>  $k_{\text{SiH}}/k_{\text{SiD}}$  (e.g., 1.15 for triphenylsilane in wet piperidine at 25°), are small compared to the maximum estimated from complete loss of the isotopic zero-point energy in the reactant stretching mode ( $k_{\text{H}}/k_{\text{D}}$  about 4)<sup>7</sup> so that it has been presumed that the transition state is unsymmetrical, i.e., either very reactant-like (strong Si-H, weak H-H) or very product-like (weak Si-H, strong H-H). Kaplan and Wilzbach<sup>6b</sup> suggested that the H-H bond is completely formed on the basis of simple model calculations, but their only "reactant-like" model was hydride-ion-like rather than having a strong Si-H bond. Thornton<sup>8</sup> arrived at the opposite conclusion (strong Si-H bond, weak H-H bond) by estimating the equilibrium isotope effect for complete formation of products as  $K_{\text{H}}/K_{\text{D}} = 1.7$ . If the isotope effect indeed passes smoothly from 1.00 for an exactly reactant-like transition state through a maximum of about 4 for a "symmetrical" transition state and down to 1.7 for an exactly product-like structure, then the observed isotope effect of 1.15, being less than 1.7, could correspond only to a reactant-like structure. The problem with this conclusion is that the assumption of the smooth rise and fall of the isotope effect about

(1) Catalysis in Organosilicon Chemistry. III. For part II, see R. L. Schowen and K. S. Latham, *J. Amer. Chem. Soc.*, **89**, 4677 (1967).

(2) This research was supported by the National Science Foundation and the National Aeronautics and Space Agency (University of Kansas Institutional Grant). Data reduction was carried out at the University of Kansas Computation Center. For further details, see K. O'Donnell, Ph.D. Thesis, University of Kansas, 1968, and R. Bacon, M.S. Thesis, University of Kansas, 1970.

(3) Holder of a Research Career Development Award of the National Institute of General Medical Sciences.

(4) (a) R. L. Schowen and R. Bacon, *Tetrahedron Lett.*, 4177 (1970), demonstrated the bonding of solvent proton to expelled hydride to be concerted with Si-H cleavage. The reaction has long been known. Its fundamental aspects were reviewed in (b) C. Eaborn, "Organosilicon Compounds," Butterworths, London, 1960, Chapter 6.

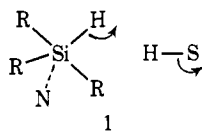
(5) (a) H. Gilman and G. E. Dunn, *J. Amer. Chem. Soc.*, **73**, 3404 (1951); (b) G. Schott and C. Harzdorf, *Z. Anorg. Allg. Chem.*, **306**, 180 (1960); (c) O. W. Steward and O. R. Pierce, *J. Amer. Chem. Soc.*, **83**, 1916 (1961); (d) G. Schott and D. Gutschick, *Z. Anorg. Allg. Chem.*, **325**, 175 (1963); (e) J. Hetflejš, F. Mares, and V. Chvalovsky, *Collect. Czech. Chem. Commun.*, **30**, 1643 (1965); (f) G. Schott, P. Hansen, S. Kuhlá, and P. Zwierz, *Z. Anorg. Allg. Chem.*, **351**, 37 (1967).

(6) (a) L. Kaplan and K. E. Wilzbach, *J. Amer. Chem. Soc.*, **74**, 6152 (1952); (b) L. Kaplan and K. E. Wilzbach, *ibid.*, **77**, 1297 (1955); (c) C. Brynko, G. E. Dunn, H. Gilman, and G. S. Hammond, *ibid.*, **78**, 4909 (1956); (d) L. H. Sommer, D. R. Weyenberg, and P. G. Campbell, Abstracts of the 135th Meeting of the American Chemical Society, Boston, Mass., 1959, p 23M.

(7) The stretching frequencies are  $2120 \text{ cm}^{-1}$  ( $(\text{C}_6\text{H}_5)_3\text{SiH}$ ) and  $1549 \text{ cm}^{-1}$  ( $(\text{C}_6\text{H}_5)_3\text{SiD}$ ), as determined in this work and in agreement with L. Kaplan, *J. Amer. Chem. Soc.*, **76**, 5880 (1954).

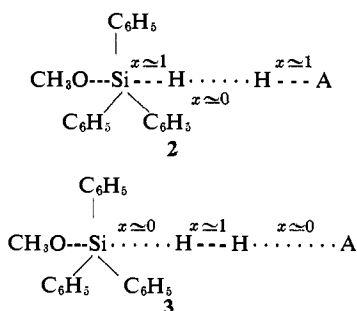
(8) E. R. Thornton, *J. Org. Chem.*, **27**, 1943 (1962).

the "symmetrical" value and the estimated magnitude of the maximum effect derive from a linear, triatomic model of the hydride-transfer transition state.<sup>9</sup> It is possible that the hydride transfer involves a bent transition state (1) because of the absence of a lone pair on



the hydridic hydrogen atom and the affinity of the electrophilic solvent proton for the Si-H  $\sigma$ -bonding electron pair.<sup>10</sup> This will lead to small isotope effects even for "symmetrical" structures, which, as More O'Ferrall has shown, may in fact give smaller isotope effects than "unsymmetrical" structures.<sup>11</sup>

We have used two methods to investigate the state of the leaving group assembly in this reaction. If we assume that bond order at hydrogen is conserved, as shown by agreement of experiment with predictions based on this assumption for hydrogen atom transfers in the gas phase<sup>12</sup> and as observed for proton transfers in solution,<sup>13</sup> then a strong Si-H bond (bond order  $x \simeq 1$ ) and weak H-H bond ( $x \simeq 0$ ) will imply a strong H-A bond ( $x \simeq 1$ ) in the proton donor, as shown in structure 2 for the methanolysis of triphenylsilane. A product-like structure, such as 3, would have a weak H-A bond ( $x \simeq 0$ ). Since structures 2 and 3 corre-



spond to general acid catalysis by HA, the strength of the H-A bond will be measured by the Brønsted coefficient.<sup>14</sup> A value  $\alpha = 1$ , signifying complete dissociation of HA in the transition state, means  $x_{\text{HA}} = 0$ , as in 3, while  $\alpha = 0$  (HA undissociated in the transition state) means  $x_{\text{HA}} = 1$ , as in 2. Thus  $x_{\text{HA}} = 1 - \alpha$ . Now the reaction also involves a methoxide ion, which we are confident is tightly bound (see above), so that the expected kinetic law in methanol solution is that of eq 1, i.e., "kinetic general base catalysis" corresponding to specific base-general acid catalysis. Inserting the Brønsted law,<sup>15</sup>  $k_{\text{HA}} = G_{\text{HA}}K_{\text{HA}}^{\alpha}$ , into eq 1, recalling

$$v/[R_3SiH] = k_{\text{HA}}[CH_3O^-][HA] = k_{\text{HA}}(K_{\text{CH}_3\text{OH}}/K_{\text{HA}})[A^-] = k_A[A^-] \quad (1)$$

(9) F. H. Westheimer, *Chem. Rev.*, **61**, 265 (1961).

(10) E. S. Lewis and M. C. R. Symons, *Quart. Rev., Chem. Soc.*, **12**, 230 (1958).

(11) R. A. More O'Ferrall, *J. Chem. Soc. B*, 785 (1970).

(12) H. S. Johnston, "Gas Phase Reaction Rate Theory," Ronald Press, New York, N. Y., 1966, pp 180, 201-202, 209, 322-332.

(13) C. G. Swain and J. Grunwell, unpublished results.

(14) J. E. Leffer and E. Grunwald, "Rates and Equilibria of Organic Reactions," Wiley, New York, N. Y., 1963, pp 157-159.

(15) R. P. Bell, "The Proton in Chemistry," Cornell University Press, Ithaca, N. Y., 1959, p 155.

that  $K_A = K_{\text{CH}_3\text{OH}}/K_{\text{HA}}$ , and applying the operations of eq 2 show that  $\beta$  for the general base catalyzed reaction

$$k_A = G_{\text{HA}}K_{\text{CH}_3\text{OH}}K^{\alpha-1}_{\text{HA}} = (G_{\text{HA}}K^{\alpha}_{\text{CH}_3\text{OH}})K_A^{1-\alpha} = G_A K_A^{\beta} \quad (2)$$

is just  $1 - \alpha$ . Thus  $\beta$  directly measures  $x_{\text{HA}}$  for the transition state.

Our second technique uses the methoxide-catalyzed reaction in methanol, in the absence of buffer, so that  $A = \text{CH}_3\text{O}^-$  in 2 and 3. Notice that 2 contains no methoxide-like moiety while 3 contains a fully formed methoxide ion ( $A^-$ ). We know from the nmr studies of More O'Ferrall<sup>16</sup> and our own previous work<sup>17</sup> that reactions of methoxide ion to form a transition state in which it is tightly bound and its solvation shell is dispersed will proceed more rapidly in  $\text{CH}_3\text{OD}$  than in  $\text{CH}_3\text{OH}$  by factors up to 2.3. The secondary solvent isotope effect expected for structure 2 is thus  $k_{\text{CH}_3\text{OD}}/k_{\text{CH}_3\text{OH}} = 2.3$ . For structure 3, little or no effect is anticipated since the reactant methoxide ion is completely duplicated in the transition state and solvation effects should cancel. Of course, in order to use this probe we must somehow separate the primary isotope effect of the transferring proton from the secondary effect of the solvating molecules.

In both cases, Brønsted coefficient and secondary solvent isotope effect, intermediate values between the extremes are evidence for intermediate magnitudes of  $x_{\text{HA}}$  in the transition state and thus for structures intermediate between 2 and 3.

## Results

**Kinetics.** Reactions at constant ionic strength of triphenylsilane, tribenzylsilane, and tributylsilane with methanol containing sodium methoxide, to yield hydrogen and the corresponding methoxysilane, eq 3, were



examined kinetically by a titrimetric technique (oxidation of silane by excess iodine and thiosulfate determination of remaining iodine)<sup>18</sup> and by an automatic manometric technique.<sup>19</sup> All reactions obeyed the kinetic law of eq 4, exhibiting first-order kinetics within

$$v = k_M[CH_3O^-][R_3SiH] \quad (4)$$

a run since methoxide was not consumed. Second-order rate constants, obtained from the slopes of plots of observed first-order constants *vs.* methoxide concentration, agreed to within  $\pm 7\%$  between titrimetric and manometric techniques, although determined by three different experimentalists over a 5-year period. Table I contains a compilation of second-order rate constants for protiated and deuterated silanes at various temperatures, measured by the titrimetric technique.

**Activation Parameters.** Table II shows the values of free energy, enthalpy and entropy of activation obtained for the methoxide-catalyzed reactions by least-squares fitting of the  $k_M$  to the Eyring equation.<sup>20</sup> The

(16) R. A. More O'Ferrall, *Chem. Commun.*, 114 (1969).

(17) C. G. Mitton, M. Gresser, and R. L. Schowen, *J. Amer. Chem. Soc.*, **91**, 2045 (1969).

(18) Adapted from the method of H. Westermark, *Acta Chem. Scand.*, **8**, 1086 (1954).

(19) R. Bacon and R. L. Schowen, *Anal. Biochem.*, **41**, 277 (1971).

(20) S. Glasstone, K. J. Laidler, and H. Eyring, "The Theory of Rate Processes," McGraw-Hill, New York, N. Y., 1941, pp 195 ff.

**Table I.** Second-Order Rate Constants for the Methanolysis of 0.01–0.02 *M* R<sub>3</sub>SiH in Methanol at 0.0008–0.1 *M* Sodium Methoxide ( $\mu = 0.100$  *M*)<sup>a</sup>

| R   | L | Temp, <sup>b</sup> °C | 10 <sup>4</sup> <i>k</i> <sub>M</sub> , <sup>c</sup> M <sup>-1</sup> sec <sup>-1</sup> |
|---|---|-----------------------|--|
| C <sub>6</sub> H <sub>5</sub>                 | H | 15.0                  | 1700   |
|   |   | 20.0                  | 2190   |
|   |   | 25.0                  | 2780   |
|   |   | 30.0                  | 4010   |
|   |   | 36.7                  | 5680   |
|   |   | 24.8                  | 2460   |
| C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> | D | 15.0                  | 37.3   |
|   |   | 20.0                  | 52.2   |
|   |   | 27.3                  | 96.5   |
|   |   | 30.3                  | 108  |
|   | H | 35.2                  | 140  |
|   |   | 40.0                  | 194  |
|   |   | 45.2                  | 284  |
|   |   | 25.0                  | 56.1   |
| <i>n</i> -C <sub>4</sub> H <sub>9</sub>       | D | 24.7                  | 5.49   |
|   |   | 35.2                  | 10.2   |
|   |   | 40.0                  | 15.7   |
|   | H | 45.2                  | 24.4   |
|   |   | 63.0                  | 63.0   |
|   |   | 25.0                  | 3.93   |

<sup>a</sup> Ionic strength maintained by added lithium perchlorate. <sup>b</sup> Temperatures are accurate to 0.2° and precise to 0.02°. <sup>c</sup> Standard deviations of the second-order rate constants are ±2–7%.

**Table II.** Activation Parameters for the Methoxide-Catalyzed Methanolysis of R<sub>3</sub>SiH in Methanol<sup>a</sup>

| R   | $\Delta G^*_{298}$ , kcal/mol | $\Delta H^*$ , kcal/mol | $\Delta S^*$ , gibbs/mol |
|---|-------------------------------|-------------------------|--------------------------|
| C <sub>6</sub> H <sub>5</sub>                 | 18.17 ± 0.02                  | 9.4 ± 0.3               | -29.5 ± 1.8              |
| C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> | 20.33 ± 0.02                  | 11.4 ± 0.3              | -30.0 ± 1.8              |
| <i>n</i> -C <sub>4</sub> H <sub>9</sub>       | 21.89 ± 0.02                  | 12.3 ± 0.5              | -32.1 ± 3.2              |

<sup>a</sup> Standard states are 1 *M* in methanol solution for solutes and pure liquid for methanol.

**Table III.** First-Order Rate Constants for the Methanolysis of R<sub>3</sub>SiH in Methanolic Buffers of Phenol and Sodium Phenoxide ( $\mu = 0.100$  *M*)<sup>a</sup>

| R (temp, °C)  | 10 <sup>3</sup> [C <sub>6</sub> H <sub>5</sub> OH], <i>M</i> | 10 <sup>3</sup> [C <sub>6</sub> H <sub>5</sub> ONa], <i>M</i> | 10 <sup>3</sup> [CH <sub>3</sub> ONa], <i>M</i> | 10 <sup>6</sup> <i>k</i> <sub>0</sub> , <sup>b</sup> sec <sup>-1</sup> | 10 <sup>3</sup> <i>k</i> <sub>0</sub> /[CH <sub>3</sub> ONa] |
|---|--|---|---|--|--|
| C <sub>6</sub> H <sub>5</sub> (25.2°)                 | 102.1  | 97.9  | 2.11  | 676  | 320  |
|   | 80.6   | 19.5  | 0.53  | 187  | 352  |
|   | 61.4   | 38.6  | 1.38  | 455  | 329  |
|   | 18.6   | 91.3  | 10.78   | 3490   | 324  |
|   | 11.9   | 43.1  | 7.97  | 2660   | 334  |
|   | 4.62   | 61.5  | 29.3  | 258  | 8.80   |
| C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> (27.3°) | 4.28   | 42.0  | 21.6  | 183  | 8.48   |
|   | 4.12   | 35.5  | 19.0  | 152  | 8.02   |
|   | 3.69   | 22.7  | 13.6  | 115  | 8.47   |
|   | 2.29   | 50.8  | 48.8  | 419  | 8.58   |
|   | 2.21   | 35.0  | 34.8  | 298  | 8.56   |
|   | 2.04   | 19.2  | 20.7  | 169  | 8.18   |
|   | 1.76   | 8.86  | 11.1  | 92   | 8.27   |
|   | 96.2   | 97.8  | 2.23  | 1.52   | 0.680  |
| <i>n</i> -C <sub>4</sub> H <sub>9</sub> (24.7°)       | 60.9   | 81.0  | 2.93  | 1.66   | 0.567  |
|   | 45.0   | 76.3  | 3.73  | 2.08   | 0.558  |
|   | 36.3   | 37.7  | 2.29  | 1.62   | 0.708  |
|   | 29.6   | 92.1  | 6.84  | 3.96   | 0.579  |
|   | 16.4   | 17.6  | 2.37  | 1.60   | 0.676  |
|   | 6.53   | 7.48  | 2.52  | 1.63   | 0.647  |

<sup>a</sup> Ionic strength maintained by added lithium perchlorate. <sup>b</sup> Standard deviations of the rate constants average 2%.

standard states are thus 1 *M* in methanol for solutes and pure liquid for methanol.

**Kinetics in Buffered Solutions.** In Table III are given titrimetric first-order rate constants *k*<sub>0</sub> in phenol-sodium phenoxide buffers. For all three substrates, the quantity 10<sup>3</sup>*k*<sub>0</sub>/[CH<sub>3</sub>ONa] is constant with an average

deviation from the mean of only a few per cent (332 ± 9 for (C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>SiH, 8.4 ± 0.2 for (C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>)<sub>3</sub>SiH, and 0.63 ± 0.05 for (*n*-C<sub>4</sub>H<sub>9</sub>)<sub>3</sub>SiH) showing that the reactions are not subject to general catalysis within the precision of these results. The quantities 10<sup>3</sup>*k*<sub>0</sub>/[CH<sub>3</sub>ONa] differ only a few per cent from the corresponding values of *k*<sub>M</sub> at the same temperature (298 for (C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>SiH, 9.65 for (C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>)<sub>3</sub>SiH, and 0.55 for (*n*-C<sub>4</sub>H<sub>9</sub>)<sub>3</sub>SiH), confirming the absence of a buffer effect.

**Solvent Isotope Effects.** The automatic manometric technique was used to obtain second-order rate constants, *k*<sub>n</sub>, *i.e.*, *k*<sub>M</sub> at mole fraction *n* of CH<sub>3</sub>OD in binary mixtures of CH<sub>3</sub>OH and CH<sub>3</sub>OD. The results are given in Table IV for both (C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>SiH and (C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>SiD.

## Discussion

**Brønsted Coefficient.** The rate of triphenylsilane methanolysis was unaffected to within 3% by sodium phenoxide concentrations as high as 0.1 *M* and was essentially equal to the methoxide-catalyzed rate. This means that the phenoxide catalysis (rate constant *k*<sub>P</sub>[0.1]) amounts to less than 0.03*k*<sub>M</sub>[CH<sub>3</sub>O<sup>-</sup>] or that *k*<sub>P</sub>/*k*<sub>M</sub> < (0.03[CH<sub>3</sub>O<sup>-</sup>]/0.1). The methoxide concentration in the most concentrated buffer was 0.002 *M* so that *k*<sub>P</sub>/*k*<sub>M</sub> < 6 × 10<sup>-4</sup> = 10<sup>-3.22</sup>. Now the Brønsted law (eq 2) can be restated as eq 5, in which *K*<sub>P</sub> = 10<sup>-14.26</sup>

$$k_P/k_M = (K_M/K_P)^\beta \quad (5)$$

for ionization of phenol in methanol<sup>21</sup> and *K*<sub>M</sub> = 10<sup>-18.31</sup> (the autoprotolysis constant of methanol,<sup>22</sup> 10<sup>-16.92</sup>, is corrected by log [CH<sub>3</sub>OH]<sub>pure</sub> = 1.39 to convert it to the dimensions of *K*<sub>P</sub>). Thus for triphenylsilane, from insertion of all values into eq 5, β > 0.8. For tribenzylsilane, a corresponding calculation yields β > 0.5, the lower value arising primarily because only

rather basic buffers were employed. In the case of tri-butylsilane, β > 0.7 is obtained. From the argument above, the bond order *x*<sub>HA</sub> in the transition state is

(21) R. L. Schowen and K. S. Latham, Jr., *J. Amer. Chem. Soc.*, **88**, 3795 (1966).

(22) E. Grunwald and E. Price, *ibid.*, **86**, 4517 (1964).

**Table IV.** Second-Order Rate Constants for the Sodium Methoxide Catalyzed Methanolysis of 0.0307 M (C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>SiL in Binary Mixtures of CH<sub>3</sub>OH and CH<sub>3</sub>OD (Mole Fraction *n*) at 25.00 ± 0.05° (*μ* = 0.100 M)<sup>a</sup>

| <i>n</i> | L | 10 <sup>4</sup> <i>k<sub>n</sub></i> , M <sup>-1</sup> sec <sup>-1</sup> |
|----------|---|--|
| 0.000    | H | 3114 ± 37  |
| 0.000    | D | 2380 ± 135   |
| 0.098    | H | 2959 ± 113   |
| 0.246    | H | 2947 ± 50  |
| 0.297    | D | 2098 ± 67  |
| 0.495    | H | 2755 ± 59  |
| 0.495    | D | 2215 ± 64  |
| 0.653    | H | 2628 ± 39  |
| 0.693    | D | 1601 ± 33  |
| 0.730    | H | 2413 ± 41  |
| 0.818    | H | 2111 ± 46  |
| 0.883    | H | 1936 ± 48  |
| 0.891    | D | 1371 ± 11  |
| 0.982    | H | 1643 ± 21  |
| 0.990    | D | 1156 ± 48  |

<sup>a</sup> Ionic strength maintained by lithium perchlorate.

greater than 0.7–0.8 (certainly greater than 0.5), which clearly favors structure 2.

**Solvent Isotope Effects.** Table IV gives rate constants for methanolysis of triphenylsilane in mixtures of CH<sub>3</sub>OH and CH<sub>3</sub>OD. The observed isotope effects are (in principle) mixtures of secondary solvation isotope effects and primary isotope effects for proton transfer from solvent to departing hydride. The general formula (including both primary and secondary effects) for the rate constant *k<sub>n</sub>* in binary mixed isotopic solvent<sup>23</sup> having mole fraction *n* of deuterium and mole fraction (1 - *n*) of protium in exchangeable positions is given by eq 6. In eq 6, *k<sub>0</sub>* is the rate constant in pure

$$k_n = k_0 \prod_i (1 - n + n\phi_i^*) / (1 - n + n\phi_i^R) \quad (6)$$

protiated solvent (*n* = 0), the index *i* counts all exchangeable hydrogens (including solvent positions) involved in conversion of reactants to transition state, and the  $\phi_i^*$ 's ( $\equiv \{[D]_i/[H]_i\} / \{n/(1-n)\}$ ) are the *isotopic fractionation factors* measuring the deuterium preference of the *i*th position ( $\phi_i^*$  in the transition state,  $\phi_i^R$  in the reactant state) relative to solvent. The  $\phi_i^R$ 's can be measured by an nmr method,<sup>24</sup> by relative solubilities or by other probes of relative affinity for isotopic molecules in solvation sites.<sup>25</sup> The  $\phi_i^*$ 's must be inferred from rate data.

For both transition-state structures 2 and 3 (and all intermediate structures), the reactants are triphenylsilane (for the solvation shell of which all  $\phi_i^R = 1$ ) and methoxide ion (triply solvated, with each  $\phi_i^R = 0.76$ ).<sup>26</sup>

(23) (a) A. J. Kresge, *Pure Appl. Chem.*, **8**, 243 (1964); (b) V. Gold, *Advan. Phys. Org. Chem.*, **7**, 259 (1969).

(24) (a) V. Gold, *Proc. Chem. Soc., London*, 141 (1963); (b) A. J. Kresge and A. L. Allred, *J. Amer. Chem. Soc.*, **85**, 1541 (1963).

(25) E. M. Arnett and D. R. McKelvey in "Solute-Solvent Interactions," J. F. Coetzee and C. D. Ritchie, Ed., Marcel Dekker, New York, N. Y., 1969.

(26) More O'Ferrall<sup>16</sup> has determined from nmr studies that CH<sub>3</sub>OH is preferred over CH<sub>3</sub>OD in a single position of the methoxide ion solvation shell by a factor of 1.32 (i.e.,  $\phi = 0.76$ ). The ion is thus less stable and more reactive in CH<sub>3</sub>OD; reactions in which the solvating methanols are dispersed completely to bulk solvent at the transition state will be faster in CH<sub>3</sub>OD by (1.32)<sup>*m*</sup> where *m* is the solvation number of the reactant methoxide ion. Measurements of  $k_{CH_3OD}/k_{CH_3OH}$  in carbonate and acetate ester reactions with methoxide ion gave values of 1.7–2.1 indicating that *m* = 3 (structurally plausible since CH<sub>3</sub>O<sup>-</sup> has three lone pairs of electrons).<sup>17</sup>

Thus for both structures, the denominator of eq 6 is just (1 - *n* + 0.76*n*).<sup>3</sup>

In the formation of 2, the methoxide ion itself binds tightly to the silicon, one of its solvating methanols becomes (formally) the H—A moiety, and the other two solvating methanols are released to the bulk solution. The latter two methanols will thus have  $\phi_i^* = 1$ . The H—A methanol may give rise to a primary isotope effect for proton transfer, corresponding to an unknown fractionation factor  $\phi_{pri}^*$ . Thus if structure 2 is correct, *k<sub>n</sub>* should be given by eq 7.

$$k_n = k_0(1 - n + \phi_{pri}^*n) / (1 - n + 0.76n)^3 \quad (7)$$

The formation of 3 consists formally of tight binding of the methoxide ion to silicon and extensive donation of a proton to the departing hydride by one of the three original solvating methanols so that a new methoxide ion is generated at the A<sup>-</sup> position. One of the lone pairs of A<sup>-</sup> still points in the direction of the proton and the other two are available for solvation: these sites will be solvated by the remaining two methanol molecules with  $\phi_i^* = 0.76$ . The proton undergoing transfer will again generate an unknown primary isotope effect  $\phi_{pri}^*$ . Thus the numerator of eq 6, applied to structure 3, is (1 - *n* + 0.76*n*)<sup>2</sup>(1 - *n* +  $\phi_{pri}^*n$ ). If structure 3 is correct, the mixed solvent isotope effects should obey eq 8.

$$k_n = k_0(1 - n + \phi_{pri}^*n) / (1 - n + 0.76n) \quad (8)$$

Values of  $\phi_{pri}^*$  required for each transition state structure can be found by noting that  $k_n/k_0 = \phi_{pri}^*/(0.76)^3$  when *n* = 1.00 for structure 2 (eq 7) and  $k_n/k_0 = \phi_{pri}^*/(0.76)$  when *n* = 1.00 for structure 3 (eq 8). From Table IV, *k<sub>0</sub>* = 0.311 for (C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>SiH and *k<sub>1</sub>* = 0.158 for the same compound (brief linear extrapolation to pure CH<sub>3</sub>OD). Therefore, structure 2 requires  $\phi_{pri}^* = 0.22$  (a primary isotope effect  $k_H/k_D$  of  $(\phi_{pri}^*)^{-1} = 4.5$ ) while structure 3 requires  $\phi_{pri}^* = 0.38$  (primary isotope effect  $k_H/k_D = 2.6$ ).

With the requisite values of  $\phi_{pri}^*$  eq 7 and 8 are plotted along with experimental points in Figure 1. The same fractionation factors are also used to construct plots for (C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>SiD.<sup>27</sup> The experiments are quantitatively consistent with the prediction for structure 2 and not consistent with the prediction for structure 3.

**Enthalpy Changes and Transition-State Structure.** The conversion of reactants to transition state requires 9–12 kcal/mol of energy (Table II). Estimation of the equilibrium enthalpy change from bond energies<sup>28</sup> yields  $\Delta H^\circ = -34$  kcal/mol, showing that conversion of transition state to reaction products releases 43–46 kcal/mol of energy. According to Hammond's postulate,<sup>29</sup> such a strongly exothermic process should have a reactant-like transition state if formation of the Si—O bond, cleavage of the Si—H bond, formation of the H—H bond, and cleavage of the H—O bond were all con-

(27) If the rule of the geometric mean (cf. V. Gold, *Trans. Faraday Soc.*, **64**, 2770 (1968); W. J. Albery and M. H. Davies, *ibid.*, **65**, 1059 (1969)) holds, the isotope effects for the transferring hydrogen and solvating methanols should be independent of the hydride isotopic identity. The rule may hold less well in hydrogen-forming reactions than it usually does.<sup>11</sup>

(28) T. L. Cottrell, "The Strengths of Chemical Bonds," 2nd ed, Academic Press, New York, N. Y., 1958, gives *E*(SiH) = 76 kcal/mol, *E*(SiO) = 108 kcal/mol, *E*(OH) = 102 kcal/mol, and *E*(HH) = 104 kcal/mol.

(29) G. S. Hammond, *J. Amer. Chem. Soc.*, **77**, 334 (1955).

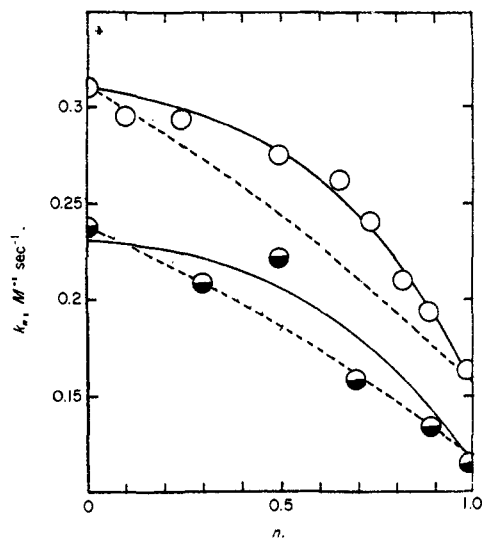


Figure 1. Second-order rate constants for methoxide-catalyzed methanolysis of  $(\text{C}_6\text{H}_5)_3\text{SiH}$  (open circles) and  $(\text{C}_6\text{H}_5)_3\text{SiD}$  (half-filled circles) in binary mixtures of  $\text{CH}_3\text{OD}$  (mole fraction  $n$ ) and  $\text{CH}_3\text{OH}$ . The solid lines are plots of eq 7 with  $\phi^*_{\text{pri}} = 0.22$ ,  $k_0 = 0.311$  for  $(\text{C}_6\text{H}_5)_3\text{SiH}$ , and  $k_0 = 0.230$  for  $(\text{C}_6\text{H}_5)_3\text{SiD}$ . The solid lines thus correspond to transition-state structure 2. The dashed lines plot eq 8 with  $\phi^*_{\text{pri}} = 0.38$ ,  $k_0 = 0.311$  for  $(\text{C}_6\text{H}_5)_3\text{SiH}$  and  $k_0 = 0.238$  for  $(\text{C}_6\text{H}_5)_3\text{SiD}$ , corresponding to transition-state structure 3. Both lines fit the data for  $(\text{C}_6\text{H}_5)_3\text{SiD}$  but the more extensive data set for  $(\text{C}_6\text{H}_5)_3\text{SiH}$  clearly distinguishes the two structures and gives a quantitative fit for 2.

certed with each other. Our data are in fact consistent with a very reactant-like structure in the leaving-group assembly, but the substituent effects indicate extensive formation of the Si–O bond. The clearest stable analog of transition state 2 is thus a quinquevalent-silicon, trigonal-bipyramidal compound.<sup>30</sup> If such a species is a high-energy intermediate in this reaction,<sup>31</sup> the transition state, by Hammond's postulate, should resemble it strongly, as seems to be true. Stereochemical data also favor a geometry for 2 close to the  $\text{sp}^3\text{d}$  structure.<sup>32</sup>

**Hydride Isotope Effects.** The relative rate constants for  $\text{R}_3\text{SiH}$  and  $\text{R}_3\text{SiD}$  ( $1.20 \pm 0.08$  (titrimetric) or  $1.30 \pm 0.09$  (manometric) for triphenylsilane,  $1.35 \pm 0.09$  for tribenzylsilane, and  $1.40 \pm 0.10$  for tributylsilane) are (a) small, confirming the previous work,<sup>6</sup> and (b) insensitive to substituent. The smallness is consistent with a tight Si–H bond as in 2, although if the transition state for hydride transfer is triangular, as in 1, then the effects might not be large for any degree of transfer of the hydride. The insensitivity to substituent may de-

(30) (a) J. E. Ferguson, D. K. Grant, R. H. Hickford, and C. J. Wilkins, *J. Chem. Soc. A*, 99 (1959); (b) C. L. Frye, G. E. Vogel, and J. A. Hall, *J. Amer. Chem. Soc.*, 83, 996 (1961); (c) C. L. Frye, *ibid.*, 86, 3170 (1964); (d) D. I. Cook, R. Fields, M. Green, R. N. Haszeldine, B. R. Isles, A. Jones, and M. J. Newlands, *J. Chem. Soc. A*, 887 (1966); (e) C. L. Frye, G. A. Vincent, and G. L. Hauschildt, *J. Amer. Chem. Soc.*, 88, 2727 (1966); (f) R. Rudman, W. C. Hamilton, S. Novick, and T. D. Goldfarb, *ibid.*, 89, 5157 (1967); (g) F. Klanberg and E. L. Muetterties, *Inorg. Chem.*, 7, 155 (1968); (h) J. W. Turley and F. P. Boer, *ibid.*, 90, 4026 (1968); (i) F. P. Boer, J. W. Turley, and J. J. Flynn, *ibid.*, 90, 5102 (1968); (j) F. P. Boer, J. J. Flynn, and J. W. Turley, *ibid.*, 90, 6973 (1968); (k) J. W. Turley and F. P. Boer, *ibid.*, 91, 4129 (1969); (l) F. P. Boer and J. W. Turley, *ibid.*, 91, 4134 (1969); (m) F. P. Boer and F. P. van Remsortere, *ibid.*, 92, 801 (1970); (n) C. L. Frye, *ibid.*, 92, 1205 (1970).

(31) (a) C. G. Swain, R. M. Esteve, and R. H. Jones, *ibid.*, 71, 965 (1949); (b) L. H. Sommer and D. L. Bauman, *ibid.*, 91, 7045 (1969).

(32) The classical work of Sommer's group is reviewed in L. H. Sommer, "Stereochemistry, Mechanism and Silicon," McGraw-Hill, New York, N. Y., 1965.

rive from this same principle, but even if the transfer is linear, hydride-transfer isotope effects are expected to be less affected by structure changes than proton-transfer isotope effects.<sup>33</sup> The mobile electrons in a hydride transfer are in a bonding molecular orbital and are less polarizable than those in a proton transfer, half of which are in a nonbonding or antibonding orbital.<sup>33</sup>

## Conclusions

The hydride ion, an archetypally poor leaving group, might be thought in serious "need" of electrophilic catalytic assistance.<sup>34</sup> We have found that it does not receive much assistance from electrophiles in its displacement from silicon by methoxide ion although far less basic leaving groups such as methoxide or aryl oxide enjoy easily detectable general catalysis.<sup>35</sup> Instead two factors other than "need" govern the catalytic mechanism. First, proton donation to hydride is concerted with fission of the reactant Si–H  $\sigma$  bond because there is no lone electron pair to serve as a locus for prior protonation or as an organizing site for catalysis by solvation without concurrent proton transfer.<sup>36</sup> Second, the transition state for the concerted proton transfer will have the proton very close to the donor and far from the more basic incipient hydride ion as is expected from proton transfers at carbon<sup>37</sup> and on the basis of the Swain–Thornton reacting bond rule<sup>38</sup> and Hammond's postulate.<sup>29</sup> Thus the Brønsted  $\alpha$  will be very small and general catalysts weak competitors with solvent.

## Experimental Section

**Materials.** Methanol (anhydrous, ACS analyzed reagent from Matheson Coleman and Bell, Baker and Adamson, Fisher Scientific, and J. T. Baker), phenol (analytical reagent, Mallinckrodt), and lithium perchlorate (anhydrous reagent, G. Frederick Smith) were used as obtained. In about one-half the runs, methanol was purified by distillation from magnesium according to Lund and Bjerrum,<sup>39</sup> followed by distillation from benzoic acid. No differences were detectable in rate measurements in purified and unpurified solvents. All unlabeled organosilicon compounds were supplied by Peninsular ChemResearch. Triphenylsilane was recrystallized twice from 95% ethanol (mp 44.5–45.5°, lit.<sup>40</sup> 44–45°); tribenzylsilane (mp 88.5–90°, lit.<sup>41</sup> 90–91°) and tri-*n*-butylsilane (bp 210–215°, lit.<sup>42</sup> 215–220°) were used as obtained without further purification. Methanol-*d* was prepared from dimethyl

(33) C. G. Swain, R. A. Wiles, and R. F. W. Bader, *J. Amer. Chem. Soc.*, 83, 1945 (1961). Insensitivity to substituent is also characteristic of isotope effects in hydride abstraction from silicon by carbonium ions: F. A. Carey and C. L. W. Hsu, *J. Organometal. Chem.*, 19, 29 (1969).

(34) From the data of W. M. Latimer ("Oxidation Potentials," 2nd ed, Prentice-Hall, New York, N. Y., 1952) we can estimate that  $\text{H}^-$  is the conjugate base of an acid ( $\text{H}_2$ ) of  $\text{p}K_a \sim 38$ .

(35) We showed the methanolysis of aryloxysilanes to be general base catalyzed by a protolytic mechanism.<sup>21</sup> This is either proton donation by an acid to the departing aryl oxide or proton removal from an attacking methanol by a base. In the latter case, an acid donates a proton to a departing methoxide ion in the microscopic reverse reaction. Although the average Brønsted slope  $\beta$  is large (0.7) in this reaction, the value for  $\text{CH}_3\text{O}^-$  and  $\text{C}_6\text{H}_5\text{O}^-$  (the bases used here) is only 0.4. Thus phenol is far more competitive with methanol as a catalyst for alkoxide or aryl oxide displacement than for hydride displacement.

(36) C. G. Swain, D. A. Kuhn, and R. L. Schowen, *J. Amer. Chem. Soc.*, 87, 1553 (1965).

(37) R. P. Bell, ref 15, Chapter X.

(38) C. G. Swain and E. R. Thornton, *J. Amer. Chem. Soc.*, 84, 817 (1962); E. R. Thornton, *ibid.*, 89, 2915 (1967).

(39) H. Lund and I. Bjerrum, *Ber.*, 64, 210 (1931).

(40) H. Gilman and H. W. Melvin, Jr., *J. Amer. Chem. Soc.*, 71, 4050 (1949).

(41) J. W. Jenkins, N. L. Lavery, P. R. Guenther, and H. W. Post, *J. Org. Chem.*, 13, 648 (1948).

(42) H. Gilman, D. H. Miles, L. O. Moore, and C. W. Gerow, *ibid.*, 24, 219 (1959).

carbonate according to Streitwieser, Verbit, and Stang.<sup>43</sup> Isotopic analyses were performed by J. Nemeth of Urbana, Ill.

**Triphenylsilane-*d*** was prepared by reduction of chlorotriphenylsilane by lithium aluminum deuteride as described by Gilman and Dunn.<sup>5a</sup>

**Tribenzylsilane-*d***. According to the foregoing procedure for the preparation of the triphenyl compound, lithium aluminum deuteride (0.087 g, 2.07 mmol) and tribenzylchlorosilane (1.33 g, 3.94 mmol) were caused to react, resulting in 1.175 g (3.89 mmol) of crude product and 0.813 g (2.68 mmol, 68%) of pure tribenzylsilane-*d*, mp 87.5–88.5°, ir (CHCl<sub>3</sub>) 1550 cm<sup>-1</sup> (s), near absence of absorption at 2135 cm<sup>-1</sup>.

**Tri-*n*-butylsilane-*d***. According to the same procedure the reaction of 0.228 g (11.1 mmol) of lithium aluminum deuteride and 2.593 g (11.0 mmol) of tri-*n*-butylchlorosilane afforded several milliliters of a clear, colorless liquid product. Distillation through a short-path microassembly gave 1.643 g (8.16 mmol, 74%) of pure tri-*n*-butylsilane-*d*, bp 210–215°, ir (CHCl<sub>3</sub>) 1520 cm<sup>-1</sup> (s), no absorption at 2045 cm<sup>-1</sup>.

**Titrimetric Kinetic Method.** A sampling technique was developed for this investigation which has two major advantages over the usual manometric method: (a) reactions can be studied over a wider temperature range with better temperature control; and (b) much slower reactions can be studied, which greatly increases the number of silanes open to investigation. The main disadvantages are (a) the requirement of a large volume (50–100 ml) of reaction solution; (b) the limited number of samples in single kinetic runs; and (c) only moderately good precision (1–2%) of first-order rate constants. Although these are not generally serious problems, they are undesirable in isotopic work.

Our analytical method for the quantitative determination of silane is an adaptation of an iodimetric technique reported by Westermark.<sup>18</sup> Triorganosilanes react with iodine to form iodosilanes. Thus, by treating the silane with a known excess amount of iodine, the silane concentration can be deduced by titration of the remaining iodine with standard sodium thiosulfate.

(43) A. Streitwieser, Jr., L. Verbit, and P. Stang, *ibid.*, **29**, 3706 (1964).

A 10-ml sample was removed from the reaction flask by pipet and allowed to drain into a 125-ml erlenmeyer flask containing about 3 ml of glacial acetic acid to quench the reaction. In long kinetic runs, an ampoule was removed from a thermostated collection and broken, and the contents were washed with methanol into 3 ml of acetic acid for analysis. About 4 ml of saturated aqueous sodium acetate solution was added as a buffer, and methanol was added to effect solution of any silane precipitate. It was necessary to maintain a delicate balance of methanol and water throughout the analysis to keep both organic and inorganic materials in solution. Iodine was generated *in situ* as triiodide ion by adding first 1 ml of 0.03361 *M* aqueous potassium iodate solution with a tuberculin syringe and then roughly 0.25 g of solid potassium iodide. The flask was heated on a hot plate just to boiling to effect solution and to create an atmosphere of methanol and water above the liquid, stoppered with a cork stopper, and allowed to sit out of direct light to complete the reaction. The reactions of triphenyl-, tribenzyl-, and tri-*n*-butylsilane with iodine required 45, 30, and 15 min, respectively. After the allotted time the stopper was carefully removed to avoid splashing, and the excess iodine was titrated with 0.02681 *M* sodium thiosulfate to the colorless end point. Starch indicator cannot be used in alcoholic solutions because of the decomposition of the starch-iodine complex.

Rate constants were calculated by subjecting the data to a linear least-squares computer program.

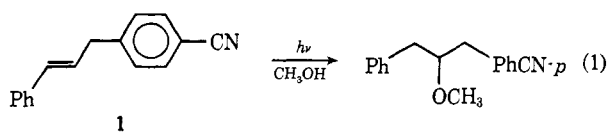
**Manometric Kinetic Method.**<sup>19</sup> A Datametrics Corporation Type 1023 electronic manometer with Barocel pressure sensor, Model 523-11, equipped with solvent shields, was connected to a Heath Model AUW-2 servo-recorder. A flask of methanol was attached to the reference side of the electronic manometer; a two-neck flask with a pressure equalizing pipet in one neck was attached through the other neck to the sample side of the manometer. The sample flask was stirred magnetically and both flasks were immersed in a constant-temperature bath. Substrate stock solution was thermally equilibrated in the sample flask, with catalyst solution in the pipet. Runs were initiated by draining the pipet contents into the sample flask. The apparatus has been fully described elsewhere.<sup>19</sup> Rate constants were treated as above.

## Communications to the Editor

### Excited State Interactions between Nonconjugated Chromophores. Unusual Polar Photochemical Methanol Additions and Reductions in the 1,3-Diarylpropene System

Sir:

Until recently, reported examples of the photochemical addition of methanol to olefins in a polar fashion had been restricted to those cases where the double bond was either contained within a six-eight-membered ring or was conjugated to an electron-withdrawing group or where the addition required the presence of added acid.<sup>1a-d</sup> We have recently reported an unusual exception to these generalities in that 3-(*p*-cyano-phenyl)-1-phenylpropene (**1**) photochemically adds



(1) (a) J. A. Marshall, *Accounts Chem. Res.*, **2**, 33 (1969); (b) S. F. Nelsen and P. J. Hintz, *J. Amer. Chem. Soc.*, **91**, 6190 (1969), and references therein; (c) H. Kato and M. Kawanisi, *Tetrahedron Lett.*, 865 (1970); (d) N. Miyamoto, M. Kawanisi, and H. Nozaki, *ibid.*, 2565 (1971).

methanol in an anti-Markovnikov fashion in the absence of added acid (eq 1).<sup>2</sup> We now report (1) further studies on the photochemical addition of methanol to 1,3-diarylpropenes which provide strong evidence that an interaction between the nonconjugated chromophores comprising these molecules is involved in the addition, and (2) a novel polar photoreduction occurring simultaneously with the addition.

The irradiation<sup>3</sup> of a 0.01 *M* methanol solution of *trans*-3-(*p*-methoxyphenyl)-1-phenylpropene (**2**)<sup>4</sup> was monitored closely by gc and nmr, which revealed a gradual buildup of at least two products along with the transient appearance and disappearance of *cis*-**2** and of small amounts of *cis*- and *trans*-cyclopropanes **3**.<sup>5</sup> Silica gel chromatography of the reaction mixture after all **2** had disappeared provided 21% of a compound whose nmr and ir spectra and gc retention times were identical with those of reduction product **4**,<sup>6</sup> indepen-

(2) S. S. Hixson, *ibid.*, 4211 (1971).

(3) Irradiations were carried out under nitrogen with Vycor-filtered light from a Hanovia 450-W medium-pressure mercury arc.

(4) C. S. Rondstvedt, *J. Amer. Chem. Soc.*, **73**, 4509 (1951).

(5) S. S. Hixson, *ibid.*, **93**, 5293 (1971).

(6) R. Royer, P. Demerseman, J.-P. Lechartier, and A. Cheutin, *J. Org. Chem.*, **27**, 3808 (1962).