problem has been the lack of fundamental information on the molecular biology of the target cells. The basic principles of biology at the molecular level are still not always clear.

Just as in solid-state research, the quickest and most effective way for the organometallic chemist to become effective in this area is to form a partnership with an appropriate biologist (immunologist, radiologist, enzymologist, ...). The collaboration can be very stimulating, but it requires openness on the part of both parties to learn the other's jargon and idiosyncratic thought patterns.

Summary

The role of the organometallic chemist in industry is changing substantially. While the traditional role of providing expertise for design of organometallic and coordination catalysts will remain important, the objectives will shift to production of smaller volume, higher value products such as pharmaceuticals, agrichemicals, and specialty polymers. Attractive opportunities are emerging in organometallic approaches to preparation of sensors, ceramics, and semiconductors.

As the American chemical industry moves toward businesses in health care products and electronic and optical materials, opportunities arise in some relatively unexplored areas of organometallic science. Although the chemical properties of organometallics are well-explored, much less research has been done on the biological and physical properties (e.g., conductivity, magnetism, optical). Work in these new areas will be multidisciplinary in nature. It will require initiative on the part of the organometallic chemist to work effectively with ceramists, physicists, and molecular biologists. In general, the effort required to establish such collaborations will be rewarded with new opportunities in both fundamental science and applied technology.

It is clear that the future of organometallic chemistry in industry is not a simple extrapolation of past trends. The chemical industry is changing character rapidly, and organometallic chemistry is strongly affected. The future appears bright for those willing to grasp the opportunities presented by these changes.

Photolysis of Acylpolysilanes Containing α-Hydrogens. Formation of Linear Head-to-Head Silene Dimers

Kim M. Baines and A. G. Brook*

Lash Miller Chemical Laboratories, Department of Chemistry, University of Toronto, Toronto M5S 1A1, Canada

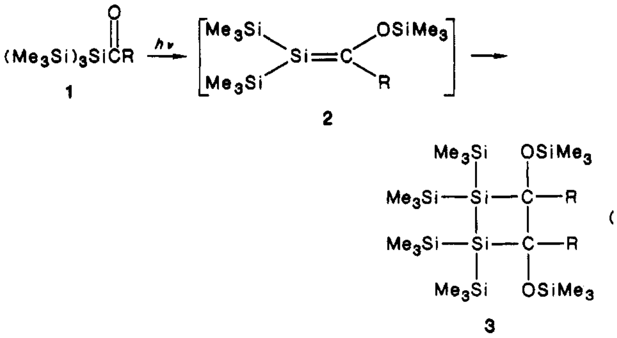
Received October 27, 1986

The photolysis of a series of acylpolysilanes, $(Me_3Si)_3SiCOR$ (R = CH_2CH_3, $CH(CH_3)_2$, CH_2Ph (**1b–d**)), containing α-hydrogens has been investigated. The photoproducts, linear (**4b–d**) and cyclic (**3c,d**) head-to-head dimers of the intermediate silenes $(Me_3Si)_2Si{=}C(OSiMe_3)R$, were fully characterized by IR and ^1H, ^{13}C, and ^{29}Si NMR spectroscopy and mass spectrometry.

Introduction

The chemistry of silenes has been a very active area of research over the last 20 years;[1] however, only recently has the isolation and characterizations of solid, stable silenes been accomplished.[2] Most often, the existence of silenes as reactive intermediates has been proven by the isolation and characterization of their trapping products. Alcohols (e.g. methanol) or dienes (e.g. 2,3-dimethylbutadiene) trap silenes cleanly and in high yield and thus have been used frequently for this purpose.[1] In the absence of trapping reagents, the common fate of these reactive species is head-to-tail dimerization to give 1,3-disilacyclobutanes. Again, this reaction proceeds cleanly and in high yield and thus has also been used as proof of an intermediate silene.[1]

Silenes, derived from the photolysis of acyltris(trimethylsilyl)silanes, are unusual since they consistently undergo head-to-head dimerization in the absence of a trapping reagent to give 1,2-disilacyclobutanes (eq 1).[3]



(1)

A second type of head-to-head dimer has been observed when the intermediate silene contains α-hydrogens in the R group. Thus, when acetyltris(trimethylsilyl)silane (**1a**, R = Me) was photolyzed in inert solvent, a linear

---

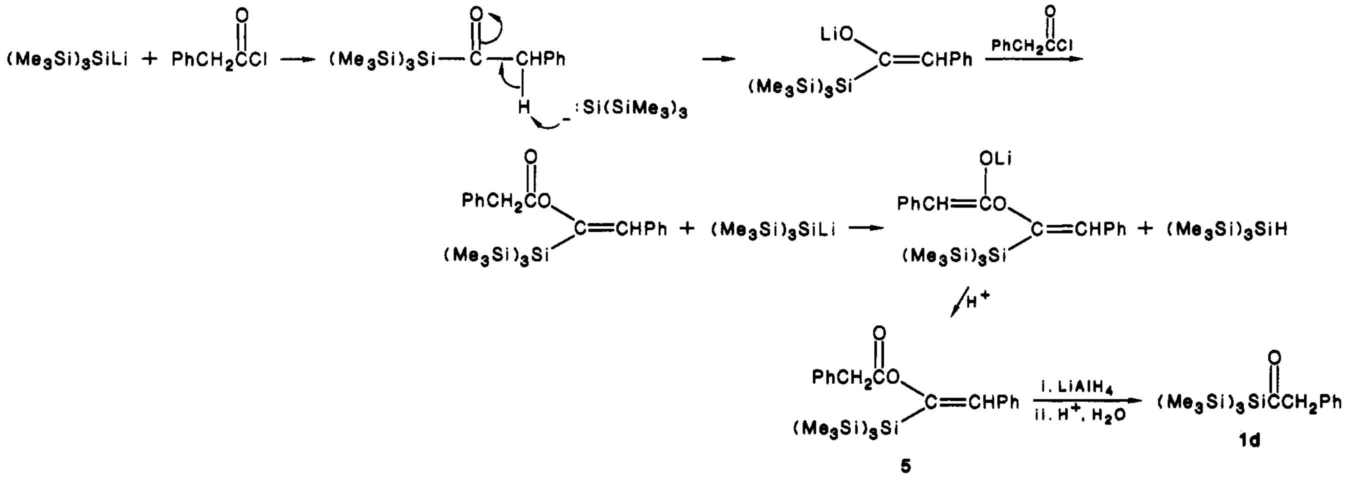
(1) For recent reviews see: (a) Brook, A. G.; Baines, K. M. *Adv. Organomet. Chem.* **1986**, *25*, 1. (b) Raabe, G.; Michl, J. *Chem. Rev.* **1985**, *85*, 419. (c) Wiberg, N. *J. Organomet. Chem.* **1984**, *273*, 141.

(2) (a) Brook, A. G.; Nyburg, S. C.; Abdesaken, F.; Gutekunst, B.; Gutekunst, G.; Kallury, R. K. M. R.; Poon, Y. C.; Chang, Y.-M.; Wong-Ng, W. *J. Am. Chem. Soc.* **1982**, *104*, 5667. (b) Nyburg, S. C.; Brook, A. G.; Abdesaken, F.; Gutekunst, G.; Wong-Ng, W. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1985**, *C41*, 1632. (c) Wiberg, N.; Wagner, G.; Muller, G. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 229. (d) Wiberg, N.; Wagner, G. *Chem. Ber.* **1986**, *119*, 1455. (e) Wiberg, N.; Wagner, G. *Chem. Ber.* **1986**, *119*, 1467.

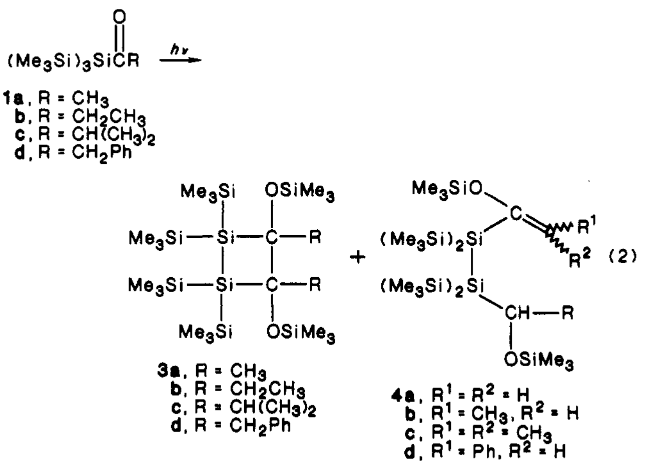
(3) (a) Brook, A. G.; Harris, J. W.; Lennon, J.; El Sheikh, M. *J. Am. Chem. Soc.* **1979**, *101*, 83. (b) Brook, A. G.; Kallury, R. K. M. R.; Poon, Y. C. *Organometallics* **1982**, *1*, 987.

0276-7333/87/2306-0692$01.50/0 © 1987 American Chemical Society

Scheme I



"disproportionated"[4] head-to-head dimer, **4a**, was obtained[3a,5] (eq 2). This type of dimer has also been observed by Barton.[6]



In the present study, the photolysis of a series of acyltris(trimethylsilyl)silanes (**1**) containing α-hydrogens in the acyl group (i.e. R = CH_2CH_3, $CH(CH_3)_2$, CH_2Ph) was investigated in order to determine the generality of this linear dimerization process.

Results and Discussion

The syntheses of the acylpolysilanes **1b**,**c** were straightforward with only minor modifications being made to the published general procedure.[3] Application of the same methodology, in an attempt to synthesize the acylpolysilane **1d**, R = CH_2Ph, resulted instead in the isolation of the enol ester **5** as well as tris(trimethylsilyl)silane in a 1/2 ratio. A reasonable mechanism for the formation of this compound is given in Scheme I. Reduction of the ester moiety of the enol ester **5** regenerated the enolate of the acylsilane which, after workup under acidic conditions, gave the desired product.

Photolysis of the propionylsilane **1b** in inert solvent (eq 2) resulted in clean conversion to the expected linear dimers **4b**. The geometric isomers obtained could not be separated easily and thus were analyzed as a mixture and identified by using IR and ^1H, ^{13}C, and ^{29}Si NMR spectroscopy as well as mass spectrometry. The infrared spectrum showed a characteristic C=C stretch at 1604 cm^{-1}. The ^{13}C NMR spectrum of the dimer mixture contained resonances characteristic of the sp^2-hybridized carbons of a silyl enol ether moiety at 155.00, 156.92 and 115.94, 118.00 ppm[7] as well as those of a siloxy-substituted carbon at 71.27 and 70.93 ppm. Twelve different methylsilyl carbons were observed as expected for two geometric isomers having two different siloxy groups and two pairs of diastereotopic trimethylsilyl groups each. Finally, the ^{13}C NMR spectrum contained two methylene carbons and four different methyl signals between 14 and 33 ppm. Two of the methyl signals could be assigned to (1) the methyl of an ethyl group and (2) a vinylic methyl group (14.26 and 17.95 ppm, respectively) by heteronuclear 2D chemical shift correlation NMR spectroscopy. The remaining signal cross sections could not be resolved. The ^{29}Si NMR spectrum was also consistent with the proposed structures. Thus, again due to two isomers, there were four different trimethylsiloxy resonances ranging from 13.5 to 14.5 ppm, six different silyl-substituted trimethylsilyl resonances ranging from −10.9 to −12.3 ppm, and four resonances characteristic of silicons attached to three other silicons (−63.0 to −77.9 ppm). The chemical shift ranges of these three different types of silicons are consistent with other model compounds.[8] The ^1H NMR spectrum of the mixture of isomers was fairly difficult to interpret. There were 9 different methylsilyl signals, three of which represented two accidentally equivalent trimethylsilyl groups each, as well as two quartets (5.36 and 5.00 ppm (J = 7.01 and 7.03 Hz, respectively)) and two doublets (1.68 and 1.59 ppm (J = 7.01 and 7.03 Hz, respectively)) representing the vinylic hydrogens and the vinylic methyl groups, respectively. The remaining hydrogens (CH_3CH_2CH–) are part of two superimposed ABC_3X spin systems that could not be fully analyzed due to their overlap.

Photolysis of the isobutyrylsilane **1c** in inert solvent again led to a mixture of dimers. However, in this case, both a cyclic head-to-head dimer, **3c**, and a linear "disproportionated" dimer, **4c**, were obtained. The linear dimer could not be separated from the cyclic dimer, but the cyclic dimer could be obtained pure by successive recrystallizations. The spectral characteristics of the linear dimer were totally consistent with the proposed structure. The 1,2-disilacyclobutane, presumably with a trans orientation of the alkyl groups by analogy with the *tert*-bu-

---

[4] The diradical ($-Si(SiMe_3)_2-\dot{C}(OSiMe_3)R)_2$ has been proposed as an intermediate in the dimerization of 1,1-bis(trimethylsilyl)-2-(trimethylsiloxy)-1-silaethenes. When R = Me, this diradical may undergo intramolecular disproportionation yielding the observed linear dimer **4a**.[3a,5]

[5] Brook, A. G.; Harris, J. W. *J. Am. Chem. Soc.* **1976**, *98*, 3381.

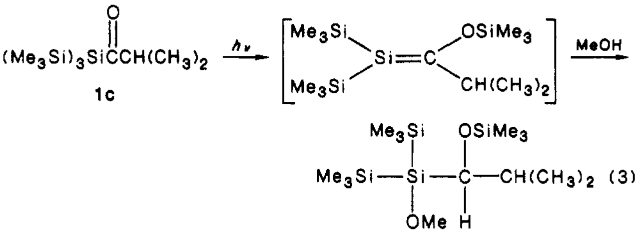
[6] Barton, T. J.; Hoekman, S. K. *J. Am. Chem. Soc.* **1980**, *102*, 1584.

[7] (a) Baigrie, L. M.; Lenoir, D.; Seikaly, H. R.; Tidwell, T. T. *J. Org. Chem.* **1985**, *50*, 2105. (b) House, H. O.; Prabhu, A. V.; Phillips, W. V. *J. Org. Chem.* **1976**, *41*, 1209.

[8] Marsmann, H. *NMR: Basic Princ. Prog.* **1981**, *17*, 65.

tyl-substituted cyclic dimer,[9] could be easily identified from a comparison of its spectral data with the data of other known 1,2-disilacyclobutanes of similar structure.[3b] The most characteristic feature of these ring systems is the chemical shift of the ring carbon (106.16 ppm) and the ring silicon (−47.48 ppm). The presence of diastereotopic methyl groups in the isopropyl groups is further evidence of the head-to-head structure. Due to symmetry, all the isopropyl methyl groups in a head-to-tail dimer would be magnetically equivalent, thus giving one NMR signal. The cyclic dimer isolated in this case has two different methyl groups, seen in both the ^1H and ^{13}C NMR spectra.

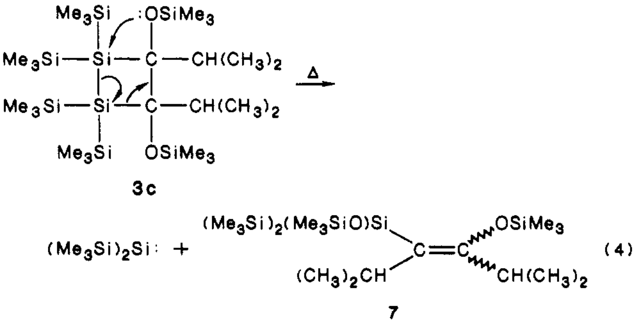
Cophotolysis of the isobutyrylsilane **1c** and methanol gave the expected trapping products of the postulated intermediate silene. The methanol adduct **6** was readily identified by ^1H NMR spectroscopy and by a comparison of its ^1H NMR spectrum with those of analogous compounds.[3a]



1c

6

The 1,2-disilacyclobutanes obtained previously from head-to-head dimerization of the 1,1-bis(trimethylsilyl)-2-(trimethylsiloxy)-1-silaethenes fall apart readily at room or reflux temperature in THF containing methanol to give their corresponding methanol adducts.[3] The thermal stability of the new cyclic isopropyl-substituted dimer was also investigated. Surprisingly, when dimer **3c** was refluxed for 140 h in C_6D_6 in the presence of methanol, the corresponding methanol adducts were not obtained, and instead the alkene **7** (see eq 4) was isolated as well as some unreacted starting material. The same alkene was the only product isolated from a preparative gas chromatography column while attempting to separate the cyclic and linear dimer mixture obtained from the photolysis of the isobutyrylsilane. A mechanism for its formation that involves the expulsion of a silylene, for which some analogy exists,[10] can be postulated (see eq 4). No product derived from



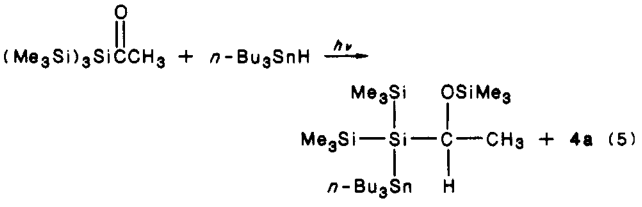
3c

7

the bis(trimethylsilyl)silylene was found. Thus, it appears that when the steric demands of the R group are decreased, the tendency for the 1,2-disilacyclobutane ring to dissociate back to a monomer also diminishes.

Photolysis of the (phenylacetyl)silane **1d** in inert solvent also gave a mixture, this time with three components: the two geometric isomers of the expected linear dimer that were analyzed as a mixture and a cyclic head-to-head dimer, again presumably the trans isomer.[9] The hydrogens at the saturated ends of the linear dimers (i.e. $PhCH_2CH$) constituted two ABX spin systems in the ^1H NMR spectrum; however, in this case, the two spin systems were well-resolved and could be fully analyzed. Interpretation of the remaining spectral data of the dimers was straightforward.

The linear "disproportionated" dimers formed by the silenes studied could be the result of an intermolecular "ene" reaction between two silene molecules (pathway A, Scheme II) or a radical dimerization pathway involving two molecules of silene[3a] (pathway B, Scheme II). An attempt was made to ascertain whether the dimerization pathway involves diradicals by conducting the photolysis of acetyltris(trimethylsilyl)silane (**1a**) in the presence of 1 or 15 equiv of tri-*n*-butyltin hydride, an effective radical trap;[13] however, the results were not definitive. While the tin hydride added to the silene regiospecifically in accordance with a radical mechanism (i.e. hydrogen to carbon and n-Bu_3Sn to silicon of the silene double bond, as shown by NMR spectroscopy), in each case, the linear "disproportionated" dimer **4a** was also formed. No



8

products related to the trapping of an intermediate diradical and no hexabutylditin were detected. Further work is currently underway in this laboratory investigating the mechanism of silene dimerization as well as other [2 + 2] cycloaddition reactions.

The current results clearly show that silenes, derived from the photolysis of acylsilanes, with nonbulky R groups containing α-hydrogens (R = CH_3, CH_2CH_3) exclusively form linear head-to-head dimers, but as the steric bulk of the R group increases, or the number of α-hydrogens decreases, there is an increasing tendency to form cyclic 1,2-disilacyclobutane-type dimers (R = $CH(CH_3)_2$, CH_2Ph) as also observed when the silene contains no α-hydrogens (e.g. R = $C(CH_3)_3$, Ph, etc.).[3]

Experimental Section

All reactions were carried out in oven-dried glassware under an atmosphere of dry argon. Solutions were transferred with syringes. THF and Et_2O were distilled from the sodium ketyl of benzophenone, pentanes and benzene (C_6D_6/C_6H_6) were distilled from $LiAlH_4$, and MeOH was distilled from magnesium methoxide prior to use. MeLi was obtained from Aldrich Co.. The acid chlorides were prepared by reaction of the corresponding carboxylic acids with thionyl chloride and distilled prior to use. NMR spectra were recorded on a Varian CFT-20, XL-200, or XL-400 or Bruker WP-80 spectrometer by using deuteriated benzene as a solvent unless otherwise noted. The standards used are as follows: residual C_6D_5H, δ 7.15 for ^1H NMR spectra; C_6D_6, central transition, δ 128.00 for ^{13}C NMR spectra; Me_4Si as an external standard, δ 0.00 for ^{29}Si NMR spectra. IR spectra were measured by using a Nicolet 5DX FT instrument, and mass spectra were recorded by using a Du Pont 21-490 mass spectrometer. Elemental analyses were performed by Galbraith Laboratories Inc., Knoxville, TN.

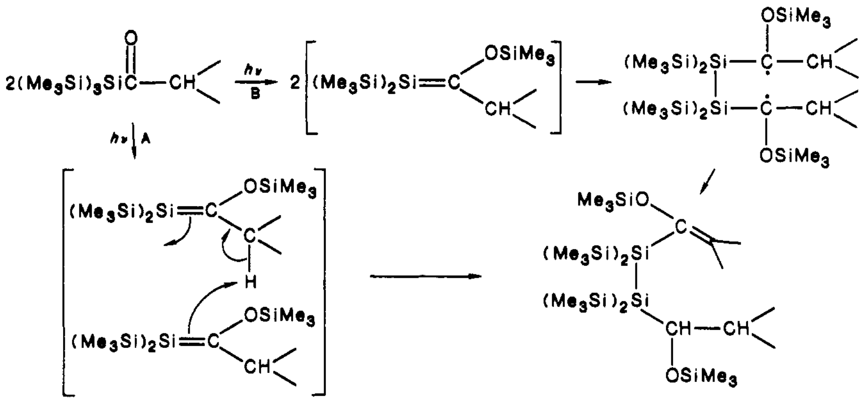
Photolyses were carried out by using two to four 100-W Par38 mercury spot lamps (Blak-Ray, Ultraviolet Products Inc., λ > 360 nm). Sample solutions were photolyzed under an atmosphere of

---

[9] Brook, A. G.; Nyburg, S. C.; Reynolds, W. F.; Poon, Y. C.; Chang, Y.-M.; Lee, J.-S.; Picard, J.-P. *J. Am. Chem. Soc.* **1979**, *101*, 6750.

[10] Brook, A. G.; Chatterton, W. J.; Sawyer, J. F.; Hughes, D.; Vorspohl, K. *Organometallics*, in press.

Scheme II



argon in Pyrex Schlenk or NMR tubes immersed in a cold water bath (10–15 °C).

Synthesis of Acylsilanes.[11] In a typical procedure, MeLi (17 mL, 25 mmol) in Et_2O was added to a solution of $Si(SiMe_3)_4$ (8.05 g, 25 mmol) in THF (110 mL). The mixture was left to stir overnight at room temperature. The yellow silyllithium reagent solution was then transferred via syringe to a dropping funnel and added dropwise to a dry ice/acetone cooled solution of propionyl chloride (2.4 mL, 28 mmol) in pentanes (100 mL). The reaction mixture, protected from light, was stirred in the cold 30 min and then was warmed to room temperature and stirred for 3 h. The reaction was worked up under acidic conditions, and the product was purified by using chromatography (70/30 hexanes/CH_2Cl_2; silica gel).

Propionyltris(trimethylsilyl)silane (1b): colorless semisolid; yield 72%; mp 96–99 °C; ^1H NMR δ 0.22 (s, 27 H, Me_3Si), 0.93 (t, 3 H, CH_3, J = 7.2 Hz), 2.47 (q, 2 H, CH_2, J = 7.2 Hz); ^{13}C NMR δ 1.31 (Me_3Si), 6.93 (CH_3), 48.52 (CH_2), 241.91 (C=O); ^{29}Si NMR δ -12.00 ($SiMe_3$), -75.80 (Si); IR (Nujol) 1636 cm^{-1} (C=O); MS M^+ 304.1515, $C_{12}H_{32}Si_4O$ requires 304.1530.

Isobutyryltris(trimethylsilyl)silane (1c): colorless solid; yield 54%; mp 156–158 °C; ^1H NMR δ 0.26 (s, 27 H, Me_3Si), 0.93 (d, 6 H, CH_3, J = 6.7 Hz), 2.77 (sept, 1 H, CH, J = 6.9 Hz); ^{13}C NMR δ 1.52 (Me_3Si), 16.81 (CH_3), 49.78 (CH), 245.75 (C=O); ^{29}Si NMR δ -11.69 (Me_3Si), -76.53 (Si); IR (Nujol) 1632 cm^{-1} (C=O); MS, *m/e* (relative intensity) 303 (M^+ – Me, 14), 247 (M^+ – Me_2CHCO, 41).

2-Phenyl-1-(tris(trimethylsilyl)silyl)ethenyl phenylacetate (5): pale yellow oil; yield 60%; ^1H NMR δ ($CDCl_3$) 0.26 (s, 27 H, Me_3Si), 3.64 (s, 2 H, CH_2), 6.31 (s, 1 H, vinylic CH), 7.10–7.26 (m, 5 H, Ph); ^{13}C NMR ($CDCl_3$) δ 2.13 ($SiMe_3$), 43.13 (CH_2), 154.32, 169.19 (C=O and OC=), 128.07, 128.14, 129.22, 129.30, 129.51, 130.70, 133.40, 134.15, 135.82 (phenyl and vinylic carbons); ^{29}Si NMR ($CDCl_3$) δ -11.88 (Me_3Si), -75.45 (Si); IR (neat) 1743 cm^{-1} (C=O); MS, *m/e* (relative intensity) 469 (M^+ – Me, 2), 411 (M^+ – Me_3Si, 33).

Preparation of (Phenylacetyl)tris(trimethylsilyl)silane (1d). $LiAlH_4$ (220 mg) was added to a solution of **5** (3.5 g, 7.2 mmol) in Et_2O (75 mL). The resulting mixture was refluxed for 2 h and then poured slowly into 100 mL of a 5 M HCl–ice solution. After workup the acylsilane was purified by using chromatography (50/50 hexanes/CH_2Cl_2; silica gel): pale yellow-green oil; yield 68%; ^1H NMR δ 0.23 (s, 27 H, Me_3Si), 3.83 (s, 2 H, CH_2), 7.10 (b s, 5 H, Ph); ^{13}C NMR δ 1.30 (Me_3Si), 60.93 (CH_2), 126.87, 128.56, 130.15, 133.75 (phenyl), 238.90 (C=O); ^{29}Si NMR δ -11.81 ($SiMe_3$), -72.72 (Si); IR (neat) 1642 cm^{-1} (C=O); MS, *m/e* (relative intensity) 293 (M^+ – Me_3Si, 2).

Photolyses of Acylsilanes. In a typical procedure, a solution of propionyltris(trimethylsilyl)silane (**1b**) (300 mg) in C_6H_6 (2 mL) was photolyzed for 3 h. The yield of the photoproducts **4b** (*E* and *Z* isomers) was >95%, and the ratio of the geometric isomers was 54/46 as determined by ^1H NMR spectroscopy. The mixture of isomers was isolated in 50% yield after removal of the solvent and purification by chromatography (cyclohexane; silica gel).

4b (mixture of geometric isomers):[12] ^1H NMR δ 0.23, 0.27, 0.399, 0.402, 0.407, 0.414, (s, Me_3Si), 0.21, 0.395, 0.44 (s, 2 Me_3Si), 1.59 (d, CH_3C=, J = 7.03 Hz), 1.68 (d, CH_3C=, J = 7.01 Hz), 5.00 (q, HC=, J = 7.03 Hz), 5.36 (q, HC=, J = 7.01 Hz), 1.78–2.20 (AB part), 4.24–4.33 (X part), 1.09, 1.10 (C part, of two superimposed ABC_3X spin systems (CH_3CH_2CH)); ^{13}C NMR δ 1.04, 1.59, 1.65, 2.60, 2.73, 2.74, 2.78, 2.84, 3.20, 3.31, 3.60, 3.62 (Me_3Si), 14.03, 14.15 (CH_3), 14.26 ($\mathit{C}H_3CH_2$), 17.95 ($\mathit{C}H_3CH$=), 32.55, 32.56 (CH_2), 70.93, 71.27 ($\mathit{C}HOSiMe_3$), 115.94, 118.00 (=$\mathit{C}HCH_3$), 155.00, 156.92 (=$\mathit{C}(OSiMe_3)Si$); ^{29}Si NMR δ 13.55, 14.26, 14.39, 14.46 ($OSiMe_3$), –10.90, –11.46, –11.52, –11.91, –12.12, –12.30 ($SiMe_3$), –62.98, –63.56, –71.12, –77.93 ($\mathit{Si}Si_3$); IR (neat) 1604 cm^{-1} (C=C); MS, *m/e* (relative intensity) 305 ($[CH_3CH_2CH(OSiMe_3)Si(SiMe_3)_2]^+$, 16), 131 ($[CH_3CH_2CH(OSiMe_3)]^+$, 38), 73 ($[Me_3Si]^+$, 100).

Photolysis of Isobutyrylsilane 1c. Photolysis of **1c** under the usual conditions gave a cyclic to linear dimer ratio of 76/24 as determined by ^1H NMR spectroscopy. The cyclic dimer **3c** was purified by successive recrystallizations from acetone.

4c:[12] ^1H NMR δ 0.23, 0.26, 0.38, 0.44, 0.46, 0.48 (s, Me_3Si), 1.16, 1.14 (d, $C\mathit{H}_3CH$), 1.96 (m, CH), 1.64, 1.79 (s, CH_3C=), 4.39 (d, $C\mathit{H}OSiMe_3$); ^{13}C NMR δ 1.91, 2.80, 3.37, 3.56, 4.09 (Me_3Si), 18.55, 23.92 ($CH(\mathit{C}H_3)_2$), 20.86, 27.29 (($\mathit{C}H_3)_2C$=), 35.40 ($\mathit{C}H(CH_3)_2$), 75.17 ($\mathit{C}HOSiMe_3$), 124.23 (=$\mathit{C}(CH_3)_2$), 148.58 (=$\mathit{C}(OSiMe_3)Si$); ^{29}Si NMR δ 12.84, 13.87 ($OSiMe_3$), –10.80, –10.85, –11.78 ($SiMe_3$), –64.05, –72.32 ($\mathit{Si}Si_3$); IR (Nujol) 1605 cm^{-1} (C=C).

3c: white crystalline solid; mp 159.5–161 °C; ^1H NMR δ 0.34, 0.41, 0.44 (s, $SiMe_3$), 1.130, 1.135 (d, CH_3), 2.53 (m, CH); ^{13}C NMR δ 3.82, 3.98, 5.79 ($SiMe_3$), 19.87, 23.48 (CH_3), 34.73 (CH), 106.16 (ring C); ^{29}Si NMR δ 1.27 ($OSiMe_3$), –12.35, –13.48 ($SiMe_3$), –47.48 (ring Si); IR (KBr disk) 2957 (s), 2894 (m), 1252 (s), 1243 (s), 835 (s), 1051 (s) cm^{-1}; MS, *m/e* (relative intensity) 348 ($[((Me_3Si)_2Si)_2]^+$, 23), 73 ($[Me_3Si]^+$, 100). Anal. Calcd for $C_{26}H_{68}Si_8O_2$: C, 48.99, H, 10.75. Found: C, 49.12; H, 10.60.

Photolysis of (Phenylacetyl)silane 1d. The yield of the photoproducts **3d** and **4d** was >95%, the ratio of **3d**/**4d** (cyclic/linear dimer) was 20/80, and the ratio of the geometric isomers of the linear dimer was 62/38, all determined by ^1H NMR spectroscopy. The linear dimers could be separated from the cyclic dimer by preparative thin-layer chromatography (pentanes; silica gel).

4d (mixture of geometric isomers):[12] colorless oil; ^1H NMR δ –0.122, –0.116, 0.00, 0.24, 0.28, 0.36, 0.46, 0.50 (s, $SiMe_3$) 0.51 (s, representing four Me_3Si groups, i.e. two coincidental pairs of unresolved diastereotopic $SiMe_3$ groups), 6.25, 6.65 (s, =CH), 7.03–7.33 (m, phenyl), the remaining hydrogens (CH_2CH) form two superimposed ABX spin systems (system "A", H_A, 3.48, H_B, 3.15, H_X, 4.87 ppm, J_{AB} = (–)14.69, J_{AX} = 0.81, J_{BX} = 11.69 Hz; system "B", H_A, 3.34, H_B, 3.17, H_X, 4.87 ppm, J_{AB} = (–)16.50, J_{AX} = 0.42, J_{BX} = 11.60 Hz); ^{13}C NMR δ 1.45, 1.51, 2.27, 2.91, 2.99,

---

[11] The acylsilanes **1b–d** decomposed after a few days in air and did not give satisfactory elemental analyses even when mailed to the analyst in sealed vials under argon. Compound **1b** could be analyzed by high resolution MS, but **1c**,**d** lacked molecular ions.

[12] The linear dimer **4c** could not be obtained pure and therefore was not analyzed. The linear dimers **4b** and **4d** were mixtures of geometric isomers that slowly decomposed in the air. Due to lack of molecular ions these compounds could not be analyzed by high-resolution MS.

[13] (a) Franz, J. A.; Alnajjar, M. S.; Barrows, R. D.; Kaisaki, D. L.; Camaioni, D. M.; Suleman, N. K. *J. Org. Chem.* **1986**, *51*, 1446. (b) Neumann, W. P. In *The Organic Chemistry of Tin*; Wiley: London, 1970.

3.03, 3.33, 3.53, 3.59 (Me_3Si), 46.19, 46.83 (CH_2), 69.14, 70.11 ($\mathit{C}HOSiMe_3$), 157.30, 159.97 ($=\mathit{C}(OSiMe_3)Si$), 125.98, 126.82, 126.76, 129.69, 129.80, 130.11, 130.29, 137.74, 137.99, 141.39, 141.54 (phenyl and remaining vinylic carbons, some signals obscured by C_6D_6); ^{29}Si NMR δ 14.92, 15.00, 15.72, 16.45 ($OSiMe_3$), −11.24, −11.33 (double intensity), −11.48, −11.90, −12.66 ($SiMe_3$), −59.06, −59.50, −68.77, −72.33 ($\mathit{Si}Si_3$); IR (neat) 1603 cm^{-1} (C=C); MS, *m/e* (relative intensity) 367 ($[PhCH_2CH(OSiMe_3)Si(SiMe_3)_2]^+$, 76), 191 ($[Me_3SiOC{=}CHPh]^+$, 20).

3d: white solid; mp 216–218 °C; ^1H NMR δ 0.06, 0.16, 0.58 (s, $SiMe_3$), CH_2 (AB spin system) (H_A, 3.65, H_B, 3.71 ppm, J_{AB} = (−)19.05 Hz), 7.00–7.53 (m, phenyl); ^{13}C NMR δ 2.59, 3.56, 3.95 ($SiMe_3$), 41.19 (CH_2), 93.09 (ring C), 126.10, 128.68, 130.01, 140.37 (phenyl); ^{29}Si NMR δ 6.69 ($OSiMe_3$), −10.67, −12.02 ($SiMe_3$), −48.29 (ring Si); IR (KBr disk) 2952 (m), 2895 (m), 3026 (w), 3061 (w), 1250 (m), 1261 (m), 837 (s), 1045 (s) cm^{-1}; MS, *m/e* (relative intensity) 384 ($[((Me_3SiO)(PhCH_2)C)_2]^+$, 3), 366 ($[(Me_3Si)_2Si{=}C(OSiMe_3)(CH_2Ph)]^+$, 10), 348 ($[((Me_3Si)_2Si)_2]^+$, 69).

Cophotolysis of Isobutyrylsilane 1c with Methanol. A solution of isobutyrylsilane **1c** (45 mg, 0.14 mmol) in methanol (0.5 mL) containing one drop of pyridine was photolyzed for 2.5 h. The solvent was then removed under vacuum and the major product, the methanol adduct **6**, purified by chromatography (80/20 hexanes/CH_2Cl_2; silica gel).

(α-(Trimethylsiloxy)isobutyl)bis(trimethylsilyl)methoxysilane (6): colorless oil; yield 25%; ^1H NMR δ 0.21, 0.31, 0.34 (s, $SiMe_3$), 1.06, 1.10 (d, CH_3), 1.85–2.36 (m, CH), 3.40 (s, OCH_3), 4.02 (d, $C\mathit{H}OSiMe_3$); IR (neat) 2957 (s), 2896 (s), 2826 (s), 1248 (s), 840 (s), 1083 (s), 1039 (s) cm^{-1}.

Thermolysis of the Isopropyl-Substituted Dimer 3c. Method A. A solution of isobutyrylsilane **1c** (0.5 g) in C_6D_6 (1 mL) was photolyzed for 3.5 h. The solvent was then removed and the residue dissolved in a minimal amount of *n*-pentane. An attempt was then made to separate the photoproducts **3c** and **4c** by preparative gas chromatography (OV-101 column operating at 230 °C). The major product isolated from the column was identified as the alkene **7**.

Method B. A solution of the dimer **3c** (100 mg) in C_6D_6 (5 mL) containing methanol (1.5 mL) and one drop of pyridine was refluxed for a total of 140 h. The solvents were removed under vacuum, and the major products, the alkene **7** and unreacted starting material, were isolated by using chromatography (80/20 hexanes/CH_2Cl_2; silica gel). 2,5-Dimethyl-3-(bis(trimethylsilyl)(trimethylsiloxy)silyl)-4-(trimethylsiloxy)-3-hexene (**7**): colorless oil; ^1H NMR δ 0.23, 0.26 (s, $OSiMe_3$), 0.28 ($(SiMe_3)_2$), 1.08, 1.33 (d, CH_3, J = 6.7 and 7.1 Hz, respectively), 2.34, 2.85 (sept, CH, J = 6.7 and 7.1 Hz, respectively); ^{13}C NMR δ 0.07 ($SiMe_3$), 1.81, 3.08 ($OSiMe_3$), 21.84, 22.22 ($CH(\mathit{C}H_3)_2$), 28.56, 34.80 ($\mathit{C}H(CH_3)_2$), 118.63 ($=\mathit{C}(CH(CH_3)_2)Si$), 158.34 ($=\mathit{C}(OSiMe_3)(CH(CH_3)_2)$; ^{29}Si NMR δ 6.04, 11.99 ($OSiMe_3$), −7.24 ($\mathit{Si}(OSiMe_3)Si_2$), −19.29 ($\mathit{Si}Me_3$); IR (neat) 2959 (s), 2898 (s), 1261 (s), 841 (s), 1078 (s), 1043 (s), 1597 (m), 1582 (m) cm^{-1}; MS, *m/e* (relative intensity) 447 ($M^+ - Me$, 2), 389 ($M^+ - Me_3Si$, 18), 190 ($[(Me_3Si)(Me_3SiO)Si]^+$, 55), 279 (94).

Cophotolysis of Acetylsilane 1a with Tri-*n*-butyltin Hydride. Experiment 1. A solution of acetylsilane **1a** (90 mg, 0.31 mmol) and freshly distilled *n*-Bu_3SnH (0.1 mL, 0.37 mmol) in C_6D_6 (0.7 mL) was photolyzed for 2.5 h. The ratio of the products, linear dimer **4a**/tin hydride adduct 8, was approximately 1/1 as determined by ^1H NMR spectroscopy.

Experiment 2. A solution of acetylsilane **1a** (50 mg, 0.17 mmol) and freshly distilled *n*-Bu_3SnH (0.7 mL, 2.6 mmol) in C_6D_6 (0.3 mL) was photolyzed for 3 h. The excess *n*-Bu_3SnH was removed by trap-to-trap distillation. The ratio of the products, linear dimer **4a**/tin hydride adduct 8, was approximately 1/3 as determined by ^1H NMR spectroscopy.

The tin hydride adduct 8 could be isolated from either reaction mixture by preparative gas chromatography (5% OV-101 on Chromosorb G HP 80/100, operating at 250 °C).

((α-Trimethylsiloxy)ethyl)bis(trimethylsilyl)(tri-*n*-butylstannyl)silane (8): colorless oil; ^1H NMR δ 0.15, 0.32 0.36 (all s, $SiMe_3$), 0.80–1.79 (m, butyl and CH_3), 4.33 (q, CH, J = 7.3 Hz); ^{13}C NMR δ 1.05, 1.88, 2.09 (Me_3Si), 10.24 (CH_2, $^1J(^{119}Sn{-}^{13}C)$ = 252.6 Hz), 30.71 (CH_2, $^2J(^{119}Sn{-}^{13}C)$ = 17.9 Hz), 28.20 (CH_2, $^3J(^{119}Sn{-}^{13}C)$ = 57.8 Hz), 13.90 (CH_3), 26.47 ($\mathit{C}H_3CHOSiMe_3$), 62.74 ($CH_3\mathit{C}HOSiMe_3$); ^{29}Si NMR δ 15.13 ($OSiMe_3$), −11.21 ($SiMe_3$, $^2J(^{119}Sn{-}^{29}Si)$ = 23.6 Hz), −11.73 ($SiMe_3$, $^2J(^{119}Sn{-}^{29}Si)$ = 23.5 Hz), −63.58 ($\mathit{Si}Si_2Sn$).

Acknowledgment. We are grateful to the Natural Science and Engineering Research Council for financial support and for a scholarship to K.M.B.

Registry No. **1a**, 60154-96-3; **1b**, 106821-57-2; **1c**, 106821-58-3; **1d**, 106821-59-4; **3c**, 106821-66-3; **3d**, 106821-68-5; **4a**, 60155-05-7; (*E*)-**4b**, 106821-64-1; (*Z*)-**4b**, 106821-65-2; **4c**, 106821-67-4; (*E*)-**4d**, 106821-69-6; (*Z*)-**4d**, 106821-70-9; **5**, 106821-60-7; **6**, 106821-61-8; **7**, 106821-62-9; **8**, 106821-63-0; *n*-Bu_3SnH, 688-73-3; $Si(SiMe_3)_4$, 4098-98-0; CH_3CH_2COCl, 79-03-8; $(CH_3)_2CHCOCl$, 79-30-1; $PhCH_2COCl$, 103-80-0; $(Me_3Si)_3SiH$, 1873-77-4.

Dehydrogenation of Alkanes to Arenes by Iridium Complexes

Robert H. Crabtree,* Charles P. Parnell, and Richard J. Uriarte

Department of Chemistry, Yale University, New Haven, Connecticut 06511

Received July 21, 1986

Dehydrogenation of cyclohexanes to arenes using $[IrH_2(Me_2CO)_2(PAr_3)_2]SbF_6$ without a solvent is described. The chlorinated solvents previously used for reactions of this type are shown to transfer chloride to the metal to give chloro-bridged binuclear species. P–C bond cleavage in the phosphines limits the efficiency of the alkane reactions, which seem to involve the interface between the crystal of iridium complex and the alkane. Their yield is found to be strongly dependent on the counterion used, SbF_6 being the best we have tried.

Alkane activation is an area of great current interest;[1] selective catalytic functionalization of alkanes is one important goal in this area.[2] We have looked at the approach of using ligand deficient low-valent metal complexes in combination with a hydrogen acceptor.[1] These can stoichiometrically dehydrogenate alkanes and, as has been shown more recently, catalytically dehydrogenate alkanes to alkenes.[3,4a,5] We found *tert*-butylethylene (tbe) to be

---

(1) Crabtree, R. H. *Chem. Rev.* **1985**, *85*, 245. Janowicz, A. H.; Bergman, R. G. *J. Am. Chem. Soc.* **1982**, *104*, 352.

(2) Groves, J. T.; Nemo, T. E. *J. Am. Chem. Soc.* **1981**, *103*, 2884.

(3) Baudry, D.; Ephritikine, M.; Felkin, H. *J. Chem. Soc., Chem. Commun.* **1982**, *606*, 1980, 1243, 1983, 788. Baudry, D.; Ephritikine, M.; Felkin, H.; Zakrzewski, J. *J. Chem. Soc., Chem. Commun.* **1982**, 1235, *Tetrahedron Lett.* **1984**, 1283.

0276-7333/87/2306-0696$01.50/0 © 1987 American Chemical Society