broadened considerably, indicating the formation of a nondiscrete mixture of products.

A separate reaction was carried out in which *n*-butyllithium (0.64 mL of a 1.6 M solution in hexane, 1.03 mmol) was added dropwise to a THF (100 mL) solution of **23** (0.5 g, 0.51 mmol), which had been cooled to −78 °C with a dry ice/acetone bath. After the addition was complete, a molar excess of 2-propanol was added and the mixture was allowed to warm to room temperature. Removal of the solvent on a rotary evaporator left a semisolid material. Mass spectral analysis of the product mixture showed the following peaks of interest: *m/e* 972 – **23**; 930 – $N_4P_4(OCH_2CF_3)_7(CH_2CH_2CH_2CH_3)$, in addition to peaks above *m/e* 1600 that could correspond to fragments of coupled products.

Acknowledgment. This work was supported by a grant from the Office of Naval Research.

Registry No. **1**, 13053-90-2; **2**, 55975-50-3; **3**, 1065-05-0; **4**, 7736-61-0; **5**, 82918-20-5; **5**, 82932-64-7; **7**, 82918-21-6; **8**, 82918-22-7; **9**, 82918-23-8; **10**, 82918-24-9; **14**, 82918-25-0; **15**, 82918-26-1; **16**, 82918-27-2; **17**, 82918-28-3; **18**, 82918-29-4; **19**, 82918-30-7; **20**, 82918-31-8; **21**, 82932-65-8; **22**, 82918-32-9; **23**, 1065-05-0; $(NPCl_2)_3$, 940-71-6; $(CH_3)_2CHOD$, 3979-51-9; BuLi, 109-72-8; $(CH_3)_2CHOH$, 67-63-0; Ph_3SnCl, 639-58-7; CH_3I, 74-88-4; sodium trifluoroethoxide, 420-87-1; sodium phenoxide, 139-02-6.

Silanes in Organic Synthesis. 18. Preparation and Reactivity of Optically Active Vinyl- and Dienylsilanes[1]

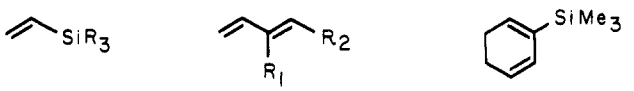
Rhys G. Daniels[2] and Leo A. Paquette*

Evans Chemical Laboratories, The Ohio State University, Columbus, Ohio 43210

Received July 16, 1982

The ((2,4,6-triisopropylphenyl)sulfonyl)hydrazones of four saturated and one α,β-unsaturated ketone have been transformed via the Shapiro reaction to the corresponding optically active vinyl- and dienylsilanes by condensation with (+)-1-naphthylphenylmethylchlorosilane. Inversion of configuration at asymmetric silicon is assumed on the basis of extensive literature analogy with other organolithium reagents. As a result of the silicon-bound aryl substituents, the double bonds are seen to be more electron deficient than those in the trimethylsilyl analogues. Greater steric crowding is also present. Consequently, the chemical reactivity of these systems is greatly attenuated. In addition, low levels of asymmetric induction were observed in two different reactions of these compounds, the implication being that chirality transfer from silicon to carbon may be generally inefficient in the absence of template effects.

In recent years, vinylsilanes (1) have gained increasing popularity as valued synthetic intermediates.[3] Some of the many tactical advantages offered by 1 have been sought with silyl-substituted 1,3-butadienes **2a**, **2b**, and their homologues.[4,5] The utilitarian nature of 2-silyl-1,3-cyclohexadienes, e.g., **3**,[6] has been virtually unexplored.[7]

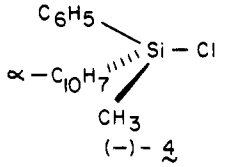


1 2a, $R_1 = H$, $R_2 = SiMe_3$ 3

b, $R_1 = SiMe_3$, $R_2 = H$

Oddly enough, there can be found no report of attempts to prepare optically active derivatives of **1–3** with the ultimate aim of transferring chirality from asymmetric silicon to carbon. Our interest in this question, coupled with the intriguing possibility of developing a recyclable chiral silicon pool, has prompted an examination of methods for preparing optically active vinyl- and dienylsilanes.[8]

Not long ago, we[6a,9] and others[6b,10] reported that vinyllithium reagents, generated regiospecifically from ketone (phenylsulfonyl)hydrazones Shapiro reaction[11] with *n*-butyllithium in TMEDA or TMEDA–hexane solvent systems, condense readily with chlorotrimethylsilane to provide unsaturated silanes. This efficient enesilylation[12] methodology encouraged us to examine comparable condensation reactions with (+)-1-naphthylphenylmethylchlorosilane (**4**).[13] More relevantly, Sommer, Korte, and



(−)-4

Rodewald had previously demonstrated that reaction of 4 with organolithiums proceeds with clean inversion of stereochemistry at asymmetric silicon.[14] Corriu has generalized on these findings by establishing that analogous stereochemical results materialize upon condensation of lithium and Grignard reagents with (−)-1-naphthyl-

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(13) For the absolute configurational assignment, see: Sommer, L. H.; Frye, C. L.; Parker, G. A.; Michael, K. W. *J. Am. Chem. Soc.* **1964**, *86*, 3271.

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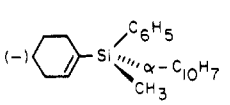
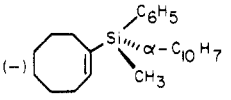
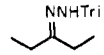
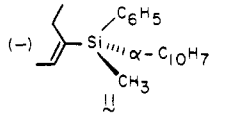
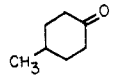
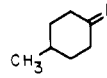
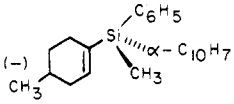
Table I. Preparation of Optically Active Vinylsilanes

ketone	trishydrazone	yield, %	vinylsilane	yield, %
	 5	86	 9	69
	 6	84	 10	46
	 7	79	 11	34
	 8	77	 12	53

phenyl-(−)-menthoxysilane,[15,16] (−)-1-naphthylphenylchloro-(−)-menthoxysilane,[16,17] and (−)-1-naphthylphenylmethoxy-(−)-menthoxysilane.[16,17]

Synthetic Considerations. For the present purposes, use was made of Bond's ((2,4,6-triisopropylphenyl)sulfonyl)hydrazone (trishydrazone) modification of the Shapiro procedure[6b] because these conditions lend themselves most suitably to quenching of the organometallic with a stoichiometric quantity of the valued electrophile. Owing to the established absolute configuration of (−)-4[13] and the precedent for clean inversion of configuration, it was considered that assignments of absolute configuration to our products could be made with a reasonable level of confidence.

Beginning with the saturated ketones given in Table I, each of the optically active vinylsilanes (**9–12**) was isolated as a clear colorless levorotatory oil. In three of the examples, comparison of the olefinic proton chemical shift was made relative to that in the corresponding trimethylsilyl analogue (Table II). Substantial deshielding is clearly evident in the chiral systems due to the presence of the silicon-bound aromatic substituents.

In the case of 4,4-dimethylcyclohexenone (**13**), direct condensation with ((2,4,6-triisopropylphenyl)sulfonyl)hydrazine proceeded without serious complication from side reactions to give trishydrazone **14** in 49% yield. Subsequent sequential treatment with *sec*-butyllithium (TMEDA–hexane, −78 °C) and **4** yielded **15** (57%), shown to be homogeneous by ^{13}C NMR analysis.

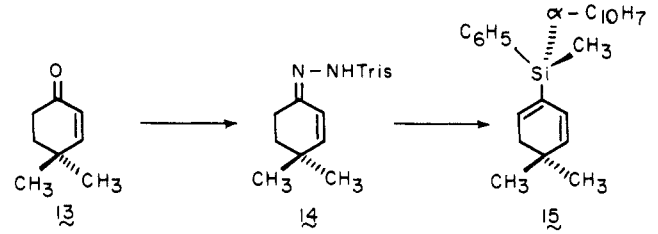
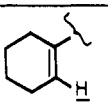
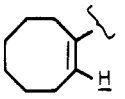
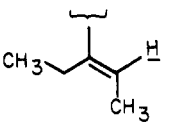
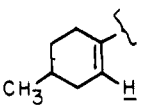
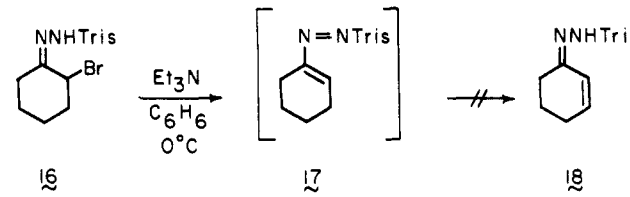


Table II. ^1H NMR Shifts of the Vinyl Proton in 9–12

R	chem shifts (δ, $CDCl_3$) Me_3Si-R	(−)-α-NpPhMeSi-R	Δδ[a]
	6.12	6.62	+0.50
	6.28		
	(5.76)[b]	5.97	(+0.21)
	5.84	6.29	+0.45

[a] $\Delta\delta = \delta(\alpha\text{-NpPhMeSi-R}) - \delta(Me_3Si\text{-R})$. [b] The value cited is for the *Z* isomer.

As expected,[18] comparable attempts to prepare **18** directly from 2-cyclohexenone were frustrated by facile competing Michael addition of the (phenylsulfonyl)hydrazine. Recourse was therefore made to the procedure of Dondoni[19] as modified by Lightner and co-workers.[20] Upon treatment of 2-bromocyclohexanone with trishydrazine, **16** was obtained. When this intermediate was allowed to react with triethylamine in benzene at 0 °C, the usual precipitate of triethylammonium bromide was observed. However, 2,4,6-triisopropylbenzenesulfinic acid and not **18** was isolated in striking contrast to the "normal" behavior of the benzenesulfonylhydrazone.[7]



A possible clue to this dichotomy has been provided by Cusack et al., who investigated the relative stabilities of selected (phenylsulfonyl)hydrazines.[21] They found that the *p*-toluenesulfonyl derivative reacts with triethylamine in methanol-d_4 under pseudo-first-order conditions to liberate *p*-toluenesulfinic acid with a half-life of 120 h. For the 2,4,6-triisopropyl example, decomposition occurred with $t_{1/2}$ = 19 min or approximately 380 times faster. Therefore, the probable fate of **17** upon deprotonation is loss of the sulfinic acid in preference to prototropic shift. Alternatively, **18** may be subject to accelerated 1,1-elimination.

Reactivity. Previously, vinyltrimethylsilanes were shown to undergo regiospecific singlet oxygenation.[12,22]

(15) Corriu, R. J. P.; Lanneau, G. F.; Leard, M. *J. Chem. Soc D* **1971**, 1365.
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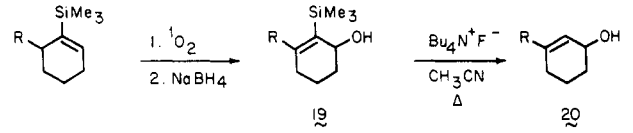
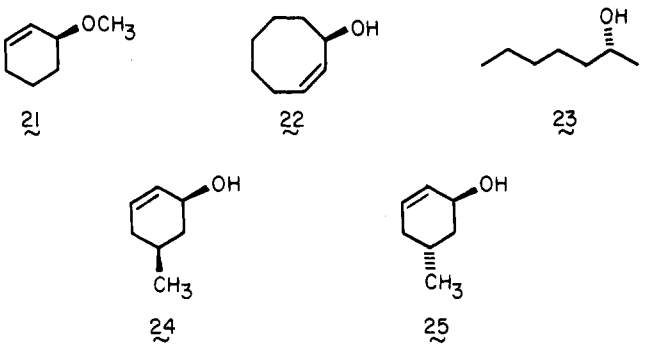
Sodium borohydride reduction of the hydroperoxide product gives the β-silylated alcohol resulting from ene reaction, e.g., **19**, which is in turn convertible to the transposed allylic alcohol **20** on treatment with tetra-*n*-butylammonium fluoride in dry acetonitrile.



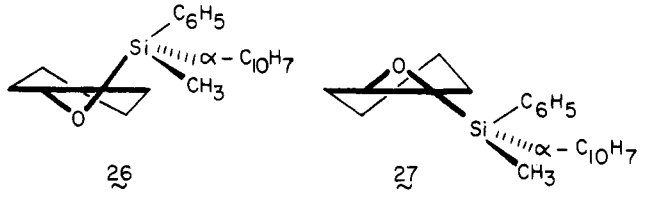
19 **20**

In order to learn more about the reactivity of the bulkier optically active vinylsilanes **9–12** and concomitantly probe the feasibility of chirality transfer from silicon to carbon during such oxidations, varied photooxygenation conditions were investigated. The substrates were carefully chosen so as to provide end products relatable to known allylic alcohols or their derivatives, i.e., **21**,[23] **22**,[23b,c,24] **23**,[25] and **24**/**25**,[26] whose absolute configurations are well established. Unfortunately, all attempts at photooxygenation proved fruitless. Although several minor components were seen to develop over long periods of irradiation, the chiral vinylsilanes were recovered largely intact.



21 **22** **23** **24** **25**

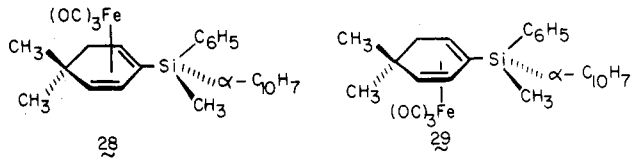
In a possible alternative approach, the epoxidation of **9** was examined. With buffered *m*-chloroperbenzoic acid, a 43:57 mixture of the diastereomeric α,β-epoxysilanes **26** and **27** was obtained in 97% yield. While a variety of procedures have been developed to effect the conversion of epoxides to allylic alcohols, attempts to extend them to these systems proved unsuccessful. Thus, treatment with ethanolic sodium phenylselenide followed by hydrogen peroxide oxidation,[27] with lithium diisopropylamide,[28] with trimethylsilyl triflate,[29] and with iodotrimethylsilane as generated from hexamethyldisilane–iodine[30] or from chlorotrimethylsilane–sodium iodide[31] all failed to effect the desired transformation.



26 **27**

While the unwillingness of the epoxide to undergo ring opening is unclear in its origins, the unreactivity of the vinylsilanes toward singlet oxygen may be attributable to several factors. Some possibilities include reduced electron density within the vinylsilane double bond (note downfield shifting of vinyl protons in Table I) as the result of π-electron donation through the silicon d orbitals into the aromatic rings, quenching of singlet oxygen by the same aromatic substituents, and/or the steric bulk of the 1-naphthylphenylmethylsilyl substituent.

In another context, it is interesting to note that reaction of **15** with diiron enneacarbonyl in refluxing petroleum ether afforded the diastereomeric tricarbonyliron complexes **28** and **29** as an approximately 50:50 mixture of diastereomers (^{1}H NMR analysis). The lack of stereocontrol in the complexation step parallels the poor stereoselectivity realized in formation of epoxides **26** and **27**. Taken together, these results bode ill for attempts to effect chirality transfer from asymmetric silicon to carbon, at least in the absence of template effects. Investigations aimed at the utilization of such auxiliary agents have been initiated.



28 **29**

Experimental Section

Proton magnetic resonance spectra were recorded with Varian EM-390 and Bruker HX-90 spectrometers. Apparent splittings are given in all cases. Carbon-13 magnetic resonance spectra were recorded on a Bruker HP-90 instrument. Infrared and mass spectra (70 eV) were determined with Perkin-Elmer Model 457 and AEI-MS9 spectrometers, respectively. Optical rotations were taken on a Perkin-Elmer 241 polarimeter. Elemental analyses were performed at the Scandinavian Microanalytical Laboratory, Herlev, Denmark.

Cyclohexanone ((2,4,6-Triisopropylphenyl)sulfonyl)hydrazone (5). A rapidly stirred suspension of 14.93 g (50.0 mmol) of ((2,4,6-triisopropylphenyl)sulfonyl)hydrazine (trishydrazine)[21] in 50 mL of methanol was treated with 4.91 g (50.0 mmol) of freshly distilled cyclohexanone. Addition of 0.5 mL of concentrated hydrochloric acid induced rapid clearing of the reaction mixture which subsequently was chilled (−20 °C) overnight. The crystalline product was collected by suction filtration, washed with a little cold methanol, and dried in vacuo to give 16.25 g (85.8%) of **5** as fine white crystals: mp 124–124.5 °C dec (lit.[6b] mp 123–124 °C dec); ^{1}H NMR ($CDCl_3$) δ 7.16 (s, 2 H), 4.22 (sept, J = 7 Hz, 2 H), 2.88 (sept, J = 7 Hz, 1 H), 2.38–1.98 (br s, 4 H), 1.71–1.42 (br s, 6 H), 1.27 (d, J = 7 Hz, 18 H); *m/e*(calcd) 378.2341, *m/e*(obsd) 378.2336.

(−)-1-(1-Naphthylphenylmethylsilyl)cyclohexene (9). To a cold (−75 °C) suspension of 2.00 g (5.28 mmol) of **5** in 20 mL of 50% tetramethylethylenediamine (TMEDA)–hexane was added dropwise under nitrogen 11.4 mL (10.6 mmol) of a freshly titrated 0.93 M solution of *sec*-butyllithium in cyclohexane (Foote Mineral Co.). The reaction mixture was stirred at −78 °C for 2 h and at

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(24) (a) Bach, R. D.; Mazur, U.; Brummel, R. N.; Lin, L.-H. *J. Am. Chem. Soc.* **1971**, *93*, 7120. (b) Luche, J.-L.; Damiano, J.-C.; Crabbé, P. *J. Chem. Res., Synop.* **1977**, 32. (c) Damiano, J.-C.; Luche, J.-L.; Crabbé, P. *Tetrahedron* **1978**, *34*, 3137.
(25) (a) Lemieux, R. U.; Giguerre, J. *Can. J. Chem.* **1951**, *29*, 678. (b) Doering, W. von E.; Young, R. W. *J. Am. Chem. Soc.* **1952**, *74*, 2997. (c) Novak, E. R.; Tarbell, D. S. *J. Am. Chem. Soc.* **1967**, *89*, 73.
(26) (a) Goering, H. L.; Blanchard, J. P. *J. Am. Chem. Soc.* **1954**, *76*, 5405. (b) Goering, H. L.; Nevitt, T. D.; Silversmith, E. F. *Ibid.* **1955**, *77*, 4042.
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0 °C for 30 min (vigorous evolution of nitrogen). Subsequently, a solution of 1.50 g (5.30 mmol) of (-)-1-naphthylphenylmethylchlorosilane (**4**) in 10 mL of dry hexane was added dropwise, and the reaction mixture was allowed to warm to room temperature and stir for 8 h prior to addition to 25 mL of water. The layers were separated, the aqueous layer was extracted with 3 × 25 mL of pentane, and the combined organic layers were washed with 3 × 25 mL of saturated copper(II) sulfate solution and 25 mL of brine, dried, and evaporated to yield 2.04 g of a clear yellow oil. Chromatography on silica gel (50 g, elution with hexane) afforded 1.188 g (68.5%) of **9** as a viscous, clear colorless oil: $[\alpha]_D$ -23.4° (*c* 4.13, cyclohexane); ^{1}H NMR ($CDCl_3$) δ 8.57–7.55 (m, 12 H), 6.62 (br t, 1 H), 2.85–2.35 (br m, 4 H), 2.14–1.94 (br m, 4 H), 1.29 (s, 3 H); IR (CCl_4, cm^{-1}) 3050, 2920, 2850, 2825, 1615, 1500, 1445, 1425, 1315, 1245, 1215, 1140, 1100, 1055, 1015, 975, 930, 815, 595, 575; *m/e*(calcd) 328.1647, *m/e*(obsd) 328.1639.

Cyclooctanone ((2,4,6-Triisopropylphenyl)sulfonyl)hydrazone (6). Reaction of 6.51 g (50.0 mmol) of 97% cyclooctanone with 14.93 g (50.0 mmol) of trishydrazine as described above gave 17.11 g (84.2%) of **6** as a white crystalline solid: mp 116–117 °C dec; ^{1}H NMR ($CDCl_3$) δ 7.15 (s, 2 H), 4.20 (sept, *J* = 7 Hz, 2 H), 2.83 (sept, *J* = 7 Hz, 1 H), 2.43–2.30 (m, 4 H), 1.28 (d, *J* = 7 Hz, 18 H), 2.00–1.00 (m, 10 H).

(-)-1-(1-Naphthylphenylmethylsilyl)cyclooctene (10). Reaction of 2.00 g (4.92 mmol) of **6** with 10.6 mL (9.86 mmol) of a 0.93 M solution of *sec*-butyllithium in cyclohexane with quenching by 1.40 g (4.95 mmol) of **4** as previously described afforded 809 mg (46.1%) of **10** as a viscous, clear colorless oil: $[\alpha]_D$ -4.04° (*c* 4.63, cyclohexane); ^{1}H NMR ($CDCl_3$) δ 8.34–7.31 (m, 12 H), 6.28 (t, *J* = 8 Hz, 1 H), 2.80–2.15 (br m, 4 H), 1.85–1.30 (br m, 8 H), 1.03 (s, 3 H); IR (CCl_4, cm^{-1}) 3050, 2990, 2920, 2845, 1610, 1585, 1500, 1465, 1445, 1425, 1355, 1315, 1245, 1210, 1140, 1100, 1015, 990, 975, 895, 700, 695; *m/e*(calcd) 356.1960, *m/e*(obsd) 356.1952.

3-Pentanone ((2,4,6-Triisopropylphenyl)sulfonyl)hydrazone (7). Reaction of 4.31 g (50.0 mmol) of freshly distilled 3-pentanone with 14.93 g (50.0 mmol) of trishydrazine as described above gave 14.42 g (78.7%) of **7** as a white crystalline solid: mp 116–117 °C dec (lit.[6b] mp 115–116 °C dec); ^{1}H NMR ($CDCl_3$) δ 7.01 (s, 2 H), 4.18 (sept, *J* = 7 Hz, 2 H), 2.90 (sept, *J* = 7 Hz, 1 H), 2.15 (qrt, *J* = 7 Hz, 4 H), 1.27 (d, *J* = 7 Hz, 18 H), 0.93 (t, *J* = 7 Hz, 6 H); *m/e*(calcd) 366.2341, *m/e*(obsd) 366.2333.

(-)-3-(1-Naphthylphenylmethylsilyl)-(*Z*)-2-pentene (11). Reaction of 2.00 g (5.46 mmol) of **7** with 11.8 mL (11.0 mmol) of a 0.93 M solution of *sec*-butyllithium in cyclohexane with quenching by 1.55 g (5.48 mmol) of **4** as previously described afforded 591 mg (34.2%) of **11** as a viscous, clear colorless oil: $[\alpha]_D$ -12.7° (*c* 5.48, cyclohexane); ^{1}H NMR ($CDCl_3$) δ 8.22–7.21 (m, 12 H), 5.97 (qrt, *J* = 6 Hz, 1 H), 2.41 (qrt, *J* = 7 Hz, 2 H), 1.87 (d, *J* = 6 Hz, 3 H), 0.99 (t, *J* = 7 Hz, 3 H), 0.94 (s, 3 H); IR (CCl_4, cm^{-1}) 3050, 2960, 2925, 2850, 1615, 1585, 1500, 1445, 1425, 1365, 1315, 1245, 1215, 1135, 1100, 1015, 975, 905, 705, 695; *m/e*(calcd) 316.1647, *m/e*(obsd) 316.1639.

4-Methylcyclohexanone ((2,4,6-Triisopropylphenyl)sulfonyl)hydrazone (8). Reaction of 5.61 g (50.0 mmol) of freshly distilled 4-methylcyclohexanone with 14.93 g (50.0 mmol) of trishydrazine as described above gave 15.17 g (77.3%) of **8** as a white crystalline solid: mp 115–116 °C dec; ^{1}H NMR ($CDCl_3$) δ 7.15 (s, 2 H), 4.19 (sept, *J* = 7 Hz, 2 H), 2.88 (sept, *J* = 7 Hz, 1 H), 2.52–1.48 (m, 9 H), 1.25 (d, *J* = 7 Hz, 18 H), 0.87 (d, *J* = 5 Hz, 3 H).

(-)-1-(1-Naphthylphenylmethylsilyl)-4-methylcyclohexene (12). Reaction of 2.00 g (5.09 mmol) of **8** with 11.0 mL (10.2 mmol) of a 0.93 M solution of *sec*-butyllithium in cyclohexane with quenching by 1.45 (5.13 mmol) of **4** as previously described afforded 930 mg (53.4%) of **12** as a viscous, cllear colorless oil: $[\alpha]_D$ -22.9° (*c* 6.29, cyclohexane); ^{1}H NMR ($CDCl_3$) δ 8.02–7.20 (m, 12 H), 6.29 (br s, 1 H), 2.59–1.33 (m, 7 H), 1.27–1.22 (br d, 3 H), 0.98 (s, 3 H); IR (CCl_4, cm^{-1}) 3050, 3000, 2950, 2900, 2865, 2840, 1615, 1585, 1400, 1480, 1445, 1425, 1370, 1315, 1245, 1215, 1140, 1100, 1055, 1015, 975, 925, 895, 700, 695; *m/e*(calcd) 342.1805, *m/e*(obsd) 342.1811.

4,4-Dimethyl-2-cyclohexenone ((2,4,6-Triisopropylphenyl)sulfonyl)hydrazone (14). A rapidly stirred suspension of 7.46 g (25.0 mmol) of trishydrazine in 50 mL of methanol was treated with 3.10 g (25.0 mmol) of 4,4-dimethyl-2-cyclohexenone (**13**)[32] and 5 drops of concentrated hydrochloric acid. The clear pale yellow reaction mixture was chilled (-20 °C) overnight and the crystalline product was collected by suction filtration, washed with a little cold methanol, and dried in vacuo to yield 5.01 g (49.5%) of **14** as a white crystalline solid: mp 145–147 °C dec; ^{1}H NMR ($CDCl_3$) δ 7.05 (s, 1 H), 5.81 (s, 1 H), 4.21 (sept, *J* = 7 Hz, 2 H), 2.86 (sept, *J* = 7 Hz, 1 H), 2.42–2.10 (m, 2 H), 1.74–1.38 (m, 2 H), 1.26 (d, *J* = 7 Hz, 18 H), 1.00 (s, 6 H).

(-)-2-(1-Naphthylphenylmethylsilyl)-5,5-dimethyl-1,3-cyclohexadiene (15). Reaction of 2.00 g (4.97 mmol) of **14** with 11.0 mL (10.0 mmol) of a 0.91 M solution of *sec*-butyllithium in cyclohexane with quenching by 1.41 g (4.98 mmol) of **4** as previously described afforded 998 mg (56.6%) of **15** as a viscous, clear colorless oil; $[\alpha]_D$ -6.41° (*c* 5.13, cyclohexane). Analytical purification was achieved by MPLC (Lobar Li-Chroprep Si-60, elution with light petroleum ether) to give a clear colorless oil: $[\alpha]_D$ -6.35° (*c* 0.096, cyclohexane); ^{1}H NMR ($CDCl_3$) δ 8.27–7.40 (m, 12 H), 6.26 (d, *J* = 5 Hz, 1 H), 6.05 (d, *J* = 10 Hz, 1 H), 5.65 (d, *J* = 10 Hz, 1 H), 2.32 (d, *J* = 5 Hz, 2 H), 1.19 (s, 6 H), 0.97 (s, 3 H); ^{13}C NMR (ppm, $CDCl_3$) 138.71, 136.96, 136.67, 136.13, 135.21, 130.26, 129.19, 129.00, 128.85, 127.83, 125.55, 125.35, 125.11, 124.19, 39.18, 30.30, 27.72, -3.01; IR (CCl_4, cm^{-1}) 3045, 3010, 2950, 2860, 1585, 1555, 1535, 1500, 1460, 1425, 1370, 1355, 1315, 1300, 1245, 1210, 1190, 1140, 1100, 1055, 1015, 920, 812, 700, 690; *m/e*(calcd) 354.1804, *m/e*(obsd) 354.1812.

Anal. Calcd for $C_{25}H_{26}Si$: C, 84.69; H, 7.39. Found: C, 84.21; H, 7.46.

3-Bromocyclohexanone ((2,4,6-Triisopropylphenyl)sulfonyl)hydrazone (16). A solution of 8.50 g (52.8 mmol) of 2-bromocyclohexanone[33] in 50 mL of diethyl ether was added to a cold (0 °C) rapidly stirred suspension of 14.92 g (50.0 mmol) of trishydrazine in 200 mL of diethyl ether. The reaction mixture was stirred at 0 °C for 2 h, chilled (-20 °C, no crystallization of product observed), and evaporated, giving 20.20 g (84.0%) of crude **16** as a yellow-brown oil having a compatible ^{1}H NMR spectrum.

Treatment of a solution of this oil (20.20 g, 44.4 mmol) in 400 mL of benzene with a solution of 6.2 mL (45 mmol) of triethylamine in 40 mL of benzene at 0 °C gave the usual precipitate of triethylammonium bromide. Treatment of the filtrate with 62 mL (450 mL) of triethylamine at room temperature for 42 h yielded a yellow-brown oil which on filtration through silica gel (30 g, elution with ethyl acetate–hexane, 1:1) afforded g of impure 2,4,6-triisopropylbenzenesulfinic acid as a brown semisolid. Recrystallization from hot methanol furnished 7.72 g of pure acid as white needles:[21] mp 111.5–112 °C; ^{1}H NMR ($CDCl_3$) δ 7.03 (d, *J* = 5 Hz, 2 H), 4.09–3.32 (m, 2 H), 2.86 (sept, *J* = 7 Hz, 1 H), 1.26 (d, *J* = 7 Hz, 6 H), 0.99 (d, *J* = 7 Hz, 6 H).

1-(1-Naphthylphenylmethylsilyl)-7-oxabicyclo[4.1.0]heptane (26/27). A cold (0 °C) solution of 93 mg (0.28 mmol) of **9** in 5 mL of dry dichloromethane containing 25 mg (3.0 mmol) of sodium bicarbonate was treated portionwise with 50 mg (2.9 mmol) of *m*-chloroperoxybenzoic acid (MCPBA). The reaction mixture was stirred at 0 °C for 1 h, second equimolar portions of bicarbonate and peracid were added, and the reaction mixture was stirred at room temperature for 5 h. The reaction mixture was diluted with 20 mL of diethyl ether, washed with 10 mL of saturated sodium sulfite solution, 3 × 10 mL of saturated sodium bicarbonate solution, and 10 mL of brine, and the organic phase was dried and evaporated. Chromatography of the residual yellow oil (130 mg) on silica gel (10 g, elution with ethyl acetate–hexane, 1:9) yielded 95 mg (97%) of a clear, colorless, oily 43:75 mixture of diastereomers **26/27** which crystallized on standing to give fine white needles: mp 118–121 °C; ^{1}H NMR ($CDCl_3$) δ 8.19–7.15 (m, 12 H), 3.20–3.02 (br t, 1 H), 2.22–1.66 (m, 4 H), 1.59–1.00 (m, 4 H); *m/e*(calcd) 344.1596, *m/e*(obsd) 344.1605.

(-)-Tricarbonyl[1–4-η-2-(1-naphthylphenylmethylsilyl)-5,5-dimethyl-1,3-cyclohexadienyl]iron (28/29). Reaction of 962 mg (2.71 mmol) of **15** and 4.00 g (11.0 mmol) of diiron no-

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nacarbonyl in the usual manner[7] provided 633 mg (47.2%) of an ca. 50:50 (by ^{1}H NMR) mixture of diastereomers **28**/**29** as a golden oil: $[\alpha]_D$ −3.93° (*c* 3.41, cyclohexane); ^{1}H NMR ($CDCl_3$) δ 8.05–7.80 (m, 12 H), 5.07 (dt, *J* = 8 and 2 Hz, 1 H), 3.10 (t, *J* = 6 Hz, 2 H), 2.75 (t, *J* = 3 Hz, 2 H), 1.10 (s, 3 H), 0.87 (2s, 3 H), 0.78 (2s, 3 H); IR ($CHCl_3$, cm^{-1}) 3045, 3030, 2945, 2910, 2840, 2030, 1940, 1585, 1500, 1455, 1445, 1422, 1365, 1315, 1280, 1260, 1250, 1180, 1135, 1115, 1100, 1010, 952, 945, 860, 815, 740, 660, 605, 590, 585, 575; *m*/*e*(calcd) 494.1000, *m*/*e*(obsd) 494.1020.

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Kinetics and Mechanism of Pyrolysis of 1,1,3,3,4,4-Hexamethyl-1,3,4-trisilacyclopentane

Iain M. T. Davidson* and F. Timothy Lawrence

Department of Chemistry, The University, Leicester, Great Britian

Gerhard Fritz and Eberhard Matern

Institute of Inorganic Chemistry, The University, Karlsruhe, FRG

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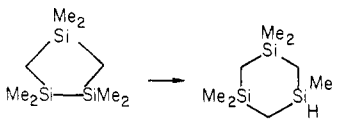
Pyrolysis of the title compound, which is known to give a ring expansion isomer at atmospheric pressure, proceeds differently at low pressure, the main product being 1,1,3,3-tetramethyl-1,3-disilacyclobutane formed in a first-order reaction with $\log_{10} A/s^{-1} = 16.1 \pm 0.6$ and E/kJ mol^{-1} = 316 ± 11. A mechanism is suggested to rationalize the results at high and low pressure.

Introduction

Pyrolysis of 1,1,3,3,4,4-hexamethyl-1,3,4-trisilacyclopentane (HTSP) at 773 K and ca. 1 atm of pressure is known[1] to give the ring expansion isomer, 1,1,3,3,5-pentamethyl-1,3,5-trisilacyclohexane (PTSH), thus



Although reasonable suggestions as to mechanism have been made,[1] no detailed kinetic work had been done; we have now undertaken a gas kinetic investigation by low-pressure pyrolysis (LPP) with analysis by mass spectrometry,[2] to elucidate the mechanism of this interesting pyrolysis.

Results

HTSP was pyrolyzed at initial pressures of 0.1–0.2 mmHg (1 mmHg = 133.3 N m^{-2}) between 879 and 1036 K. The decomposition of HTSP was first order with the following Arrhenius parameters: $\log_{10} A/s^{-1} = 16.1 \pm 0.6$ and E/kJ mol^{-1} = 316 ± 11. These parameters were derived from measurements between 939 and 992 K, the range within which the rate constants had optimum values for reliable measurement by LPP.[2]

In contrast to the original experiments at higher pressure[1] the ring expansion product PTSH was not observed, the main product being 1,1,3,3-tetramethyl-1,3-disilacyclobutane (TDSB) instead. TDSB accounted for 77% of the HTSP decomposed at 889 K, diminishing to ca. 16% at 924 K, partly because of secondary decomposition of TDSB (vide infra) and partly because of the tendency for loss of silicon from the gas phase, which is a feature of the pyrolysis of organosilicon compounds,[3] especially by LPP.[2] Other products were methane (ca. 17% at 924 K) and some hydrogen. Both of these products arose from decomposition of polymer at the surface of the reaction vessel; but in separate experiments it was established that they also came from secondary decomposition of TDSB.[4] In keeping with this explanation the yields of methane and hydrogen increased with increasing temperature relative to the yield of TDSB.

It is not unusual in silicon chemistry for the product composition of a pyrolysis to be drastically affected by variation in pressure. For example, pyrolysis of hexamethyldisilane gives an isomer, $Me_3SiCH_2Si(H)Me_2$, as a principal product at relatively high pressure[5] but gives TDSB instead at low pressure.[6,7] Vinyltrimethylsilane is a major product of the pyrolysis of allyltrimethylsilane at high pressure,[8] but not at low.[9] In both cases the differences arise because of the effect of pressure on the rate of a bimolecular radical–molecule reaction relative to a competing unimolecular reaction. The likelihood that a similar explanation was responsible for the formation of TDSB at low pressure and PTSH at high pressure in the pyrolysis of HTSP was investigated in a LPP experiment at 689 K (well below the pyrolysis temperature for HTSP) in which methyl radicals were generated by pyrolysis of dimethylmercury in the presence of HTSP, thus giving a high concentration of radicals, even at low pressure. PTSH was indeed formed, with no TDSB.

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