**Table I. Melting Points of 2-Bromoacids**

| | compound | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | 2A | 2B | 2C | 2D | 2E | 2F | 2G | 2H |
| mp, °C | 23.5–25 | 28–30 | 31.5–32 | 42–43 | 53–54 | 60–61 | 61–62 | 64.5–65.5 |

**Table II. Characteristics of 2-(2-Hydroxyethylamino) Fatty Acids**

| compd | yield, % | mp, °C | surf. tension, dyn $cm^{-1}$ | cmc,[a] $10^{-4}$ × mol $L^{-1}$ |
|---|---|---|---|---|
| 3A | 84 | 187.5–190 | 48 | 50 |
| 3B | 54 | 200–202 | 34 | 5 |
| 3C | 78 | 171.5–173 | 37 | 80 |
| 3D | 71 | 152–153.5 | 26 | 0.5 |
| 3E | 82 | 158.5–160.5 | 36 | 0.3 |
| 3F | 78 | 151.5–153.5 | 41 | 0.2 |
| 3G | 55 | 164–166 | 49 | 0.1 |
| 3H | 62 | 167–169 | 51 | 0.02 |

[a] Cmc = critical micelle concentration.

product was poured into warm water and washed with warm water. The products were dried and then recrystallized from acetone (*2*). Their melting points are reported in Table I.

***2-(2-Hydroxyethylamino) Fatty Acids (3).*** The compounds **3** were synthesized by adding 2-aminoethanol to a mixture of compound **2** and potassium or sodium hydroxide in a polar solvent such as water, ethanol, and methanol to react for 7–15 h at 65–78.5 °C or reflux. After an excess of 2-aminoethanol (30–50 mmol) had been reacted with compound **2** (10 mmol), the chlorhydric acid or glacial acetic acid was added to neutralize. The resulting crystalline **3** were filtered, washed with water, and dried in a vacuum desiccator over phosphorous pentoxide. The white solid crystals of **3** were obtained. Compounds 3 were further purified by column chromatography. Their characteristics are given in Table II.

2-(2-Hydroxyethylamino)tetradecanoic acid (**3D**), as a representative sample, was prepared as follows: a mixture of 1.54 g (5 mmol) of **2D**, 1.1 mL (18 mmol) of 2-aminoethanol, and 20 mL 5% KOH ethanol solution was stirred and heated at reflux for 10 h. The solvent was removed in vacuo. The remaining residue was acidified with glacial acetic acid and then filtered, washed with water, dried in a vacuum desiccator over phosphorous pentoxide and purified by column chromatography to give a white solid 1.02 g (71%) of **3D**.

**Registry No.** 1A, 334-48-5; 1B, 112-37-8; 1C, 143-07-7; 1D, 544-63-8; 1E, 57-10-3; 1F, 57-11-4; 1G, 646-30-0; 1H, 112-85-6; **2**A, 2623-95-2; **2**B, 2623-84-9; **2**C, 111-56-8; **2**D, 10520-81-7; **2**E, 18263-25-7; **2**F, 142-94-9; **2**G, 89367-98-6; **2**H, 20828-43-7; **3**A, 67552-88-9; **3**B, 99097-95-7; **3**C, 67491-92-3; **3**D, 67491-93-4; **3**E, 67491-94-5; **3**F, 67491-95-6; **3**G, 99097-96-8; **3**H, 99097-97-9; $H_2NCH_2CH_2OH$, 141-43-5.

## Literature Cited

(1) Gawish, S. M.; Hazzaa, A. A. B.; Zourab, S. *J. Am. Oil Chem. Soc.* **1981**, *58*(6), 757.
(2) Du Xianxian; Yang Shiguang; Chen Yukang; Yin Daiyi *Huaxue Shiji* **1983**, *6*, 383–384.

Received for review April 8, 1985. Accepted September 6, 1985.

---

# Synthesis of Certain Cyclic Silanes

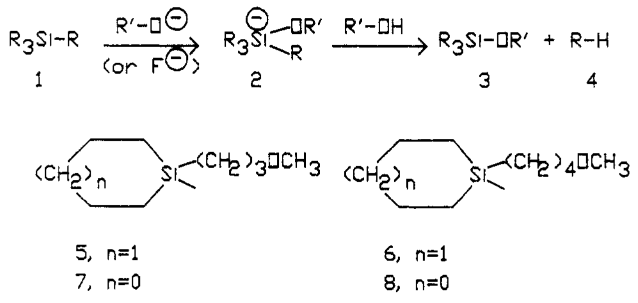
**Herbert O. House,* Joseph A. Hrable, and S. Lakshmi Narasimhan**

*School of Chemistry, Georgia Institute of Technology, Atlanta, Georgia 30332*

**The chlorotrialkylsilanes 21–24 have been synthesized as precursors to potential steric blocking groups for alkanes and cycloalkanes. Reaction of these chlorosilanes with one of the organometallic reagents methyllithium, methylmagnesium chloride, *n*-octylmagnesium bromide, or *p*-chlorobenzylmagnesium chloride formed the silanes 25–34.**

As part of our continuing interest (*1–4*) in the use of sterically bulky substituents to control reactant conformation and, in some cases, reaction stereochemistry, we initiated a study of certain trialkylsilyl substituents, $R_3Si$–. Such substituents, $R_3Si$–, have sufficient steric bulk (*5–9*) to exert control over reactant conformation in a manner similar to bulky alkyl substituents (*10*). Thus, a conformational *A* value of 2.4–2.6 kcal/mol is reported for the trimethylsilyl group (*8*, *9*). Furthermore, the susceptibility of tetraalkylsilanes **1** (Scheme I) to attack by hard nucleophiles such as $F^-$ or $R'$–$O^-$ to form successively pentacoordinate intermediates **2** and cleavage products **3** and **4** (*11–16*) suggests that selective cleavage of certain steric blocking groups, $R_3Si$–, might be possible. In order to investigate this possibility, we have studied synthetic routes to silanes incorporating the trisubstituted silyl groups **5–8**. This paper describes the synthesis and characterization of these silanes.

**Scheme I**



The syntheses began with the conversion of each dibromide **9** or **10** to the corresponding bis-Grignard reagent followed by reaction with trichlorosilane (Scheme II). Subsequent orienting experiments were performed in which 1-octene (**13**) was converted to the silane **14** via either of the hydrosilation (*17*, *18*) products **15** or **16** without rearrangement of the carbon skele-

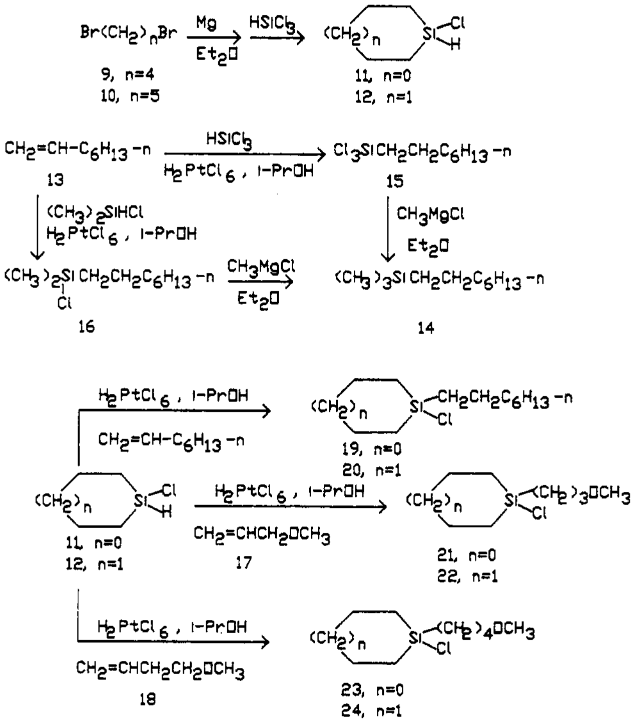
0021-9568/86/1731-0124$01.50/0

Table I. Physical Properties[a] of Compounds Prepared

| cmpd | formula | yield, % | bp (press.) | $n_D$(temp) | [ref] bp(press.), $n_D$ (temp) | analyses | MS | (EI/CI) M(Int) | IR data,[b] cm$^{-1}$ |
|---|---|---|---|---|---|---|---|---|---|
| **15** | $C_8H_{17}Cl_3Si$ | 96 | 57–58(1.2) | 1.4463(25) | [*19*] 68(1.6), 1.4458(25) | | (EI) | 246 (M, 1) | |
| **14** | $C_{11}H_{26}Si$ | 88 | 89–90(9) | 1.4222(25) | [*20*] 63(1.2), 1.4272(25) | C, H | (EI) | 186 (M, 1) | |
| **16** | $C_{10}H_{23}ClSi$ | 69 | 65–66(1.5) | 1.4341(25) | [*21*] 215–218(740), 1.4390(20) | | (EI) | 206 (M, 0.3) | |
| **12** | $C_5H_{11}ClSi$ | 69.4 | 142–143 | 1.4683(25) | [*22*] 143(760), 1.467(25) | | (EI) | 134 (M, 25) | 2180 (SiH) |
| **20** | $C_{13}H_{27}ClSi$ | 80 | 134–136(0.6–0.7) | 1.4702(25) | | | (EI) | 248 (M, 2) | |
| **26** | $C_{14}H_{30}Si$ | 78 | 71–73(0.15–0.16) | 1.4588(25) | | C,H | (EI) | 226 (M, 2) | |
| **17** | $C_4H_8O$ | 70 | 41.5–42.5 | 1.3744(25) | [*23*] 42–42.3, 1.3759(25) | | | | 1645(C=C), 914(CH=CH$_2$) |
| **22** | $C_9H_{19}ClOSi$ | 53 | 55(0.05) | 1.4701(25) | | | (EI) | 206 (M, 1.7) | |
| **29** | $C_{17}H_{36}OSi$ | 63 | ca. 100(0.05) | 1.4656(25) | | C, H | (EI) | 284 (M, 1.4) | |
| **30** | $C_{16}H_{25}ClOSi$ | 67 | ca. 170–175(0.5) | 1.5295(25) | | C, H, Cl | (CI) | 297 (M + 1, 40) | no C=O or OH |
| **11** | $C_4H_9ClSi$ | 45 | 114–116 | 1.4614(25) | | | (EI) | 120 (M, 13) | 2185 (Si–H) |
| **19** | $C_{12}H_{25}ClSi$ | 81 | 73(0.02) | 1.4650(25) | | | (EI) | 232 (M, 7) | |
| **25** | $C_{13}H_{28}Si$ | 77 | ca. 70(0.07) | 1.4552(25) | | exact mass | (EI) | 212 (M, 2) | |
| **21** | $C_8H_{17}ClOSi$ | 52 | 38–40(0.05) | 1.4622(25) | | | (EI) | no M+, 165 (32) | no C=C |
| **27** | $C_{16}H_{34}OSi$ | 84 | ca. 80–95(0.2–0.8) | 1.4624(25) | | C, H | (EI) | 270 (M, 0.5) | no OH or C=O |
| **28** | $C_{15}H_{23}ClOSi$ | 69 | ca. 160–163(0.5) | 1.5315(25) | | C, H, Cl | (EI) | 282 (M, 0.1) | no OH or C=O |
| **18** | $C_5H_{10}O$ | 62 | 71–72 | 1.3890(25) | [*24*] 71–72, 1.3910(22) | | | | 1645(C=C), 920(CH=CH$_2$) |
| **24** | $C_{10}H_{21}ClOSi$ | 81 | 60–62(0.03) | 1.4710(25) | | | (EI) | 220 (M, 0.3) | no CH=CH |
| **33** | $C_{18}H_{38}OSi$ | 69 | 125–130(0.9–1.1) | 1.4670(25) | | C, H | (EI) | 298 (M, 2) | |
| **34** | $C_{17}H_{27}ClOSi$ | 24 | ca. 145(0.3) | 1.5278(25) | | C, H, Cl | (CI) | 310 (M + 1, 27) | no OH or C=O |
| **23** | $C_9H_{19}ClOSi$ | 62 | 68–70(0.45) | 1.4675(25) | | | (CI) | 207 (M + 1, 54) | |
| **31** | $C_{17}H_{36}OSi$ | 58 | ca. 150 (0.4) | 1.4635(25) | | C, H | (EI) | 284 (M, 2) | no OH or C=O |
| **32** | $C_{16}H_{25}ClOSi$ | 30 | ca. 168–171(0.5) | 1.5279(25) | | C, H, Cl | (CI) | 297 (M + 1, 90) | no OH or C=O |
| **35** | $C_5H_{10}O_2$ | 40.1 | 90.5–91.5 | 1.3957(25) | [*25*, *26*] 96–97 | | (CI) | 103 (1.4, M + 1) | 1645(C=C), 920(CH=CH$_2$) |
| **36** | $C_6H_{12}O_2$ | 68.1 | 116–117 | 1.4026(25) | | C, H | (CI) | 117 (28, M + 1) | 1640(C=C), 918(CH=CH$_2$) |
| **37** | $C_{11}H_{15}ClSi$ | 72 | 74–75(0.05) | 1.5520(25) | | C, H, Cl | (EI) | no M+,211 (4) | 2140 (Si–H) |
| **38** | $C_{17}H_{27}ClO_2Si$ | 85 | 165(0.2) | 1.5221(25) | | C, H, Cl | (CI) | 327 (1.3, M + 1) | no OH or C=O |

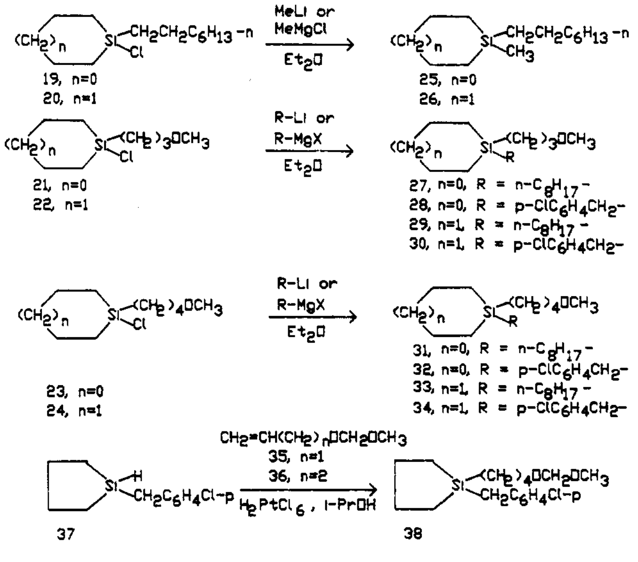
[a] Boiling point, bp, in °C. Pressure in mm. Temperature in °C. [b] In $CCl_4$.

**Scheme II**



ton. Corresponding hydrosilation reactions (*17*, *18*) employing the cyclic chlorosilanes **11** or **12** with one of the olefins **13**, **17**, or **18** yielded the set of trisubstituted chlorosilanes **19–24**.

**Scheme III**



Each of these water-sensitive chlorosilanes **19–24** was characterized by its NMR and mass spectra and by reaction with an organolithium or organomagnesium compound to form a tetrasubstituted silane (Scheme III). The $^1H$ and $^{13}C$ NMR spectra of these tetrasubstituted silanes **25–34** were used to establish that these products have been formed without rearrangement of the carbon skeletons. A related tetrasubstituted silane **38** was obtained by a hydrosilylation reaction of the trialkylsilane **37** with the terminal olefin **36**.

**Table II. NMR Spectra of Compounds Prepared**

| cmpd | (solv[a]) H NMR data | (solv[a]) C NMR data |
|---|---|---|
| **15** | (Car) 0.5–2.2 (m) | |
| **14** | (Car) 0.2–1.7 (17 H, m), –0.02 (9 H, s) | (Chl) 33.6 (t), 32.0 (t), 29.3 (t, 2 C), 24.0 (t), 22.7 (t), 16.8 (t), 14.2 (q), –1.6 (q, 3 C) |
| **16** | (Car) 0.6–1.7 (17 H, m), 0.37 (6 H, s) | |
| **12** | (Car) 4.87 (1 H, br s), 0.2–2.3 (12 H, m) | (Chl) 29.0 (t), 23.1 (t, 2 C), 14.8 (t, 2 C) |
| **20** | (Car) 0.2–2.2 (m) | |
| **26** | (Car) 0.2–2.4 (27 H, m), –0.02 (3 H, s) | (Chl) 33.7 (t), 32.0 (t), 30.2 (t), 29.4 (t, 2 C), 24.6 (t, 2 C), 23.8 (t), 22.8 (t), 14.1 (t, q, 2 C), 13.0 (t, 2 C), –4.8 (q) |
| **17** | (Car) 4.9–6.3 (3 H, m), 3.84 (d, of m), 3.23 (3 H, s) | |
| **22** | (Car) 3.30 (2 H, t), 3.25 (3 H, s), 0.4–2.2 (14 H, m) | (Chl) 74.3 (t), 58.2 (q), 29.2 (t), 23.5 (t, 2 C), 22.8 (t), 15.4 (t, 2 C), 13.1 (t) |
| **29** | (Car) 3.24 (2 H, t), 3.22 (3 H, s), 0.2–2.0(31 H, m) | (Chl) 75.5 (t), 58.2 (q)8 33.7 (t), 31.9 (t), 30.1 (t), 29.3 (t, 2 C), 24.5 (t, 2 C), 24.0 (t), 23.8 (t), 22.7 (t), 14.1 (q), 12.5 (t), 11.2 (t, 2 C), 8.5 (t) |
| **30** | (Car) 6.8–7.4 (4 H, m), 3.20 (5 H, s and t), 2.10 (2 H, s), 0.3–1.8 (16 H, m) | (Chl) 138.0 (s), 128.9 (s), 128.6 (d, 2 C), 127.6 (d, 2 C), 75.1 (t), 58.1 (q), 29.7 (t), 24.2 (t, 2 C), 23.6 (t), 22.1 (t), 10.6 (t, 2 C), 8.0 (t) |
| **11** | (Car) 5.13 (1 H, br), 0.4–2.0 (8 H, m) | (Chl) 25.7 (t, 2 C), 14.1 (t, 2 C) |
| **19** | (Car) 0.2–2.2 (m) | (Chl) 32.9 (t), 31.9 (t), 29.2 (t, 2 C), 26.0 (t, 2 C), 23.4 (t), 22.7 (t), 17.4 (t), 14.6 (t, 2 C), 14.1 (q) |
| **25** | (Car) 0.2–2.0 (25 H, m), 0.05 (3 H, s) | (Chl) 33.5 (t), 31.9 (t), 29.3 (t, 2 C), 27.3 (t, 2 C), 24.3 (t), 22.7 (t), 15.1 (t), 14.1 (q), 11.8 (t, 2 C), –3.2 (q) |
| **21** | (Car) 3.28 (2 H, t), 3.20 (3 H, s), 0.5–2.0 (12 H, m) | (Chl) 74.1 (t), 58.2 (q), 26.0 (t, 2 C), 23.5 (t), 14.6 (t, 2 C), 13.8 (t) |
| **27** | (Car) 3.28 (2 H, t), 3.23 (3 H, s), 0.2–2.0 (29 H, m) | (Chl) 75.4 (t), 58.1 (q), 33.6 (t), 31.9 (t), 29.2 (t, 2 C), 27.4 (t, 2 C), 24.4 (t, 2 C), 22.6 (t), 14.1 (t), 13.7 (q), 10.2 (t, 2 C), 9.8 (t) |
| **28** | (Chl) 6.8–7.4 (4 H, m), 3.25 (5 H, s and t), 2.10 (2 H, s), 0.3–1.8 (14 H, m) | (Chl) 138.1 (s), 129.1 (s), 128.6 (d, 2 C), 127.7 (d, 2 C), 74.9 (t), 58.1 (q), 27.1 (t, 2 C), 24.2 (t), 23.1 (t), 9.8 (t, 2 C), 9.5 (t) |
| **18** | (Car) 4.7–6.2 (3 H, m), 3.35 (2 H, t), 3.23 (3 H, s), 2.0–2.6 (2 H, m) | |
| **24** | (Car) 3.2–3.5 (5 H, m with s at 3.28), 0.3–2.1 (16 H, m) | (Chl) 72.0 (t), 58.2 (q), 32.8 (t), 29.2 (t), 23.4 (t, 2 C), 19.5 (t), 16.7 (t), 15.4 (t, 2 C) |
| **33** | (Car) 3.25 (2 H, t), 3.22 (3 H, s), 0.1–2.0 (33 H, m) | (Chl) 72.4 (t), 58.2 (q), 33.7 (t), 33.6 (t), 31.9 (t), 30.2 (t), 29.3 (t, 2 C), 24.5 (t, 2 C), 23.8 (t), 22.7 (t), 20.5 (t), 14.1 (q, ?), 12.4 (t, 2 C)8 11.3 (t, 2 C) |
| **34** | (Car) 6.6–7.4 (4 H, m), 3.0–3.4 (5 H, m with s at 3.22), 2.07 (2 H, s), 0.4–2.0 (16 H, m) | (Chl) 138.9 (s), 129.6 (s), 129.3 (d, 2 C), 128.3 (d, 2 C), 72.4 (t), 58.5 (q), 33.5 (t), 29.9 (t), 24.4 (t, 2 C), 22.3 (t), 20.3 (t), 11.8 (t), 10.8 (t, 2 C) |
| **23** | (Car) 3.30 (2 H, t), 3.23 (3 H, s), 0.2–2.0 (14 H, m) | (Chl) 72.0 (t), 58.2 (q), 32.6 (t), 26.0 (t, 2 C), 20.1 (t), 17.2 (t), 14.5 (t, 2 C) |
| **31** | (Car) 3.1–3.4 (5 H, m with s at 3.22), 0.3–1.7 (31 H, m) | (Chl) 72.4 (t), 58.2 (q), 38.5 (t, 2 C), 31.9 (t), 29.3 (t, 2 C), 27.4 (t, 2 C), 24.3 (t), 22.7 (t), 20.9 (t), 14.1 (q, ?), 13.7 (t, 2 C), 10.3 (t, 2 C) |
| **32** | (Chl) 6.8–7.4 (4 H, m), 3.2–3.6 (5 H, m with s at 3.25), 2.10 (2 H, s), 0.3–1.8 (16 H, m) | (Chl) 138.8 (s), 129.8 (s), 129.3 (d, 2 C), 128.3 (d, 2 C), 72.4 (t), 58.5 (q) 33.4 (t), 27.2 (t, 2 C), 23.3 (t), 20.8 (t), 13.2 (t), 10.0 (t, 2 C) |
| **35** | (neat) 4.9–6.3 (3 H, m), 4.59 (2 H, s), 4.05 (2 H, d of t), 3.30 (3 H, s) | (Chl) 134.6 (d), 116.9 (t), 95.8 (t), 68.3 (q), 55.2 (t) |
| **36** | (neat) 4.8–6.2 (3 H, m), 4.50 (2 H, s), 3.45 (2 H, t), 3.25 (3 H, s), 2.0–2.4 (2 H, m) | (Chl) 135.2 (d), 116.4 (t), 96.4 (t), 67.1 (t), 55.1 (q), 34.3 (t) |
| **37** | (Chl) 6.8–7.3 (4 H, m), 4.05 (1 H, m), 2.15 (2 H, d), 1.2–1.7 (4 H, m), 0.4–0.8 (4 H, m) | (Chl) 138.4 (s), 130.1 (s), 129.4 (d, 2 C), 128.5 (d, 2 C), 27.1 (t), 21.7 (t, 2 C), 8.7 (t, 2 C) |
| **38** | (Car) 6.8–7.2 (4 H, m), 4.60 (2 H, s), 3.50 (2 H, t), 3.30 (3 H, s), 2.15 (2 H, s), 1.3–1.8 (6 H, m), 0.4–0.8 (4 H, m) | (Chl) 138.7 (s), 129.7 (s), 129.1 (d, 2 C), 128.3 (d, 2 C), 96.4 (t), 67.3 (t), 55.0 (q), 33.4 (t), 27.2 (t, 2 C), 23.3 (t), 20.8 (t), 13.1 (t), 9.9 (t, 2 C) |

[a] Car = carbon tetrachloride; Chl = deuteriochloroform.

## Experimental Section

All melting points are corrected and all boiling points are uncorrected. The IR spectra were determined with a Perkin Elmer, Model 299, infrared recording spectrophotometer fitted with a grating. The $^{1}$H NMR spectra were determined at 60 mHz with a Varian, Model T-60A, NMR spectrometer or at 300 mHz with a Bruker, Model WM-300, NMR spectrometer. The $^{13}$C NMR spectra were determined at 25 mHz with a JEOL, Model PFT-100, NMR spectrometer or at 75 mHz with a Bruker, Model WM-300, NMR spectrometer. The chemical shift values are expressed in values (ppm) relative to a $Me_4Si$ internal standard. The mass spectra were obtained with either a Hitachi (Perkin Elmer), Model RMU-7, or a Varian MAT, Model 112S, mass spectrometer. All reactions involving strong bases or reactive organometallic intermediates were performed under a nitrogen atmosphere.

***Preparation and Characterization of the Silanes and Related Compounds.*** The chlorosilane intermediates whose preparations are summarized in Scheme II were characterized by their physical and spectral properties (Tables I and II), but no effort was made to obtain analytical samples of these water-sensitive materials. The silanes prepared as summarized in Scheme III were fully characterized as indicated in Tables I and II. Descriptions of the preparation and purification of each of the compounds listed in Table I are available in the supplementary material.

**Registry No.** **9**, 110-52-1; **10**, 111-24-0; **11**, 55437-96-2; **12**, 18339-91-8; **13**, 111-66-0; **14**, 3429-76-3; **15**, 5283-66-9; **16**, 18162-84-0; **17**, 627-40-7; **18**, 4696-30-4; **19**, 99165-24-9; **20**, 99165-25-0; **21**, 99165-26-1; **22**, 99165-27-2; **23**, 99165-28-3; **24**, 99165-29-4; **25**, 99165-30-7; **26**, 99165-31-8; **27**, 99165-32-9; **28**, 99165-33-0; **29**, 99165-34-1; **30**, 99165-35-2; **31**, 99165-36-3; **32**, 99165-37-4; **33**, 99165-38-5; **34**, 99165-39-6; **35**, 62322-45-6; **36**, 99165-40-9; **37**, 99165-41-0; **38**, 99165-42-1; $H_2PtCl_6$, 16941-12-1; $HSiCl_3$, 10025-78-2; MeCl, 74-87-3; $Me_2SiHCl$, 1066-35-9; $CH_2{=}CHCH_2OH$, 107-18-6; *n*-$C_8H_{17}Cl$, 111-85-3; *n*-$C_{16}H_{33}Li$, 65018-36-2; *n*-$C_{16}H_{34}$, 544-76-3; *p*-$ClC_6H_4CH_2Cl$, 104-83-6; MeLi, 917-54-4; *n*-$C_8H_{17}Br$, 111-83-1; $CH_3OCH_2Cl$, 107-30-2; $CH_2{=}CHCH_2Br$, 106-95-6; $CH_2{=}CH(CH_2)OH$, 627-27-0; HCHO, 50-00-0; *p*,*p*′-dichlorobibenzyl, 5216-35-3.

*J. Chem. Eng. Data* **1986**, *31*, 127-129

## Literature Cited

(1) House, H. O.; Lusch, M. J. *J. Org. Chem.* **1977**, *42*, 183.
(2) House, H. O.; Phillips, W. V. *J. Org. Chem.* **1978**, *43*, 3851.
(3) House, H. O.; Phillips, W. V.; VanDerveer, D. *J. Org. Chem.* **1979**, *44*, 2400.
(4) House, H. O.; Yau, C. C.; VanDerveer, D. *J. Org. Chem.* **1979**, *44*, 3031.
(5) Fessenden, R. J.; Seeler, K.; Dagani, M. *J. Org. Chem.* **1966**, *31*, 2483.
(6) Whitesides, G. M.; Sevenair, J. P.; Goetz, R. W. *J. Am. Chem. Soc.* **1967**, *89*, 1135.
(7) Ouellette, R. J.; Baron, D.; Stolfo, J.; Rosenblum, A.; Weber, P. *Tetrahedron* **1972**, *28*, 2163.
(8) Kitching, W.; Olszowy, H. A.; Drew, G. M. *J. Org. Chem.* **1982**, *47*, 5153.
(9) Berti, G.; Crotti, P.; Macchia, F.; Domiano, P. *J. Chem. Soc., Perkin Trans. 2* **1984**, 1987.
(10) Eliel, E. L.; Allinger, N. L.; Angyal, S. J.; Morrison, G. A. "Conformational Analysis"; Wiley-Interscience: New York, 1966.
(11) Corriu, R. *Organomet. Chem. Rev.* **1978**, *9*, 357.
(12) Corriu, R. J. P.; Guerin, C. *J. Organomet. Chem.* **1980**, *198*, 231.
(13) Eaborn, C.; Walton, D. R. M.; Seconi, G. *J. Chem. Soc., Perkin Trans. 2* **1976**, 1857.
(14) Macciantelli, D.; Seconi, G.; Eaborn, C. *J. Chem. Soc., Perkin Trans. 2* **1978**, 834.
(15) Eaborn, C.; Jenkins, I. D.; Seconi, G. *J. Organomet. Chem.* **1977**, *131*, 387.
(16) Andersen, N. H.; McGrae, D. A.; Grotjahn, D. B.; Gabhe, S. Y.; Theodore, L. J.; Ippolito, R. M.; Sarkar, T. K. *Tetrahedron* **1981**, *37*, 4069.
(17) Speier, J. L. *Adv. Organomet. Chem.* **1979**, *17*, 407.
(18) Benkeser, R. A.; Kang, J. *J. Organomet. Chem.* **1980**, *185*, C9.
(19) Pike, R. A. *J. Org. Chem.* **1962**, *27*, 2186.
(20) Abel, E. W.; Bush, R. P. *Trans. Faraday Soc.* **1963**, *59*, 630.
(21) Andrianov, K. A.; Izmailov, B. A.; Lodkina, A. A.; Pronchenkov, S. M. *Zh. Obshch. Khim.* **1977**, *47*, 1061.
(22) West, R. *J. Am. Chem. Soc.* **1954**, *76*, 6012.
(23) Watanabe, W. H.; Conlon, L. E.; Hua, J. C. H. *J. Org. Chem.* **1958**, *23*, 1666.
(24) Takakis, I. M.; Rhodes, Y. E. *J. Org. Chem.* **1978**, *43*, 3496.
(25) Taskinen, E.; Laehteenmaeki, H. *Tetrahedron* **1976**, *32*, 2331.
(26) Hoffmann, R. W.; Kemper, B. *Tetrahedron Lett.* **1982**, *23*, 845.

Received for review June 12, 1985. Accepted August 19, 1985. A portion of this research has been supported by Public Health Service Grant R01-GM-30735 from the National Institute of General Medical Science. The execution of this research was also assisted by Institutional Research Grants from the National Science Foundation for the purchase of a mass spectrometer and a Fourier transform NMR spectrometer.

**Supplementary Material Available:** Descriptions of the preparation and purification of each of the compounds listed in Table I (22 pages). Ordering information is given on any masthead page.

---

# Preparation of New 9-Alkylthio-1,2,3,4-tetrahydroacridine Monomers and Dimers

**Geneviève Giovannangeli, Jean-Claude Soyfer, Jean-Pierre Galy, and Jacques Barbe***

*Groupe d'Etudes et de Recherches en Chimie Thérapeutique Organique et Physique (G.E.R.C.T.O.P.), UER de Pharmacie, 13385 Marseille Cedex 5, France*

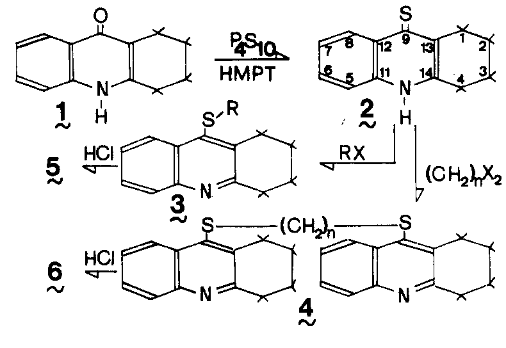
**New compounds related to 1,2,3,4-tetrahydroacridine have been prepared and characterized. These monomeric as well as dimeric derivatives are of specific interest with respect to parasites.**

From a chemical point of view, there are no extensive studies about 1,2,3,4-tetrahydro-9-acridanones. Moreover, pharmacological properties of these compounds are not yet well-known, although antimalarials have been pointed out in this series (*1*). In addition, it must be emphasized that results concerning the 9-thio-substituted derivatives are the rarest among those of the compounds under discussion, despite the biological interest of the thio group.

That is why we were interested in the preparation of the following 9-thioalkyl-1,2,3,4-tetrahydroacridines, **3**, and 9,9′-dithio-1,2,3,4-tetrahydroacridinyl-$\alpha,\omega$-alkanes, **4**, within our researches into antiparasitics.

Results regarding **3** are gathered in Table I while results regarding **4** are collected in Table II. In addition $^{13}C$ NMR data concerning hydrochlorides are presented in Table III.

Scheme I



These compounds were prepared in good yield by using phase-transfer catalysis as previously done with other acridinics (*2–4*). Starting materials were either mono- or dihalogenoalkanes and 9-thio-1,2,3,4-tetrahydroacridanone (**2**). The latter has been prepared from 1,2,3,4-tetrahydro-9-acridanone (**1**) by means of phosphorus pentasulfide thiation (*5*) (Scheme I). The synthetic pathway proposed herein is a very convenient one for the preparation of antiamoebic or trypanocidal drugs (*6*).

## General Procedure

A stirred mixture of 9-thio-1,2,3,4-tetrahydroacridanone (**2**) (10 mmol), alkylating agents (5 mmol in the case of **4**; 25 mmol in the case of **3**), triethylbenzylammonium chloride (3 mmol),

0021-9568/86/1731-0127$01.50/0 © 1986 American Chemical Society