

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; 2A, 2623-95-2; 2B, 2623-84-9; 2C, 111-56-8; 2D, 10520-81-7; 2E, 18263-25-7; 2F, 142-94-9; 2G, 89367-98-6; 2H, 20828-43-7; 3A, 67552-88-9; 3B, 99097-95-7; 3C, 67491-92-3; 3D, 67491-93-4; 3E, 67491-94-5; 3F, 67491-95-6; 3G, 99097-96-8; 3H, 99097-97-9; H₂NCH₂CH₂OH, 141-43-5.

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Synthesis of Certain Cyclic Silanes

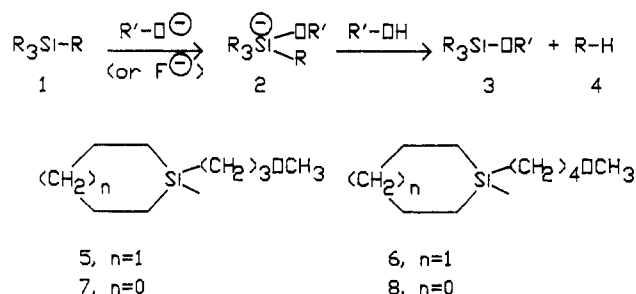
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The chlorotrialkylsilanes **21-24** have been synthesized as precursors to potential steric blocking groups for alkanes and cycloalkanes. Reaction of these chlorosilanes with one of the organometallic reagents methylolithium, methylmagnesium chloride, *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, R₃Si-. Such substituents, R₃Si-, 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, R₃Si-, might be possible. In order to investigate this possibility, we

Scheme I



have studied synthetic routes to silanes incorporating the tri-substituted silyl groups **5-8**. This paper describes the synthesis and characterization of these silanes.

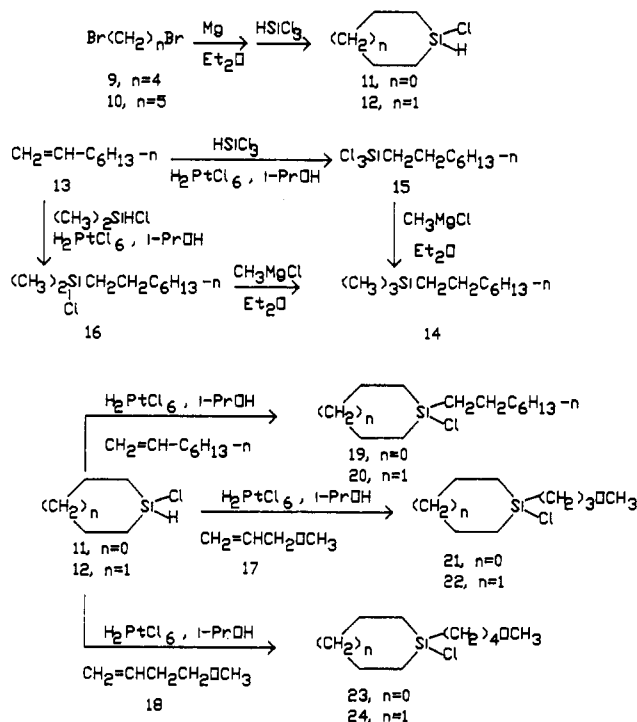
The syntheses began with the conversion of each dibromide **9** or **10** to the corresponding bis-Grignard reagent followed by reaction with trichlorosilane (Scheme II). Subsequent orienting experiments were performed in which 1-octene (**13**) was converted to the silane **14** via either of the hydrosilylation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

Table I. Physical Properties^a of Compounds Prepared

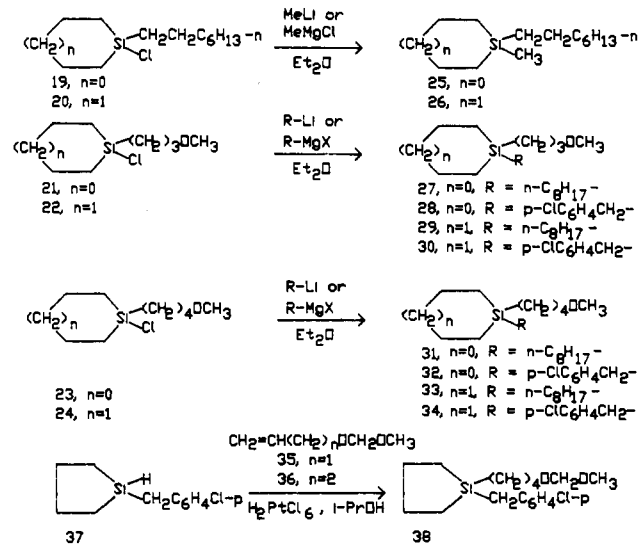
compd	formula	yield, %	bp (press.)	n_D (temp)	[ref] bp(press.), n_D (temp)	analyses	MS (EI/CI) M(Int)	IR data, ^b cm ⁻¹
15	C ₈ H ₁₇ Cl ₃ Si	96	57-58(1.2)	1.4463(25)	[19] 68(1.6), 1.4458(25)		(EI) 246 (M, 1)	
14	C ₁₁ H ₂₆ Si	88	89-90(9)	1.4222(25)	[20] 63(1.2), 1.4272(25)	C, H	(EI) 186 (M, 1)	
16	C ₁₀ 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 ₈ H 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 ₄ H ₈ O	70	41.5-42.5	1.3744(25)	[23] 42-42.3, 1.3759(25)			1645(C=C), 914(CH=CH ₂)
22	C ₉ H ₁₉ ClOSi	53	55(0.05)	1.4701(25)			(EI) 206 (M, 1.7)	
29	C ₁₇ H ₃₈ 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 ₄ H ₉ ClSi	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 ₉ H 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 ₆ H 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 ₉ H ₁₉ ClOSi	62	68-70(0.45)	1.4675(25)			(CI) 207 (M + 1, 54)	
31	C ₁₇ H ₃₈ 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 ₆ H 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 ₈ H 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 ₂ Si	85	165(0.2)	1.5221(25)		C, H, Cl	(CI) 327 (1.3, M + 1)	no OH or C=O

^aBoiling point, bp, in °C. Pressure in mm. Temperature in °C. ^bIn CCl₄.

Scheme II



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 ¹³C 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.

ton. Corresponding hydrosilylation 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.

Table II. NMR Spectra of Compounds Prepared

compd	(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 ¹H 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 ¹³C 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 Me₄Si 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, 4698-30-4; 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; H₂PtCl₆, 16941-12-1; HSiCl₃, 10025-78-2; MeCl, 74-87-3; Me₂SiHCl, 1066-35-9; CH₂=CHCH₂OH, 107-18-6; *n*-C₈H₁₇Cl, 111-85-3; *n*-C₁₀H₂₃Li, 65018-38-2; *n*-C₁₀H₂₄, 544-76-3; *p*-ClC₆H₄CH₂Cl, 104-83-6; MeLi, 917-54-4; *n*-C₈H₁₇Br, 111-83-1; CH₃OCH₂Cl, 107-30-2; CH₂=CHC-H₂Br, 106-95-6; CH₂=CH(CH₂)OH, 627-27-0; HCHO, 50-00-0; *p*,*p*'-di-chlorobenzyl, 5216-35-3.

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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

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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.

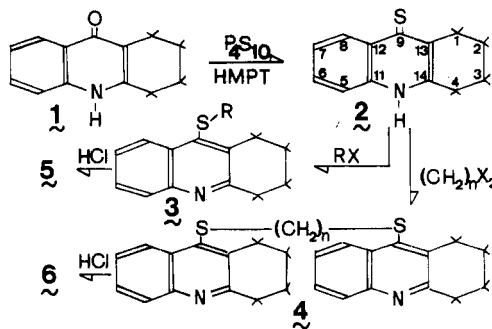
From a chemical point of view, there are no extensive studies about 1,2,3,4-tetrahydro-9-acridanones. Moreover, pharmacological properties of these compounds are not yet well-known, although antimalarials have been pointed out in this series (1). In addition, it must be emphasized that results concerning 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- α,ω -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.

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

Scheme I



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 antiamebic 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),