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PHASE TRANSFER CATALYTIC SYNTHESIS OF SILYL DERIVATIVES OF HETEROCYCLIC THIOLS

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Reactions of heteroaromatic thiols with trialkylsilylalkyl iodides in the two-phase catalytic system (solid K_2CO_3/18-crown-6/toluene) at 111°C selectively lead to formation of the corresponding (trialkylsilylalkyl)thiohetarenes. 6-Mercaptopurine in the presence of two equivalents of alkylating agent yields S,N-dialkylated derivatives.

Heteroaromatic sulfides are of interest as biologically active compounds. For example, pyridyl sulfides have diuretic [1], anti-ulcer [1-4], anti-inflammatory [1, 5], analgesic [6, 7], antidepressant [8], antihypertensive [9, 10], cardioprotective [11], gluconeogenesis inhibiting [12], leukotriene antagonist [13], anticoagulant [14], radioprotective [15], antibacterial [16, 17], tuberculostatic [18], antimycotic [19], antifungal [20-22], internal parasiticidal [23], insecticidal [24-26], pesticidal [27], and herbicidal [28-32] activity. Quinoline sulfides have anticancer [33, 34], leukotriene antagonist [35], antispasmodic [36], antithrombotic [37], 5-hydroxytryptamine antagonist [38], proteinase inhibiting [39], sedative [40], analgesic and anti-inflammatory [41, 42], antibacterial [43-46], antimalarial [47], radioprotective [48], herbicidal [49, 50], insecticidal [50], and antifungal [51] activity. HIV-1 [52] and protein kinase [53] inhibiting activity has recently been observed in pyrimidine sulfides.

Heteroaromatic S-ethers have been usually obtained by reaction of the corresponding hetarylthiols with alkyl halides in the presence of an aqueous solution of KOH [43] or NaOH [52], or NaH in dimethylformamide [38]. Recently we demonstrated that it is possible to obtain pyridyl sulfides from acetylthiopyridines in an alkyl halide/solid KOH/18-crown-6/benzene phase transfer catalytic (PTC) system [54].

We have developed a new PTC method for synthesis of (trialkylsilylalkyl)thiohetarenes VII-XII with a view toward studying them as cholesterol-lowering agents. Thus heteroaromatic thiols I-V in the trialkylsilylalkyl iodide ($R^1R^2R^3Si(CH_2)_nI$, n = 1, 3)/solid K_2CO_3/18-crown-6/toluene phase transfer catalytic system at 111°C selectively yield the corresponding silyl derivatives of thiols VII-XIa-d (Table 1).

$$\underset{\text{I–V}}{\text{HetSH}} \xrightarrow[\text{PhMe / 111 °C}]{\text{I(CH}_2)_n\text{SiR}^1\text{R}^2\text{R}^3 \,/\, \text{K}_2\text{CO}_3 \,/\, \text{18-crown-6}} \underset{\text{VIIa-d – XIa-d}}{\text{HetS(CH}_2)_n\text{SiR}^1\text{R}^2\text{R}^3}$$

But the reaction of 6-mercaptopurine VI in the presence of two equivalents of alkylating agent ($R^1R^2R^3Si(CH_2)_nI$) in the two-phase catalytic system (solid K_2CO_3/18-crown-6/toluene) leads to the corresponding S,N-dialkylated derivatives XIIa,b,d (see Table 1 and the Experimental).

* Dedicated to the 100th anniversary of the birth of Academician A. N. Nesmeyanov.

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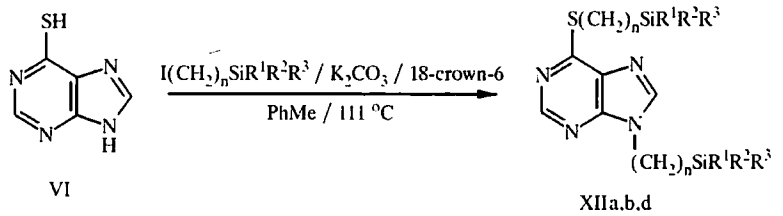
TABLE 1. Synthesis of Silyl Derivatives of Heterocyclic Thiols ($HetSH/R^1R^2R^3Si(CH_2)_nI/K_2CO_3$/18-crown-6, 1:1:2.5:0.1)

Starting thiol	Hetaryl	$SiR^1R^2R^3$	n	Reaction time, h	Product	Yield, %
I	2-Pyridyl	$SiMe_3$	1	5	VIIa	81
I	2-Pyridyl	$SiMe_3$	3	8	VIIb	66
I	2-Pyridyl	1-Methyl-1-silacyclopentyl	3	10	VIIc	40
I	2-Pyridyl	1-Methyl-1-silacyclohexyl	3	9	VIId	60
II	2-Pyrimidyl	$SiMe_3$	1	9	VIIIa	46
II	2-Pyrimidyl	$SiMe_3$	3	9	VIIIb	77
II	2-Pyrimidyl	1-Methyl-1-silacyclopentyl	3	8	VIIIc	92
II	2-Pyrimidyl	1-Methyl-1-silacyclohexyl	3	6	VIIId	73
III	2-(1-Methylimidazolyl)	$SiMe_3$	1	6	IXa	59
III	2-(1-Methylimidazolyl)	$SiMe_3$	3	8	IXb	61
IV	8-Quinolyl	$SiMe_3$	1	7	Xa	45
IV	8-Quinolyl	$SiMe_3$	3	7	Xb	33
IV	8-Quinolyl	1-Methyl-1-silacyclopentyl	3	21	Xc	20
IV	8-Quinolyl	1-Methyl-1-silacyclohexyl	3	9	Xd	24
V	2-Benzothiazolyl	$SiMe_3$	1	10	XIa	41
V	2-Benzothiazolyl	$SiMe_3$	3	10	XIb	65
V	2-Benzothiazolyl	1-Methyl-1-silacyclopentyl	3	9	XIc	70
VI	6-Purinyl*	$SiMe_3$	1	9	XIIa	26
VI	6-Purinyl*	$SiMe_3$	3	9	XIIb	35
VI	6-Purinyl*	1-Methyl-1-silacyclohexyl	3	10	XIId	38

* $HetSH:R^1R^2R^3Si(CH_2)_nI$ = 1:2; S- and N-disubstituted compounds.



VI XIIa,b,d

The (trialkylsilylalkyl)thiohetarenes obtained in our work were identified by PMR and mass spectroscopy (see Experimental).

EXPERIMENTAL

The PMR spectra were recorded on a Varian 200 Mercury spectrometer in $CDCl_3$, internal standard HMDS. The mass spectra were obtained on a GC-MS HP 6890 chromatograph/mass spectrometer (70 eV). The GLC analysis was done on a Chrom-5 chromatograph with flame-ionization detector and a glass column packed with 5% OV-101 on Chromosorb W-HP (80-100 mesh), analysis temperature 180-250°C. The 2-mercaptopyridine I, 2-mercaptopyrimidine II, 2-mercapto-1-methylimidazole III, 2-mercaptobenzothiazole V, 6-mercaptopurine VI,

(iodomethyl)trimethylsilane (all Aldrich) and 8-mercaptoquinoline IV (Reakhim) were used without additional treatment. The (γ-iodopropyl)trimethylsilane, 1-(γ-iodopropyl)-1-methylsilacyclopentane, 1-(γ-iodopropyl)-silacyclohexane were obtained by a Grignard reaction [55, 56].

Typical Procedure for Synthesis of Silyl Derivatives of Hetarylthiols VII-XIa-d Under Phase Transfer Catalytic Conditions. Powdered K_2CO_3 (3.5 g, 25 mmol) was added to a solution of 10 mmol of thiol I-V, 10 mmol of the corresponding silane, and 0.264 g (1 mmol) of 18-crown-6 in 25 ml of toluene. The mixture was boiled with vigorous stirring until the substrates completely disappeared (monitored by GLC, see Table 1), then filtered through a thin layer of silica gel, and then the toluene was evaporated under vacuum. The compounds VII-XIa-d were isolated by column chromatography (eluent benzene–EtOAc in various ratios), identified by PMR and mass spectroscopy and also by elemental analysis. The purity of the compounds obtained was confirmed by HPLC. In most cases, elemental analysis was impossible due to the high lability of the compounds.

2-[Trimethylsilylmethyl)thio]pyridine (VIIa). PMR spectrum: 0.13 (9H, s, $Si(CH_3)_3$); 2.33 (2H, s, CH_2); 6.94 (1H, m, 5-H); 7.21 (1H, m, 3-H); 7.41 (1H, m, 4-H); 8.45 ppm (1H, m, 6-H). Mass spectrum, *m/z* (I_{rel}, %): 197 (M^+, 2), 181 (14), 182 (M^+ - Me, 100), 150 (15), 78 (17), 73 (33), 51 (10), 45 (13), 43 (10). Impurities: < 1% (on Symmetry C_{18}, 3.9×150 mm, CH_3CN: 0.2 moles, acet. buffer, pH 5, 70:30).

2-[3-Trimethylsilylpropyl)thio]pyridine (VIIb). PMR spectrum: 0.13 (9H, s, $Si(CH_3)_3$); 0.72 (2H, m, CH_2Si); 1.80 (2H, m, $CH_2C\underline{H}_2CH_2Si$); 3.27 (2H, t, J = 7.6 Hz, SCH_2); 7.00 (1H, m, 5-H); 7.25 (1H, m, 3-H); 7.91 (1H, m, 4-H); 8.49 ppm (1H, m, 6-H). Mass spectrum, *m/z* (I_{rel}, %): 225 (M^+, 4), 210 (M^+ - Me, 15), 182 (12), 178 (16), 168 (37), 138 (17), 125 (19), 124 (12), 112 (16), 111 (100), 78 (22), 73 (59), 59 (11), 45 (22), 43 (14). Impurities: < 1% (on Ultrasphere, 4.6×250 mm, EtOAc–hexane, 4:96).

2-{[3-(1-Methyl-1-silacyclopentyl)propyl]thio}pyridine (VIIc). PMR spectrum: 0.18 (3H, s, $SiCH_3$); 0.73 (6H, m, $SiCH_2$); 1.69 (6H, m, $CH_2(C\underline{H}_2)_2CH_2$ for the silacycle and $CH_2C\underline{H}_2CH_2Si$); 3.20 (2H, t, J = 7.0 Hz, SCH_2); 6.97 (1H, m, 5-H); 7.22 (1H, m, 3-H); 7.47 (1H, m, 4-H); 8.49 ppm (1H, m, 6-H). Mass spectrum, *m/z* (I_{rel}, %): 251 (M^+, 3), 223 (16), 222 (50), 208 (13), 195 (15), 194 (34), 182 (13), 181 (65), 168 (17), 167 (2-$PyS(CH_2)_2$, 100), 154 (30), 153 (10), 152 (15), 138 (32), 124 (10), 111 (55), 108 (33), 99 (28), 97 (25), 93 (25), 83 (13), 78 (51), 75 (10), 71 (39), 67 (14), 59 (21), 55 (12), 53 (10), 51 (18), 45 (36), 43 (44), 41 (10), 39 (19). Impurities: < 1% (on Ultrasphere, 4.6×250 mm, EtOAc–hexane, 4:96).

2-{[3-(1-Methyl-1-silacyclohexyl)propyl]thio}pyridine (VIId). PMR spectrum: 0.20 (3H, s, $SiCH_3$); 0.80 (6H, m, $SiCH_2$); 1.81 (8H, m, $CH_2(C\underline{H}_2)_3CH_2$ for the silacycle and $CH_2C\underline{H}_2CH_2Si$); 3.38 (2H, t, J = 7.2 Hz, SCH_2); 7.11 (1H, m, 5-H); 7.35 (1H, m, 3-H); 7.62 (1H, m, 4-H); 8.64 ppm (1H, m, 6-H). Mass spectrum, *m/z* (I_{rel}, %): 265 (M^+, 13), 223 (23), 222 (100), 195 (13), 194 (38), 181 (50), 180 (34), 167 (2-$PyS(CH_2)_2$, 44), 154 (12), 152 (10), 138 (24), 113 (22), 111 (69), 110 (14), 85 (60), 78 (33), 67 (13), 59 (32), 51 (14), 45 (24), 43 (43), 41 (13), 39 (14). Impurities: 1.6% (on Symmetry C_{18}, 3.9×150 mm, CH_3CN–H_2O, 90:10).

2-[(Trimethylsilylmethyl)thio]pyrimidine (VIIIa). PMR spectrum: 0.15 (9H, s, $Si(CH_3)_3$); 2.40 (2H, s, CH_2); 6.93 (1H, t, J = 5.0 Hz, 5-H); 8.51 ppm (2H, d, J = 5.0 Hz, 4-H and 6-H). Mass spectrum, *m/z* (I_{rel}, %): 198 (M^+, 3), 184 (14), 183 (M^+-Me, 100, 73 ($SiMe_3$, 38), 72 (12), 59 (10), 45 (18), 43 (12). Impurities: 1% (on Symmetry C_{18}, 3.9×150 mm, CH_3CN–H_2O, 80:20).

2-[(3-Trimethylsilylpropyl)thio]pyrimidine (VIIIb). PMR spectrum: 0.02 (9H, s, $Si(CH_3)_3$); 0.67 (2H, m, CH_2Si); 1.73 (2H, m, $CH_2C\underline{H}_2CH_2Si$); 3.15 (2H, t, J = 7.6 Hz, SCH_2); 6.93 (1H, t, J = 5.0 Hz, 5-H); 8.51 ppm (2H, d, J = 5.0 Hz, 4-H and 6-H). Mass spectrum, *m/z* (I_{rel}, %): 226 (M^+, 13), 211 (M^+-Me, 34), 183 (22), 179 (12), 169 (65), 116 (13), 112 (54), 73 ($SiMe_3$, 100), 72 (12), 59 (20), 53 (13), 45 (30), 43 (18). Impurities: < 1% (on Symmetry C_{18}, 3.9×150 mm, CH_3CN–H_2O, 80:20).

2-{[3-(1-Methyl-1-silacyclopentyl)propyl]thio}pyrimidine (VIIIc). PMR spectrum: 0.06 (3H, s, $SiCH_3$); 0.51 and 0.74 (6H, m and m, $SiCH_2$); 1.53 (4H, m, $CH_2(C\underline{H}_2)_2CH_2$ for silacycle); 1.75 (2H, m, $CH_2C\underline{H}_2CH_2Si$); 3.36 (2H, t, J = 7.2 Hz, SCH_2); 6.92 (1H, t, J = 5.2 Hz, 5-H); 8.48 ppm (2H, d, J = 5.2 Hz, 4-H and 6-H). Mass spectrum, *m/z* (I_{rel}, %): 252 (M^+, 6), 237 (M^+-Me, 8), 224 (17), 223 (53), 219 (10), 211 (10), 210 (11), 209 (18), 196 (21), 195 (43), 183 (15), 182 (66), 181 (43), 169 (16), 168 (100), 154 (25), 153 (11), 152 (20), 138 (19), 117 (12), 113 (15), 112 (20), 107 (17), 99 (40), 97 (30), 94 (42), 79 (16), 75 (14), 71 (48), 59 (26), 57 (13), 55 (15), 53 (21), 45 (40), 43 (48), 42 (14), 41 (19). Impurities: < 1% (on Ultrasphere, 4.6×250 mm, EtOAc–hexane, 4:96).

2-{[3-(1-Methyl-1-silacyclohexyl)propyl]thio}pyrimidine (VIIId). PMR spectrum: 0.12 (3H, s, $SiCH_3$); 0.66 (6H, m, $SiCH_2$); 1.72 (8H, m, $CH_2(C\underline{H}_2)_3CH_2$ for the silacycle and $CH_2C\underline{H}_2CH_2Si$); 3.21 (2H, t, J = 7.4 Hz, SCH_2); 6.99 (1H, t, J = 5.0 Hz, 5-H); 8.56 ppm (2H, d, J = 5.0 Hz, 4-H and 6-H). Mass spectrum, *m/z* (I_{rel}, %): 266 (M^+, 10), 225 (13), 224 (22), 223 (100), 197 (10), 196 (19), 195 (40), 183 (10), 182 (47), 181 (37), 168 (37), 155 (10), 153 (10), 148 (12), 138 (14), 113 (40), 112 (17), 111 (10), 86 (11), 85 (71), 84 (12), 83 (10), 79 (11), 75 (10), 71 (13), 59 (35), 58 (11), 57 (12), 55 (11), 53 (19), 45 (28), 43 (45), 42 (12), 41 (20), 39 (10). Impurities: 1% (on Symmetry C_{18}, 3.9×150 mm, CH_3CN–H_2O, 90:10).

2-[(Trimethylsilylmethyl)thio]imidazole (IXa). PMR spectrum: 0.23 (9H, s, $Si(CH_3)_3$); 2.40 (2H, s, CH_2); 3.57 (3H, s, NCH_3); 6.96 ppm (2H, m, protons on the imidazole ring). Mass spectrum, *m/z* (I_{rel}, %): 200 (M^+, 5), 186 (14), 185 (M^+-Me, 100), 96 (14), 95 (20), 73 (30), 72 (13), 59 (14), 45 (15), 43 (14), 42 (15). Impurities: 1% (on Zorbax ODS, 4.6×250 mm, MeOH).

2-[3-Trimethylsilylpropyl)thio]imidazole (IXb). PMR spectrum: 0.03 (9H, s, $Si(CH_3)_3$); 0.91 (2H, m, CH_2Si); 1.64 (2H, m, $CH_2C\underline{H}_2CH_2Si$); 3.10 (2H, t, J = 7.0 Hz, SCH_2); 3.60 (3H, s, NCH_3); 7.20 ppm (2H, m, protons on the imidazole ring). Mass spectrum, *m/z* (I_{rel}, %): 28 (M^+, 5), 213 (M^+-Me, 10), 181 (17), 171 (39), 114 (100), 73 (49), 72 (15), 59 (11), 45 (18), 43 (10), 41 (13). Impurities: 1% (on Supelcosil LC Si, 4.6×250 mm, MeOH-EtOAc, 10:90).

8-[(Trimethylsilylmethyl)thio]quinoline (Xa). PMR spectrum: 0.15 (9H, s, $Si(CH_3)_3$); 2.11 (2H, s, CH_2); 7.33, 8.02, and 8.89 ppm (6H, all m, protons on the quinoline ring). Mass spectrum, *m/z* (I_{rel}, %): 247 (M^+, 29), 233 (19), 232 (M^+-Me, 100), 201 (12), 200 (59), 199 (10), 188 (22), 186 (21), 174 (62), 156 (17), 143 (26), 142 (75), 130 (22), 129 (24), 128 (11), 116 (10), 102 (11), 75 (11), 73 (66), 59 (10), 45 (35), 43 (17). Impurities: 1.5% (on Symmetry C_{18}, 3.9×150 mm, CH_3CN–H_2O, 80:20).

8-[(3-Trimethylsilylpropyl)thio]quinoline (Xb). PMR spectrum: 0.13 (9H, s, $Si(CH_3)_3$; 0.93 (2H, m, CH_2Si); 2.47 (2H, m, $CH_2C\underline{H}_2CH_2Si$); 3.73 (2H, t, J = 7.0 Hz, SCH_2); 7.60, 8.26, and 9.06 ppm (6H, all m, protons on the quinoline ring). Mass spectrum, *m/z* (I_{rel}, %): 275 (M^+, 4), 260 (M^+-Me, 10), 242 (23), 218 (23), 188 (48), 175 (28), 174 (100), 161 (50), 142 (10), 130 (11), 129 (24), 73 (59), 45 (23), 43 (10). Impurities: 1% (on Symmetry C_{18}, 3.9×150 mm, CH_3CN–H_2O, 80:20).

8-{[3-(1-Methyl-1-silacyclopentyl)propyl]thio}quinoline (Xc). PMR spectrum: 0.13 (3H, s, $SiCH_3$); 0.71 (6H, m, $SiCH_2$); 1.71 (6H, m, $CH_2(C\underline{H}_2)_2CH_2$ for the silacycle and $CH_2C\underline{H}_2CH_2Si$); 3.07 (2H, t, J = 7.0 Hz, SCH_2); 7.40, 8.05, and 8.92 ppm (6H, all m, protons on the quinoline ring). Mass spectrum, *m/z* (I_{rel}, %): 301 (M^+, 14), 286 (M^+-Me, 14), 272 (42), 254 (51), 244 (61), 230 (27), 217 (74), 202 (81), 188 (100), 174 (65), 161 (96), 156 (55), 141 (39), 142 (40), 129 (56), 116 (24), 99 (38), 89 (20), 71 (36), 59 (24), 45 (44), 43 (49). Impurities: < 1% (on Ultrasphere, 4.6×250 mm, EtOAc–hexane, 4:96).

8-{[3-(1-Methyl-1-silacyclohexyl)propyl]thio}quinoline (Xd). PMR spectrum: 0.04 (3H, s, $SiCH_3$); 0.76 (6H, m, $SiCH_2$); 1.67 (8H, m, $CH_2(C\underline{H}_2)_3CH_2$ for the silacycle and $CH_2C\underline{H}_2CH_2Si$); 3.00 (2H, t, J = 7.0 Hz, SCH_2); 7.36, 8.06, and 8.96 ppm (6H, all m, protons on the quinoline ring). Mass spectrum, *m/z* (I_{rel}, %): 315 (M^+, 31), 300 (M^+-Me, 10), 282 (10), 271 (25), 272 (100), 258 (10), 244 (44), 230 (40), 217 (41), 202 (39), 188 (78), 174 (88), 161 (99), 143 (23), 142 (26), 129 (50), 113 (29), 102 (17), 89 (18), 85 (86), 75 (10), 59 (43), 45 (33), 43 (54), 41 (10). Impurities: 1% (on Symmetry C_{18}, 3.9×150 mm, CH_3CN–H_2O, 90:10).

2-[(Trimethylsilylmethyl)thio]benzothiazole (XIa). PMR spectrum: 0.05 (9H, s, $Si(CH_3)_3$; 2.45 (2H, s, CH_2; 7.38 ppm (4H, m, protons on the benzothiazole ring). Mass spectrum, *m/z* (I_{rel}, %): 253 (M^+, 12), 240 (13), 239 (18), 238 (M^+-Me, 100), 206 (13), 192 (12), 149 (11), 45 (24), 43 (15). Impurities: 1.7% (on Zorbax ODS, 4.6×250 mm, MeOH).

2-[3-Trimethylsilylpropyl)thio]benzothiazole (XIb). PMR spectrum: 0.13 (9H, s, $Si(CH_3)_3$); 0.81 (2H, m, CH_2Si); 1.84 (2H, m, $CH_2C\underline{H}_2CH_2Si$); 3.46 (2H, t, J = 7.4 Hz, SCH_2); 7.46 and 7.92 ppm (4H, m, protons on the benzothiazole ring). Mass spectrum, *m/z* (I_{rel}, %): 281 (M^+, 4), 266 (M^+-Me, 8), 234 (18), 224 (25), 168 (12), 167 (100), 73 (69), 59 (10), 45 (24), 43 (10). Impurities: 1.1% (on Zorbax ODS, 4.6×250 mm, MeOH). Found, %: C 55.43; H 6.85; N 4.89. $C_{13}H_{19}NSiS_2$. Calculated, %: C 55.46; H 6.80; N 4.98.

2-{[3-(1-Methyl-1-silacyclopentyl)propyl]thio}benzothiazole (XIc). PMR spectrum: 0.08 (9H, s, $SiCH_3$); 0.53 and 0.78 (6H, m, $SiCH_2$); 1.54 and 1.85 (6H, m, $CH_2(C\underline{H}_2)_2CH_2$ for the silacycle and $CH_2C\underline{H}_2CH_2Si$); 3.34 (2H, t, J = 8.0 Hz, SCH_2); 7.33 and 7.80 ppm (4H, m, protons on the benzothiazole ring). Mass spectrum, *m/z*

(I_{rel}, %): 301 (M^+, 11), 292 (M^+-Me, 10), 280 (13), 274 (17), 265 (14), 264 (12), 263 (18), 251 (24), 250 (39), 237 (67), 236 (51), 232 (15), 223 (18), 222 (74), 209 (29), 208 (13), 207 (18), 193 (27), 179 (12), 168 (15), 167 (88), 166 (28), 165 (32), 163 (15), 162 (100), 150 (12), 149 (62), 136 (21), 134 (14), 122 (14), 117 (21), 109 (12), 108 (33), 102 (17), 99 (58), 97 (52), 95 (13), 83 (13), 75 (28), 70 (14), 69 (26), 63 (14), 59 (44), 58 (13), 57 (13), 55 (22), 45 (76), 43 (72), 41 (20), 39 (19). Impurities: < 1% (on Ultrasphere, 4.6×250 mm, EtOAc–hexane, 1:99).

Typical Procedure for Synthesis of N,S-Disilyl Derivatives of Purine Under Phase Transfer Catalytic Conditions. Powdered K_2CO_3 (3.5 g, 25 mmol) was added to a solution of 6-mercaptopurine (VI) (0.76 g, 10 mmol), the corresponding silane (20 mmol), and 18-crown-6 (0.264 g, 1 mmol) in 15 ml of toluene. The mixture was boiled with vigorous stirring until the substrates completely disappeared (monitored by GLC, see Table 1), filtered through a thin layer of silica gel; and then the toluene was evaporated on a rotary evaporator. The compounds XIIa,b,d (Table 1) were isolated by column chromatography (eluent benzene–EtOAc in various ratios), identified by PMR and mass spectroscopy, and also by elemental analysis. The purity of the compounds obtained was confirmed by HPLC.

6-[(Trimethylsilylmethyl)thio]-9-(trimethylsilylmethyl)purine (XIIa). PMR spectrum: 0.04 and 0.18 (9H, both s, $Si(CH_3)_3$); 2.50 (2H, s, SCH_2Si); 3.74 (2H, s, NCH_2Si); 7.79 (1H, s, 8-H); 8.65 ppm (1H, s, 2-H). Mass spectrum, *m/z* (I_{rel}, %): 324 (M^+, 4), 311 (14), 310 (25), 309 (M^+-Me, 100), 277 (10), 73 ($SiMe_3$, 44), 59 (34), 45 (18), 43 (12). Impurities: 2% (on Zorbax ODS, 4.6×250 mm, MeOH). Found, %: C 48.11; H 7.44; N 17.13. $C_{13}H_{24}N_4SSi_2$. Calculated, %: C 48.10; H 7.45; N 17.26.

6-[(3-Trimethylsilylpropyl)thio]-9-(3-trimethylsilylpropyl)purine (XIIb). PMR spectrum: 0.181 and 1.84 (9H, both s, $Si(CH_3)_3$; 0.34 (2H, m, $S(CH_2)_2C\underline{H}_2Si$); 0.57 (2H, m, $N(CH_2)_2C\underline{H}_2Si$); 1.67 (4H, m, $CH_2C\underline{H}_2CH_2Si$); 3.26 (2H, m, SCH_2); 4.08 (2H, m, NCH_2); 7.80 (1H, s, 8-H); 8.57 ppm (1H, s, 2-H). Impurities: 1% (on Symmetry C_{18}, 3.9×150 mm, CH_3CN–H_2O, 90:10). Found, %: C 53.75; H 8.48; N 14.67. $C_{17}H_{32}N_4SSi_2$. Calculated, %: C 53.63; H 8.47; N 14.72.

6-{[3-(1-Methyl-1-silacyclohexyl)propyl]thio}-9-[3-(1-methyl-1-silacyclohexyl)propyl]purine (XIId). PMR spectrum: -0.03 and 0.00 (9H, both s, $Si(CH_3)_3$); 0.57 (4H, m, both $C\underline{H}_2Si$); 1.62 (4H, m, both $CH_2C\underline{H}_2CH_2Si$); 3.39 (2H, t, J = 7.1 Hz, SCH_2); 4.21 (2H, t, J = 7.1 Hz, NCH_2); 7.94 (1H, s, 8-H); 8.70 ppm (1H, s, 2-H). Impurities: 1.5% (on Nova Pak Silica, 3.9×150 mm, EtOAc–hexane, 20:80). Found, %: C 59.88; H 8.97; N 11.62. $C_{23}H_{40}N_4SSi_2$. Calculated, %: C 59.95; H 8.75; N 12.16.

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