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A New Synthetic Method for 2-Silyl-Thiacycloalk-2-enes of Different Ring Size by Intramolecular Cyclization Through Silyl Thiones.

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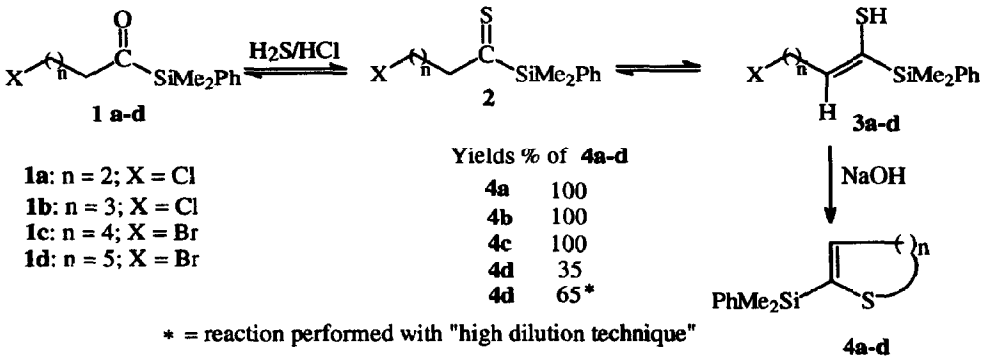
Abstract: ω-Haloacylsilanes **1a-d** were transformed by H_2S/HCl into the corresponding silyl thiones **2** which underwent enethiolization on base treatment. Enethiols **3** cyclized intramolecularly to afford the title compounds **4a-d** in high yields.

In the past years we have synthetized and have studied the chemistry of aromatic[1], t-butyl[2], methyl and cycloalkyl[3] silyl thioketones. Among these products methyltrimethylsilyl thioketone was too unstable to be isolated. Enethiolization of this thione and subsequent thiophilic addition of the enethiol form to the starting thioketone led to dimeric products[2]. This behaviour, not shown by other methyl thiones,[4] was ascribed to the presence of a silyl group, which favours enethiolization of alkyl thiones bearing a hydrogen atom at the α-carbon. This property can be used for the convenient one-pot synthesis of silylated sulfur heterocycles of different ring size, starting from acylsilanes **1** bearing a good leaving group in ω position. The reaction occurs via an intramolecular cyclization of the enethiol form of the "in situ" generated silyl thiones **2**. The starting acylsilanes **1a,b,c** were readily accessible through the reaction of the corresponding ω-halo acyl chlorides with bis(dimethylphenylsilyl)copper-zinc cyano cuprates[5], whereas the acylsilane **1d** has been prepared according with the Brook procedure.[6] Thionation of **1a-d** with H_2S-HCl was performed in ether at -30 °C. After the disappearence of the starting ketone the solution was then treated with solid sodium hydroxide, affording 2-(dimethylphenylsilyl)-thiacyclo pent-2-ene **4a**, 2-(dimethylphenylsilyl)-thiacyclo hex-2-ene **4b**, 2-(dimethylphenylsilyl)-thiacyclo hept-2-ene **4c** and 2-(dimethylphenylsilyl)-thiacyclo oct-2-ene **4d**, respectively.



1a: n = 2; X = Cl
1b: n = 3; X = Cl
1c: n = 4; X = Br
1d: n = 5; X = Br

Yields % of **4a-d**

4a	100
4b	100
4c	100
4d	35
4d	65*

* = reaction performed with "high dilution technique"

Scheme 1

Product **4a** has already been obtained by us during the thionation of cyclopropyldimethylphenylsilyl ketone in an excess of HCl followed by alkaline washing[3]. The structure assignment of the products **4b-d** was

based on correct mass measurements and NMR spectral data[7]. A ^1H NMR spectrum of the reaction mixture prior to neutralization with base showed that the thionation products obtained at low temperature were *gem*-dithiols, arising from a further addition of a molecule of hydrogen sulfide to the thiones. It is worth noting the different behaviours of the various bases used for neutralization: solid sodium hydroxide led to complete cyclization (Scheme 1). The use of sodium hydrogen carbonate led generally to the intermediate (Z)-enethiols **3**, that could be fully characterized[8] and subsequently transformed into **4** on treatment with NaOH. Enethiols, usually obtained as mixtures with thioketones, were only recently prepared in pure form.[9] The cyclization reaction could also be performed in the presence of solid sodium carbonate, although the reaction appeared to be less selective: generally mixtures of cyclic compounds **4** and enethiols **3**, whose ratio depended on the reaction time and ring size, were obtained. It should be noted that with this methodology it is possible to obtain not only the 5 to 7-membered rings, but also 8 membered heterocycles, often difficult to obtain via intramolecular cyclization. This reaction occurs, albeit in lower yield due to competitive intermolecolar dimerization.[10] Under high dilution conditions i.e., by adding the solution containing the isolated enethiol **3d** to a stirred suspension of solid NaOH in Et_2O over 13 hours, compound **4d** was obtained in a higher (65%) yield. Thionation at higher temperatures (>-10 °C) furnished thione **2** judged by its characteristic blue coloured solution which slowly faded due to enethiolization (Scheme 1). It is useful to compare our results with the recent report[11] on the synthesis of the corresponding cyclic ethers by cyclization of δ-and γ-haloacylsilanes in polar aprotic solvent at 100 °C, a reaction that fails to provide seven-membered rings.

In summary a new cyclization procedure provides easy access under mild conditions to unsaturated 5-8 membered cyclic sulfides. The presence of the vinylsilane moiety provides a handle for further functionalization of the heterocycles reported herein. We are now extending our methodology to smaller and larger ring-system as well as to other substituted derivatives.

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7. ^1H and ^{13}C NMR were recorded with a Varian Gemini 200 MHz, **4b**: δH (200 MHz, $CDCl_3$) 0.45 (s, 6H, $SiMe_2$), 1.85 (m, 2H, CH_2), 2.05 (m, 2H, CH_2), 2.85 (2H, m, CH_2), 6.00 (t, 1H, J= 8.8 and 4.4 Hz, CH=), 7.45 (m, 3H, ArH), 7.60 (m, 2H, ArH) ppm. δ ^{13}C (50.3 MHz, $CDCl_3$): -3.49 ($SiMe_2$), 21.60 (CH_2), 24.95 (CH_2), 26.55 (CH_2), 127.82, 129.32, 130.04, 131.07, 134.18, 137.35 ppm. MS: m/z= 234 (M^+), 219, 135, 99. **4c**: δH 0.40 (s, 6H, $SiMe_2$), 1.55 (m, 2H, CH_2), 1.95 (m, 2H, CH_2), 2.45 (m, 2H, CH_2), 2.65 (m, 2H, CH_2), 6.50 (t, 1H, J= 6.35 Hz, CH=), 7.35 (m, 3H, ArH), 7.60 (m, 2H, ArH) ppm. δ ^{13}C: -3.45 ($SiMe_2$), 24.43 (CH_2), 31.06 (CH_2), 32.31 (CH_2), 34.51 (CH_2), 127.81, 129.19, 134.16, 137.83, 138.94, 146.57 ppm. MS: m/z= 248, 233, 205, 135, 105. **4d**: δH: 0.45 (s, 6H, $SiMe_2$), 1.43-1.62 (m, 4H, CH_2), 1.70-1.85 (m, 2H, CH_2), 2.40-2.52 (t, 2H, CH_2S), 2.65-2.75 (m, 2H, CH_2-CH=), 7.35 (m, 3H, ArH), 7.65(m, 2H, ArH) ppm. δ ^{13}C: -3.29 ($SiMe_2$), 25.38, (CH_2), 28.55 (CH_2), 29.66 (CH_2), 36.78 (CH_2), 127.64, 129.01, 134.09, 135.11, 137.45, 152.01. MS: 262 (M^+), 205, 179, 153, 135, 94.
8. Compound (Z)-**3b**, yield 100 %: δH: 0.50 (s, 6H, $SiMe_2$), 1.95 (q, 2H, CH_2), 2.41 (q, 2H, CH_2), 2.58 (s, 1H, SH), 3.55 (t, 2H, CH_2Cl), 5.95 (t, 1H, J= 6.60 Hz, CH=), 7.40 (m, 3H, ArH), 7.555 (m, 2H, ArH) ppm. δ ^{13}C: -3.51 ($SiMe_2$), 27.71 (CH_2), 31.31 (CH_2), 44.31 (CH_2), 128.11, 129.67, 130.30, 134.26, 136.28, 137.97. MS: m/z= 234, 219, 192, 153, 135.
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