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LETTERS TO THE EDITOR

Lithiation of 3,3-Dimethyl-3-silathiane as a Route to α-Substituted Six-Membered Cyclic Organosilicon Sulfides

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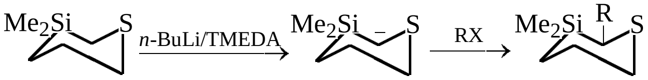
Thiasilacycloalkanes are most commonly prepared by cyclization of (α,ω-dihaloalkyl)dialkylsilanes under the action of S-nucleophiles, intramolecular cyclization of (chloroalkyl)(mercaptoalkyl)silanes, or intramolecular free-radical cyclization of (mercaptoalkyl)-alkenylsilanes [1]. In particular, these methods have been used for preparing, in good yields, a rare representative of six-membered heterocycles, 3,3-dimethyl-3-silathiane [2–5]. However, because of the inaccessibility of starting materials, the above methods have scarcely been used in the synthesis of 2-substituted 3-silatianes of which 2-methyl [6] and 2-phenyl derivatives [3] have only been described. At the same time, acyclic α-silyl sulfides are not infrequently functionalized via reactions with electrophiles of α-carbanions generated from 2-substituted 3-silathianes [1]. The latter approach was recenty applied for α-substitution of a thiane deprotonated with *n*-BuLi/KOBu-*t* [7].

We found that α-carbanion **II** generated from silathiane **I** reacts with electrophiles RX to give 2-substituted 3-silatianes **IIIa**–**IIIc** in yields depending on the nature of the base and electrophile. Thus, successive treatment of silathiane **I** with *n*-butyllithium (1.1 equiv) and methyl iodide in THF at 0°C gives heterocycle **IIIa** in 44% yield, while the deptoronation of compound **I** with the *n*-butyllithium–tetramethylenediamine complex (TMEDA) increases the yield of compound **IIIa** to 67%. However, even under such conditions and at longer reaction times, the yield of compound **IIIb** is as low as 15%. In the latter case, 1-chloro-1,2-diphenylethane $PhCHClCH_2Ph$ (**IV**) was isolated as by-product (yield 8%). The mechanism of formation of compound **IV** has been proposed in [8].



I **II** **IIIa–IIIc**

RX = MeI (**a**), $C_6H_5CH_2Cl$ (**b**), $(CH_3)_3SiCl$ (**c**).

2-Substituted 3,3-dimethyl-3-silathianes IIIa–IIIc. A 1.6 M solution of butyllithium in hexane (Merck), 7 ml, was added with stirring at 0°C to a solution of 1.46 g of 3,3-dimethyl-3-silathiane (**I**) and 1.42 g of tetramethylethylenediamine in 3 ml of THF. After 1-h stirring, a solution of halide RX (11 mmol in 2 ml of THF) was added. The reaction mixture was stirred at room temperature for 2–8 h, poured into water, and acidified with 10% HCl to pH 5. The organic layer was separated, and the aqueous layer was treated with hexane. The combined organic solutions were dried with $MgSO_4$, and the solvent was removed by rotary evaporation. Compounds **IIIa** and **IIIc** were isolated by vacuum distillation. Compound **IIIb** was purified by column chromatography on Silica gel 60 (35–70 mesh, Merck) with gradient elution (hexane, hexane–cyclohexane, and hexane–benzene).

2,3,3-Trimethyl-3-silathiane (IIIa). Physicochemical characteristics and ^1H NMR spectrum are similar to those described in [9].

2-Benzyl-3,3-dimethyl-3-silathiane (IIIb). R_f 0.41 (cyclohexane–benzene, 2 : 1), n_D^{23} 1.5172. ^1H NMR spectrum, δ, ppm: 0.00 s (3H, MeSi), 0.18 s (3H, MeSi), 0.60 d.d.d (1H, 4-CH, ^2J 14.7, ^3J 10.2 and 4.4 Hz), 0.78 d.d.d.d (1H, 4-CH, ^3J 7.7, 3.9, ^4J 0.5 Hz), 1.94 d.d.d.d.d (1H, 5-CH, ^2J 13.6, ^3J 9.6 and 2.6 Hz), 2.09 d.d. d.d.d (1H, 5-CH, ^3J 7.3 and 2.5 Hz), 2.21 d.d (1H, 2-CH, ^3J 10.1 and 6.0 Hz), 2.40 d.d.d (1H, 6-CH, ^2J 14.2 Hz), 2.58 d.d.d.d (1H, 6-CH), 2.76 d.d (1H, CH^α, $^2J_{aa}$ 14.2 Hz), 2.94 d.d (1H, CH^α), 7.30 m (5H, C_6H_5). ^{13}C NMR spectrum, δ_C, ppm: –5.6 (MeSi), –3.1 (MeSi), 13.7 (C^4), 27.0 (C^5), 30.7 (C^2), 31.1 (C^6), 35.8 (C^α), 126.2 (C_o), 128.2 (C_p), 128.8 (C_m), 140.8 (C_i). ^{29}Si NMR spectrum, δ_{Si}, ppm: –5.9. Found, %: S 14.08; Si 11.16. $C_{13}H_{20}SSi$. Calculated, %: S 13.56; Si 11.88.

3,3-Dimethyl-2-(trimethylsilyl)-3-silathiane (IIIc). Yield 50%, bp 87°C (2 mm), n_D^{20} 1.4963. ^1H NMR

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spectrum, δ, ppm: 0.03 s (3H, MeSi), 0.08 s (9H, Me_3Si), 0.22 s (3H, MeSi), 0.51 d.d.d (1H, 4-CH, ^2J 14.4, ^3J 13.4 and 4.8 Hz), 0.71 d.d.d.d (1H, 4-CH, ^3J 5.1, 3.3, ^4J 1.1 Hz), 1.26 s (1H, 2-CH), 1.87 d.d.d.d.d (1H, 5-CH, ^2J 13.2, ^3J 13.7, 10.7 and 3.4 Hz), 2.19 d.d.d.d.d (1H, 5-CH, ^3J 4.9 and 2.4 Hz), 2.45 d.d.d (1H, 6-CH, ^2J 13.6 Hz), 2.51 d.d.d (1H, 6-CH). ^{13}C NMR spectrum, δ_C, ppm: –4.01 (MeSi), –0.38 (MeSi), 0.04 (MeSi), 15.9 (C^4), 16.8 (C^2), 27.4 (C^5), 34.5 (C^6). ^{29}Si NMR spectum, δ_{Si}, ppm: –9.0, 1.7. Found, %: S 14.62; Si 25.56. $C_9H_{22}SSi_2$. Calculated, %: S 14.67; Si 25.71.

1-Chloro-1,2-diphenylethane (IV). ^1H NMR spectrum, δ, ppm: 3.36 d.d (1H, CH, ^2J 13.9, ^3J 6.9 Hz), 3.42 d.d (1H, CH, ^3J 7.7 Hz), 5.05 d.d (1H, CHCl), 7.30 m (10H, Ph).

The ^1H, ^{13}S, and ^{29}Si NMR spectra were recorded for $CDCl_3$ solutions on a Bruker DPX-400 spectrometer at 400, 100, and 80 MHz, respectively.

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