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METALATION REACTIONS. XII. ONE-POT SYNTHESIS OF 1,3-BENZOTHIASILOLES, 1,3-BENZOTHIASTANNOLES AND 1,3-BENZODITHIOLES

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__Abstract__ - The dilithiated species of (methylthio)benzene reacts with various dichlorosilanes, dichlorostannanes and sulfur chloride yielding derivatives of 1,3-benzothiasilole, 1,3-benzothiastannole and 1,3-benzodithiole respectively. By reaction with tetrachlorosilane a spirocyclic silicon compound is obtained. A description of the synthesis is given. The structures of the reaction products were determined by elemental and spectroscopic analyses.

It has been previously shown that aromatic thioethers undergo direct bimetalation reaction to give stable dilithiated derivatives.[1] This is a valuable mean to introduce, by one-pot synthesis, two electrophilic groups on substrate positions which are otherwise hardly accessible; besides, both dilithiated sites, obtained by bimetalation reaction of the (methylthio)benzene, react with the same carbon atom of an acylic halide to provide benzo[_b_]thiophene compounds.[2]

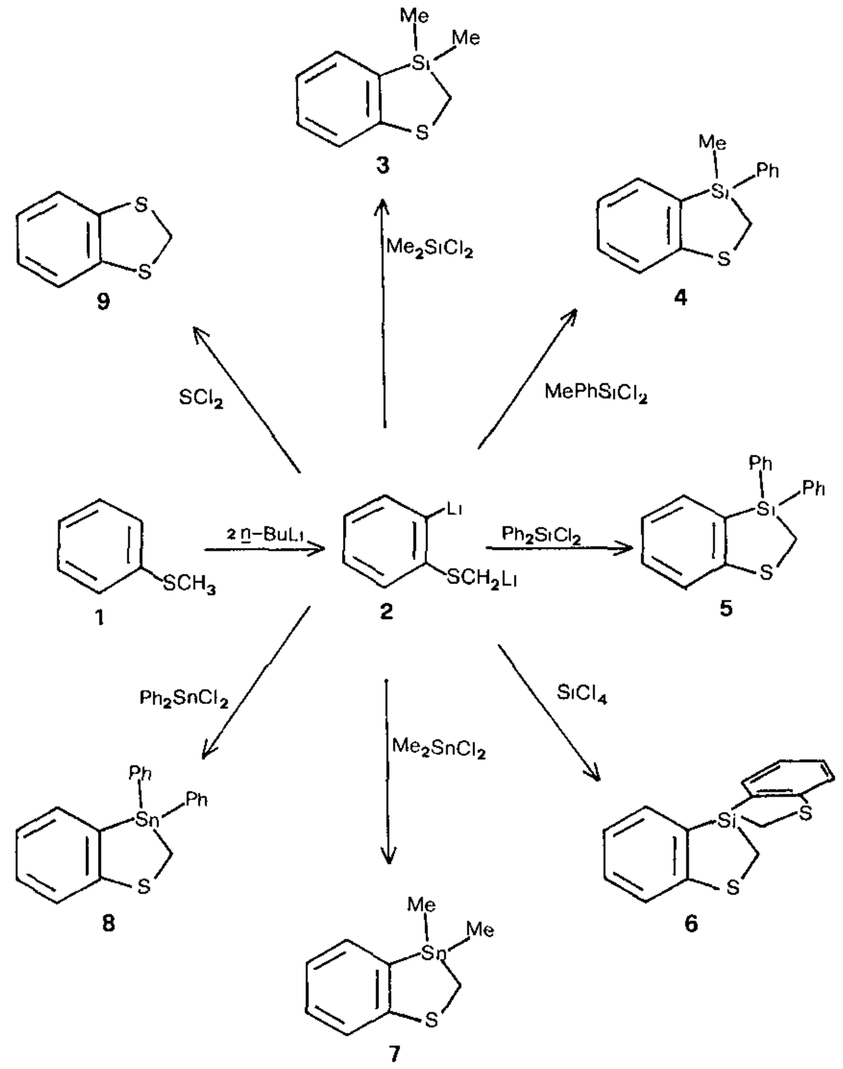
The condensation reaction of the dilithiated derivative of commercially available (methylthio)benzene (1) with various _gem_-dihalogeno compounds has been studied with the aim of devising a new preparation method for five-membered benzocondensed heterocyclic systems, containing one or two heteroatoms.

The dilithiated species (2) has been prepared by action of 2.2 moles of _n_-buthyllithium in hexane on (1). The thiomethylic carbon atom and the benzene ring carbon in _ortho_ position, with respect to thioethereal function, have been metalated.[1] By reaction of this bimetalated intermediate with dimethyl-, methylphenyl- and diphenyl-dichlorosilane, 1,3-benzothiasilole derivatives **(3-5)** have been obtained (see scheme 1), by attack of the dilithiated reagent on the same silicon atom. By reaction of two moles of (2) on the tetrachlorosilane, the formation of the spirocyclic silicon derivative **(6)** has occurred.

Stannic derivatives show the same behaviour of silicon ones; in fact, the reaction of the dimethyl- and diphenyl-dichlorostannane has provided 1,3-benzothiastannole compounds **(7, 8)**.

By reaction of (2) with sulfur chloride the expected 1,3-benzodithiole **(9)** has been obtained, when the reaction is carried out at -80°C; at higher temperatures, diphenyldisulfide **(12)** and sulfur were the only products. This fact is probably due to a first lithium-chlorine substitution on the thiomethylic carbon, providing the α-halogenothioether **(10)** (Scheme 2): this compound will then give rise to disulfide **(12)** through several steps: firstly the α-halogenothioether

Scheme 1

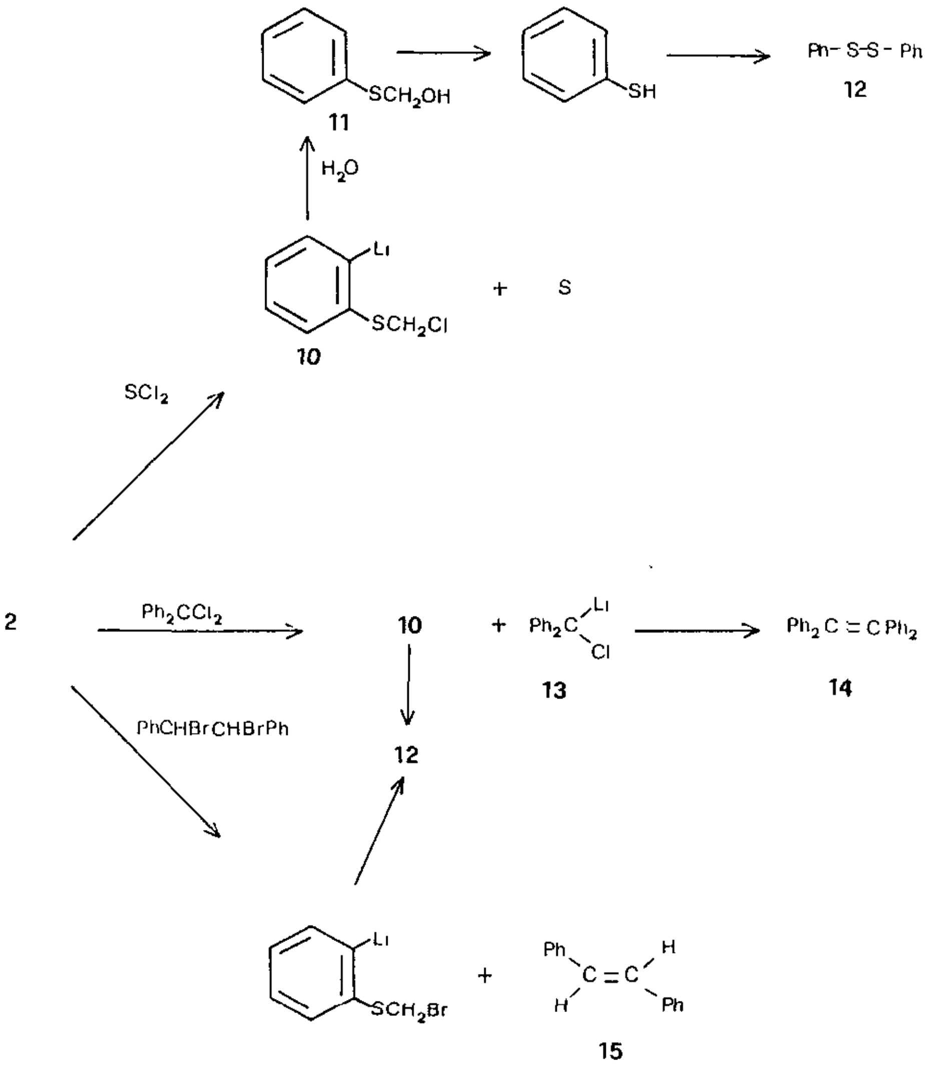


(**10**) will likely hydrolize to α-hydroxythioether (**11**), which will spontaneously give rise to benzenethiole; this will then give the disulfide (**12**) by spontaneous oxidation.

On the contrary, negative results were obtained in the attempts to synthesize benzo[b]thiophene, by reaction of dianion (2) with gem-dihalogenoalkanes. In fact, using dichlorodiphenylmethane, at room temperature, or at -10°C or at -90°C, tetraphenylethylene (**14**) and diphenyldisulfide (**12**) were exclusively isolated.

The alkene (**14**) formation can be explained via a carbenoid intermediate (**13**), resulting by a metal-halogen substitution,^{3,4} while the foregoing hypothesis

Scheme 2



(Scheme 2) can be invoked for the formation of disulfide derivative.

The attempts to obtain benzothiane compounds by using 1,2-dihalogenoalkenes failed as well: in fact, when the dianion (2) reacts with meso-1,2-dibromo-1,2-diphenylethane, only the *disulfide (12) and the trans-stilbene (15) have been* isolated (Scheme 2).

The formation of (12) can be still explained as in the foregoing reactions, while the occurrence of (15) can be likely attributed to an elimination promoted by the organometallic compound.[5]

EXPERIMENTAL

Melting points were obtained on a Kofler hot stage microscope and are uncorrected. Ir spectra were run using NaCl plates on a Perkin-Elmer 1310 grating spectrophotometer. ^{1}H-nmr spectra were recorded on a Varian EM 360A spectrometer using Me_4Si as the internal standard. Mass spectra were obtained with a "Hitachi" Perkin-Elmer RMU-6D spectrometer at 70 eV, using direct-inlet system. Elemental analyses were carried out on a Carlo Erba model 1106 Elemental Analyzer.

Materials. (Methylthio)benzene (thioanisole) (Janssen), dimethyl- (Janssen), methylphenyl- (Janssen) and diphenyl-dichlorosilane (Janssen), tetrachlorosilane (Janssen), dimethyl- (Merck) and diphenyl-dichlorostannane (Merck), sulfur chloride (Janssen), dichlorodiphenylmethane (Merck), 1,2-dibromo-1,2-diphenylethane (Janssen), diphenyldisulfide (Merck), tetraphenylethylene (Merck) trans-stilbene (Janssen) are commercially available. Solutions of *n*-buthyllithium in hexane (Janssen) were analyzed by the Gilman double titration method before use.[6] N,N,N',N'-Tetramethylethylenediamine (TMEDA) (Janssen) was distilled from calcium hydride before use. All reactions were carried out in dried glassware under an atmosphere of dry, purified nitrogen. The prepared compounds were purified by column flash-chromatography on silica G 60 (Merck).

3,3-Dimethyl-1,3-benzothiasilole (3). To a vigorously stirred solution of **1** (40 mmol), anhydrous TMEDA (90 mmol) and anhydrous ether (140 ml) was gradually added a solution of 1,2 M *n*-butyllithium in hexane (75 ml). When the addition was complete the mixture was left at room temperature for 24 h with stirring. The reaction mixture was then cooled to -10°C and treated dropwise with dichlorodimethylsilane (40 mmol). The resulting mixture was then allowed to warm and left at room temperature for 48 h with stirring. The reaction mixture was poured into water (500 ml) and the pH adjusted to 5-6 by addition of 10% hydrochloric acid. The organic layer was separated and the aqueous layer extracted with ether. The combined organic extracts were dried over anhydrous sodium sulfate and concentrated. The crude product was purified by flash-chromatography using hexane as eluent to give 3 (56%) as an oil, bp 85-86°C (2 mm); ^{1}H-nmr ($CDCl_3$), δ 6.7 (m, 4H, aromatic), 2.1 (s, 2H, SCH_2), 0.65 (s, 6H, $SiMe_2$); ms, *m/z* 180 (M^+, calcd. for $C_9H_{12}SSi$: 180.31). Anal. Calcd. for $C_9H_{12}SSi$: C, 59.95; H, 6.71; S, 17.78. Found: C, 59.83; H, 6.63; S, 17.63.

Analogously, starting from 2 and methylphenyl- and diphenyl-dichlorosilane, tetrachlorosilane, dimethyl- and diphenyl-dichlorostannane and sulfur chloride the following compounds were obtained, respectively:

3-Methyl-3-phenyl-1,3-benzothiasilole (4). Yield 75%. Flash-chromatography (hexane-ethyl acetate, 10:1); bp 163-165°C (3 mm); ^{1}H-nmr ($CDCl_3$), δ 6.5 (m, 4H, aromatic), 2.05 (s, 2H, SCH_2), 0 (s, 3H, SiMe); ms, *m/z* 242 (M^+, calcd. for $C_{14}H_{14}SSi$: 242.40). Anal. Calcd. for $C_{14}H_{14}SSi$: C, 69.37; H, 5.82; S, 13.23. Found: C, 69.21; H, 5.57; S, 13.02.

3,3-Diphenyl-1,3-benzothiasilole (5). Yield 58%. Flash-chromatography (petroleum ether); mp 82°C (from aqueous ethanol); ^{1}H-nmr ($CDCl_3$) δ 7.5 (m, 14H, aromatic), 2.7 (s, 2H, SCH_2); ms, *m/z* 304 (M^+, calcd. for $C_{19}H_{16}SSi$: 304.44). Anal. Calcd. for $C_{19}H_{16}SSi$: C, 74.95; H, 5.30; S, 10.53. Found: C, 74.94; H, 5.69; S, 10.39.

3,3'-Spirobi[1,3-benzothiasilole] (6). This compound was obtained by operating with 80 mmol of 2 and 40 mmol of tetrachlorosilane. Yield 55%. Flash-chromatography (petroleum ether); mp 112-113°C (from ethanol); ^{1}H-nmr ($CDCl_3$) δ 7.3 (m, 8H, aromatic), 2.5 (s, 4H, SCH_2); ms, m/z 272 (M^+, calcd. for $C_{14}H_{12}S_2Si$: 272.42). Anal. Calcd. for $C_{14}H_{12}S_2Si$: C, 61.72; H, 4.44; S, 23.54. Found: C, 61.43; H, 4.65; S, 23.35.

3,3-Dimethyl-1,3-benzothiastannole (7). Yield 46%. Flash-chromatography (petroleum ether); bp 120°C (2 mm); ^{1}H-nmr ($CDCl_3$) δ 7.15 (m, 4H, aromatic), 2.2 (s, 2H, SCH_2), 1.3 (s, 6H, $SnMe_2$); ms, m/z 271 (M^+, calcd. for $C_9H_{12}SSn$: 270.95). Anal. Calcd. for $C_9H_{12}SSn$: C, 39.89; H, 4.47; S, 11.83. Found: C, 39.74; H, 4.83; S, 11.68.

3,3-Diphenyl-1,3-benzothiastannole (8). Yield 54%. Flash-chromatography (hexane-ethyl acetate, 5:1); purified by sublimation (170°C, 0.6 mm); mp 195-200°C: ^{1}H-nmr (CCl_4) δ 7.3 (m, 14H, aromatic), 2.1 (s, 2H, SCH_2); ms, m/z 396 (M^+, calcd. for $C_{19}H_{16}SSn$: 395.08). Anal. Calcd. for $C_{19}H_{16}SSn$: C, 57.76; H, 4.08; S, 8.11. Found: C, 56.95; H, 4.91; S, 7.98.

1,3-Benzodithiole (9). This compound was obtained by performing the reaction at -80°C and it was identical with that of an authentic sample.[7] Yield 61%. Bp 95-96°C (1 mm).
Only the disulfide (12) and sulfur were obtained when the reaction was performed at room temperature or at -20°C.

Reaction of 2 with Dichlorodiphenylmethane.

To a vigorously stirred mixture of 2 (obtained as previously described) dichlorodiphenylmethane was gradually added at -10°C. When the addition was complete the resulting mixture was allowed to warm, left at room temperature for 48 h with stirring and worked up in the same manner as above described. The tlc analysis of the ethereal layer showed three spots. The solvent evaporation *in vacuo* gave a paste which was flash-chromatographed using petroleum ether as eluent. Elution of the first fraction afforded a small quantity of 1. Elution of the second fraction afforded diphenyldisulfide (12); yield 61%, mp 61-62°C, identical in all respects with an autenthic commercial sample. Elution of the third fraction afforded tetraphenylethylene (14), yield 72%, mp 224-225°C, identical in all respects with an authentic commercial sample.
Analogous results were obtained by performing the reaction at -80°C.

Reaction of 2 with 1,2-Dibromo-1,2-diphenylethane.

The same procedure as above described was employed starting from 2 and 1,2-dibromo-1,2-diphenylethane. The tlc analysis of the ethereal layer showed three spots. The solvent evaporation *in vacuo* gave a paste which was flash-chromatographed using petroleum ether as eluent. Elution of the first fraction afforded a small quantity of 1. Elution of the second fraction afforded diphenyldisulfide (12), yield 60%. Elution of the third fraction afforded *trans*-stilbene (15), yield 75%, mp 125-126°C, identical in all respects with an authentic commercial sample.

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