One-step Synthesis of Dodecamethylcyclohexasilane

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Summary Dodecamethylcyclohexasilane $(Me_2Si)_6$ has been conveniently prepared from Me_2SiCl_2 and Li, in tetrahydrofuran at 0 °C.

DODECAMETHYLCYCLOHEXASILANE (I) is an interesting model compound, and several methods have been described for its synthesis.[1–3] Recently, Nagai *et al.*[4] described a new method [reaction (1)] for the synthesis of (I) (60% yield crude, 40% after recrystallization) from (II) which is not, however, commercially available. The route in reaction (2) was used to prepare (II) from 'disilane residue' (resulting from the industrial synthesis of Me_2SiCl_2).[5]

$$\underset{\text{(II)}}{6(MeO)Me_2SiSiMe_2(OMe)} \xrightarrow{\text{NaOMe}} \underset{\text{(I)}}{(Me_2Si)_6} + 6(MeO)_2SiMe_2 \qquad (1)$$

$$\underset{\text{(6 mol)}}{\text{'Disilane residue'}} \xrightarrow[+\ MeHSiCl_2;\ AlCl_3]{\text{excess } Me_3SiCl} Me_3Si_2Cl_3 + Me_4Si_2Cl_2$$

$$\xrightarrow[\text{MeOH}]{130\ ^\circ C} \underset{\text{(II)}}{Me_2ClSiSiMe_2Cl} \quad \begin{matrix}\text{HCl}\\ \downarrow\\ NiCl_2(PPh_3)_2\end{matrix} \qquad (2)$$

$$\text{(2·6 mol)}$$

The route we propose [reaction (3)] is more convenient than the disilane route; from commercially available products, (I) is obtained in high yields (90% crude, 80% after recrystallization). Our process has several advantages

$$6Me_2SiCl_2 + 12\ Li \xrightarrow[0\ ^\circ C,\ 6\ h]{THF} 12\ LiCl + (Me_2Si)_6 \qquad (3)$$

over previous organometallic methods; it gives very high yields and does not require the use of a catalyst (Ph_3SiLi[3]) or the preparation of Na–K alloy.[2]

A typical procedure for the preparation of (I) is as follows. To a mixture of Li (1·6 g) in tetrahydrofuran (THF) (110 ml) at 0 °C was slowly added (1 h) Me_2SiCl_2 (13 g) in THF (40 ml) with stirring under N_2. The reaction mixture was stirred for a further 2 h at 0 °C and left overnight at room temperature; cyclohexane (100 ml) was then added and the precipitate filtered off. The THF and C_6H_{12} solvents were removed under reduced pressure, and the residue extracted with further cyclohexane (100 ml). After filtration and evaporation (I) was obtained (6 g, *ca.* 100%) and recrystallized from ethanol (4·6 g, 80%) in two crops (I), m.p. 250 °C, purity > 99%. Its physicochemical properties were identical with those reported.[2]

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