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# A SIMPLE AND CONVENIENT METHOD FOR PREPARING DI-t-BUTYLSILANES

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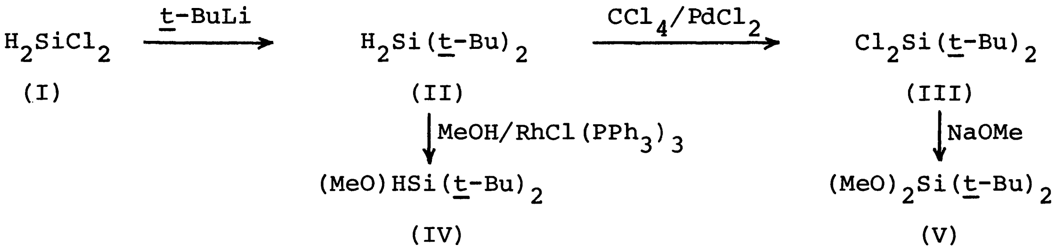
Silicon functional di-t-butylsilanes such as $(t\text{-Bu})_2SiCl_2$, $(t\text{-Bu})_2Si(OMe)_2$ and $(t\text{-Bu})_2SiH(OMe)$ were conveniently obtained in good yields via di-t-butylsilane, $(t\text{-Bu})_2SiH_2$, which can readily be prepared from the reaction of dichlorosilane, $H_2SiCl_2$, with t-butyllithium.

t-Butylchlorosilanes have recently been shown to be very useful materials in synthetic organic chemistry.[1-3] However, the reported methods usually furnish only a mixture of products.[4,5] Thus, it seems desirable to find a simple and convenient method for preparing di-t-butylsilane derivatives, the selective synthesis of which is still unestablished.

With respect to our interest in the utilization of dichlorosilane ($H_2SiCl_2$),[6] we investigated the synthesis of di-t-butylsilane derivatives from di-t-butylsilane, $(t\text{-Bu})_2SiH_2$(II), which can be readily prepared by the reaction of dichlorosilane with t-butyllithium (Scheme 1 and Table 1).

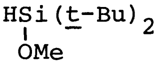
Scheme 1



The reaction of dichlorosilane with t-butyllithium proceeded quite smoothly to give di-t-butylsilane (II) in high yield (83 %). The chlorination of compound (II) with carbon tetrachloride in the presence of palladium chloride catalyst[7] gave the corresponding dichlorosilane (III) in 85% yield.

The dehydrogenative mono-methoxylation[8] of di-t-butylsilane (II) with methanol catalysed by $RhCl(PPh_3)_3$[9] readily commenced under mild conditions giving only di-t-butylmethoxysilane (IV) (67 %). On the other hand, the preparation of di-t-butyldimethoxysilane (V) could be accomplished in 64% yield by reacting di-t-butyldichlorosilane (III) with sodium methoxide in methanol, while an attempted solvolysis of III with boiling methanol was unsuccessful.

Table 1. Preparation of di-t-butylsilane derivatives

| Run | Reactants | (mmol) | Catalyst (mol %) | Conditions Temp.(°C); Time(h) | Product[a] and Yield | (%)[b] |
|---|---|---|---|---|---|---|
| 1 | (I)<br>t-BuLi | (100)<br>(200) | none | -5; 2.5<br>and r.t.; 1.5 | $H_2Si(t\text{-}Bu)_2$(II) | 83 |
| 2 | (II)<br>$CCl_4$[c] | (41) | $PdCl_2$(5) | reflux; 45 | $Cl_2Si(t\text{-}Bu)_2$(III) | 85 |
| 3 | (II)<br>MeOH[d] | (20) | $RhCl(PPh_3)_3$<br>(0.3) | r.t.; 16<br>and 60; 2 |  $HSi(t\text{-}Bu)_2(OMe)$ | 67 |
| 4 | (III)<br>NaOMe[e] | (20)<br>(40) | none | reflux; 14 | $(MeO)_2Si(t\text{-}Bu)_2$(V) | 64 |

[a] Structure was established by the usual manner (micro-analysis; IR and NMR spectral data). [b] Isolated yield by distillation. [c] Ca. 25 ml. [d] 7 ml. [e] In methanol (14 ml).

A preparative example is shown for the formation of di-t-butylsilane (II): dichlorosilane ($H_2SiCl_2$) (0.10 mol) was introduced under nitrogen into n-hexane (200 ml) which was cooled at -5 °C. To the dichlorosilane solution was added t-butyllithium (0.20 mol) at -5 °C. The mixture was stirred at -5 °C for 2.5 h and then for 1.5 h at room temperature. Work-up gave di-t-butylsilane (II), bp 128 °C, 12.7 g (83 %).

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