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CROSS-COUPLING VERSUS HOMO-COUPLING REACTIONS WITH BENZYL BROMIDE, MAGNESIUM AND CHLOROTRIMETHYLSILANE

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Abstract: The selective synthesis of benzyltrimethylsilane from $PhCH_2Br$, Mg and Me_3SiCl requires a low reaction temperature.

During recent years, we have described catalyzed oxidations of allylsilanes by Pd(II)-O_2-hv[1], Pd(II)-t.BuOOH[2] or under Wacker conditions[2], and of benzylic methylene groups by Cr(VI)-t.BuOOH[3,4]. As the former and the latter procedures are generally efficient, we decided to test them with benzyltrimethylsilane 1 as substrate.

The synthesis of 1 has been described in the literature by a cross-coupling reaction between trimethylchlorosilane and the Grignard reagent obtained from magnesium and benzyl chloride[5,6]. However, our first attempts were made using benzyl bromide instead of benzyl chloride since the former was not available in our stockroom at the time. Surprisingly, a mixture of

benzyltrimethylsilane 1 and 1,2-diphenylethane 2 with a large proportion of the unexpected homo-coupling compound was obtained under the literature conditions (see table, run 1). A recent paper[7] devoted in part to the efficient preparation of benzylic Grignard reagents has prompted us to report conditions allowing the selective formation of 1 from $PhCH_2Br$, Mg and Me_3SiCl.

A few of the unsucessful experiments attempted to improve the selectivity towards the formation of 1 are listed in the table. Finally, good yields and selectivities were achieved through a reaction carried out at -15°C by addition of $PhCH_2Br$ to a mixture of Mg and Me_3SiCl (run 5). Nevertheless, we have to point out that we obtained similar results by following the literature procedure[6] (run 6).

With 1 in hand, its oxidation by both the Pd(II)-O_2-hv[1] and the CrO_3-t.BuOOH[4] procedures have been examined: the former conditions induced a slow degradation of the substrate while the latter method led to small amounts of benzaldehyde and benzoic acid, the formation of benzoylsilane[8] has never been observed.

Experimental part:

Distilled trimethylchlorosilane (10.4 ml, 82 mmol) was added to a stirred suspension of magnesium (1.5 g) in dry tetrahydrofuran (30 ml) maintained under an argon atmosphere and then, cooled to - 15°C. Fifteen minutes later, a solution of benzyl bromide (10 g, 58 mmol) in THF (100 ml) was introduced and the mixture was kept under these conditions for 100h.

Table: Reaction of benzyl halide, magnesium and trimethylchlorosilane.

Run	Reagents, introduction order and time between additions[a]	t °C	reaction time, h	% yield 1 + 2	ratio[b] 1/2
1	EtOEt + Mg+ $PhCH_2Br$, 2 h, + TMSCl	RT	36	96	62/38
2	THF + TMSCl + Mg, 15 mn, + $PhCH_2Br$	- 5	100	98	86/14
3	THF + TMSCl + Mg, + $Pd_2(dba)_3(CHCl_3)$ (0.0005 equiv), 15 mn, + $PhCH_2Br$	- 5	100	72	74/26
4	THF + Mg + $PhCH_2Br$, 2 h, + TMSCl	- 15	100	98	80/20
5	THF + TMSCl + Mg, 15 mn, + $PhCH_2Br$	- 15	100	94	92/8
6	EtOEt + Mg + $PhCH_2Cl$, 2 h, + TMSCl	RT	36	95	91/9

[a]Ratio of $PhCH_2X$/Mg/TMSCl: 1/1.1/1.4. When no time is indicated between two reagents, that means these reagents have been added one immediately after the other.

[b]Determined by NMR.

Hydrolysis was effected by addition of ammonium chloride solution and warming to room temperature. After extraction with ether and drying the extracts over magnesium sulfate, the solvents were removed by distillation under reduced pressure. Flash-chromatography[9] of the residue, eluting with petroleum ether, furnished successively pure benzyltrimethylsilane (8.23 g, 87%) and 1,2-diphenylethane (0.72 g, 7%).

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