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Preliminary communication

The reaction of benzophenone with dimethylsilylmethylmagnesium bromide

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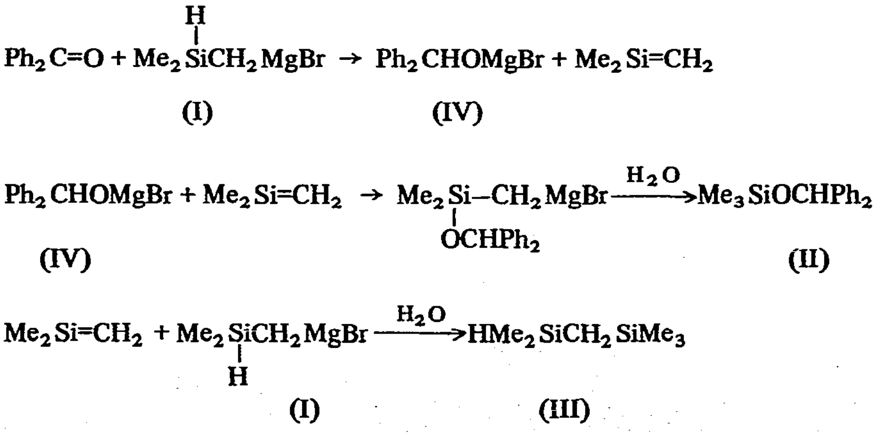
We have found that the reaction of benzophenone with dimethylsilylmethylmagnesium bromide (I) proceeds in a rather unusual fashion giving as the main product benzhydryloxytrimethylsilane (II) (89%) together with smaller quantities of (dimethylsilylmethyl)trimethylsilane (III) (12%), benzhydrol (8%) and 1,1-diphenylethylene (3%). Normally the reactions of Grignard reagents with benzophenone leads to mixture of benzopinacol, benzhydrol and tertiary alcohol[1].

The 1,1-diphenylethylene presumably arises from a normal addition reaction followed by a β-elimination. The mechanisms of formation of the other products are uncertain. The reaction of benzophenone with dimethyldeuteriosilylmethylmagnesium bromide gives deuteriobenzhydryloxytrimethylsilane and deuteriobenzhydrol. It is generally observed that reactions involving transfer of a hydrogen from a C–H bond β to a metallic centre proceed via an alkene elimination[2] and it might be expected that this reaction woud follow a similar course. The formation of a Si=C intermediate followed by its addition to $Ph_2CHOMgBr$ (IV) and to (I) would account for the formation of the observed products.



$$\underset{}{Ph_2C{=}O} + \underset{(I)}{Me_2\overset{H}{\overset{|}{Si}}CH_2MgBr} \rightarrow \underset{(IV)}{Ph_2CHOMgBr} + Me_2Si{=}CH_2 \qquad (1)$$

$$\underset{(IV)}{Ph_2CHOMgBr} + Me_2Si{=}CH_2 \rightarrow Me_2\underset{OCHPh_2}{\underset{|}{Si}}{-}CH_2MgBr \xrightarrow{H_2O} \underset{(II)}{Me_3SiOCHPh_2}$$

$$Me_2Si{=}CH_2 + \underset{(I)}{Me_2\underset{H}{\underset{|}{Si}}CH_2MgBr} \xrightarrow{H_2O} \underset{(III)}{HMe_2SiCH_2SiMe_3}$$

Another possible route to the major product is by a direct nucleophilic attack of the alkoxide (IV) at the silicon atom of (I). The alkoxide could be formed as in Eqn. (1) or from the ketyl radical, benzophenone is known to give ketyl radicals with Grignard reagents[1],

$$Ph_2C{=}O + RMgX \rightarrow Ph_2\dot{C}{-}OMgX$$

This radical could abstract a hydrogen from (I) giving the alkoxide (IV). Alkoxides do not normally react with the silanes[3] and we have established that the alkoxides IV does not react with (I) under the conditions of the reaction.

If this reaction does not involve a ketyl or a Si=C intermediate, the most reasonable route to the main product would be via a concerted rearrangement with a benzophenone–Grignard complex.

We have observed this abnormal behaviour only with benzophenone; thus acetone reacts with (I) to give the products expected from a normal addition followed by a β-elimination.

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