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Preliminary communication

FACILE MAGNESIATION OF CARBON BRØNSTED ACIDS WITH ELECTROPHILIC, DONOR-FREE ALKYLMAGNESIUM COMPOUNDS

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Summary

A solution of n-butyl (s-butyl)magnesium in an alkane reacts readily between 25 and 110°C with a series of carbon Brønsted acids to produce the corresponding unsolvated diorganomagnesium derivatives in excellent yields. Such facile magnesiations provide a superior preparative route to donor-free compounds of the R_2Mg type, where R is cyclopentadienyl, indenyl, 9-fluorenyl or 1-alkynyl. Furthermore, sulfones form isolable 1/1 complexes with n-butyl (s-butyl)magnesium and these complexes then undergo automagnesiation between 25 and 85°C. Methyl phenyl sulfone undergoes magnesiation on the methyl group, while diaryl sulfones are magnesiated at the ring carbon *ortho* to the sulfur.

The magnesiation of carbon Brønsted acids by alkyl Grignard reagent etherates is a relatively slow reaction, even at temperatures of 60—100°C and even when the ether solvent has been replaced by benzene or toluene. For example, ethylmagnesium bromide reacts with cyclopentadiene over 6 h at 60°C to yield cyclopentadienylmagnesium bromide [1]; conversion of the latter compound into dicyclopentadienylmagnesium then requires thermal decomposition under high vacuum to give only a 40% yield [2]. The direct reaction of magnesium metal with cyclopentadiene, in either of two processes, is scarcely any improvement in convenience: (1) reaction at 500—600°C gives 40% of dicyclopentadienylmagnesium [3]; or (2) the titanium-catalyzed reaction requires 20—50 h and yields a titanium-contaminated product in 60% yield [4].

In light of these difficulties in preparing dicyclopentadienylmagnesium (I), we are pleased to report that this magnesium derivative and analogous compounds can be prepared rapidly and in high yield at temperatures between 25 and 110°C. The appropriate carbon Brønsted acid dissolved in an alkane

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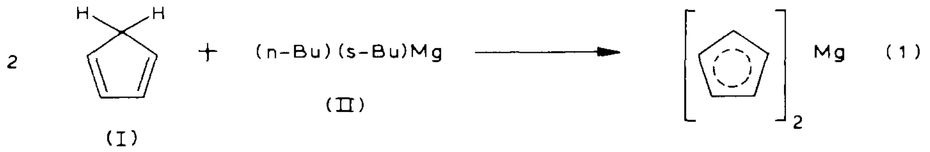
TABLE 1

PREPARATION OF UNSOLVATED DIORGANOMAGNESIUM COMPOUNDS BY THE MAGNESIATION OF CARBON BRØNSTED ACIDS BY n-BUTYL (s-BUTYL)MAGNESIUM

Substrate RH	Amount of substrate (mmol)	Amount of Bu_2Mg [a] (mmol)	Reaction temperature (°C)	Reaction time (h)	R_2Mg formed [b]	Melting point (°C)	Yield [c] (%)
Cyclopentadiene	100	46	25	1.5	$(C_5H_5)_2Mg$	178—180	82
Indene	100	50	98—108	7.0	$(C_9H_7)_2Mg$	218—221	87
Fluorene	100	50	98—108	18.0	$(C_{13}H_9)_2Mg$	[d]	95
1-Octyne	156	78	25	3.0	$(C_8H_{13})_2Mg$	viscous liq.	74
Phenylacetylene	180	90	25	1.0	$(C_8H_5)_2Mg$	170—180, dec.	93
Methyl phenyl sulfone	20	60	60—80	1.0	$PhSO_2CH_n(MgBu)_{3-n}$ [e,f]	—	40
					$PhSCH_3$		60
Diphenyl sulfone	10	10	70—85	3.0	$PhSO_2C_6H_4MgBu$ [f,g]	—	75

[a] The n-butyl (s-butyl)magnesium used was a 0.76 *M* solution in n-heptane or ISOPAR® C. The latter is a proprietary isoparaffinic hydrocarbon mixture, free of any aromatics, alcohols or ethers, offered by the Exxon Corporation, U.S.A. [b] Such isolated R_2Mg derivatives were characterized by IR spectroscopy and quantitative determination of the RH and Mg obtained upon hydrolysis. [c] The yields reported are isolated yields of pure product, except for the cases of the sulfones, where the yields are calculated on the amount of deuterated sulfur compound recovered in a D_2O work-up. [d] The product does not melt under 480° C. [e] The methyl phenyl sulfone recovered after treating the reaction mixture with D_2O was shown by mass spectral analysis to be a mixture of mono-, di-, and trideuterated products. [f] Both methyl phenyl sulfone and diphenyl sulfone form 1/1 insoluble complexes with Bu_2Mg at 25° C. Hydrolysis of these complexes with D_2O gave the undeuterated sulfone and a magnesium analysis consistent with a 1/1 complex. [g] Work-up with D_2O gave 75% of diphenyl sulfone, which was a 4/1 mixture of 2-deuterio- and 2,2′-dideuteriodiphenyl sulfones, as shown by IR, ^1H NMR and mass spectral analyses.

is simply treated with a solution of one-half an equivalent of n-butyl (s-butyl)-magnesium (II) in heptane or in an alkane of comparable volatility*. As exemplified in eq. 1 and 2 and as presented in Table 1, various substituted cyclopentadienes (cyclopentadiene, indene, and fluorene) and terminal alkynes (1-octyne and phenylethyne (III)) react smoothly to form the diorganomagnesium derivative in high yield.




$$2\,\mathrm{PhC{\equiv}CH} + \mathrm{(n\text{-}Bu)(s\text{-}Bu)Mg} \longrightarrow \mathrm{(PhC{\equiv}C)_2Mg} \qquad (2)$$

(III) (II)

The ease and convenience of these magnesiations are illustrated by the procedure for preparing diindenylmagnesium. Thus, 11.6 g (100 mmol) of freshly distilled and deoxygenated indene were placed in a 500-ml, two-necked flask provided with a reflux condenser, pressure-equalizing addition funnel and magnetic stirring. The flask was maintained under a nitrogen atmosphere while 63 ml of a 0.76 *M* solution of n-butyl (s-butyl)magnesium in n-heptane were added dropwise over 2 h. Then the solution was stirred under reflux for 7 h. The resulting pale orange suspension was cooled and collected, under nitrogen, on a glass filter frit. After washing several times with dry pentane, the off-white diindenylmagnesium weighed 11.0 g (87%) and melted at 218—221°C [6]. Hydrolysis of an aliquot gave 98% of the theoretical amount of indene (GLC, with a tetralin standard) and a magnesium content of 9.3% (expected: 9.55%).

These donor-free magnesiations have several noteworthy features, when compared with magnesiations effected by Grignard reagents in ethers. First, the rapidity of magnesiations by n-butyl (s-butyl)magnesium indicates that these reactions are promoted by the greater electrophilicity of an uncoordinated magnesium center. Second, the ease of magnesiation, as judged by the time and temperature of reaction, falls in the order: cyclopentadiene > indene > fluorene. Such a reactivity ordering is consistent with the increasing difficulty of the $\mathrm{Bu_2Mg}$-electrophile in attacking the π-electrons of the cyclopentadiene ring, as the ring is successively annulated with stabilizing benzene rings. Third, in the reaction of II with sulfones, the unsolvated nature of II leads to the formation of a 1/1 complex with the Lewis-basic $\mathrm{SO_2}$ group. In the case of diphenyl sulfone (IV), the resulting complex V undergoes automagnesiation (VI) when heated at 70—85°C (Scheme 1).

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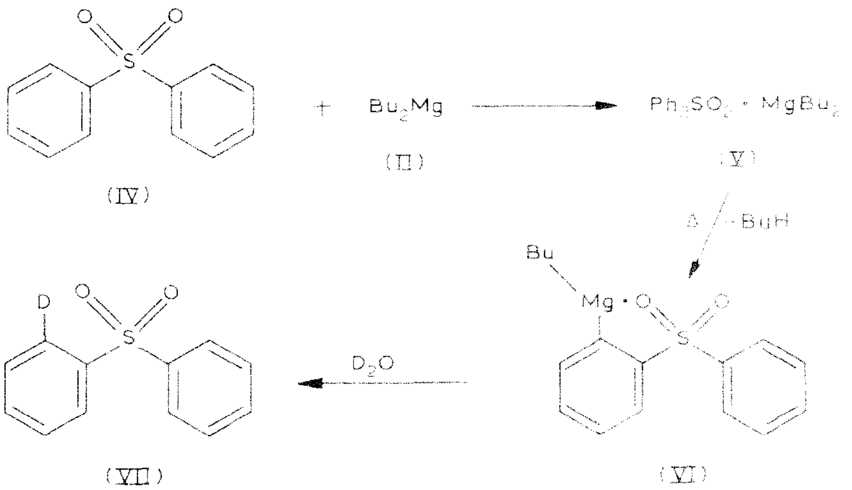
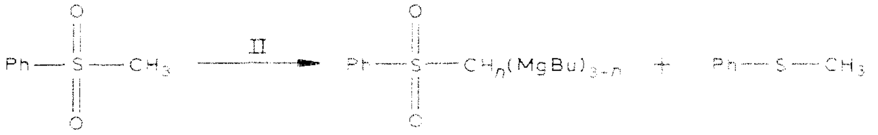
*The n-butyl (s-butyl)magnesium can be prepared in heptane according to a published procedure [5] or can be purchased from The Lithium Corporation of America, Gastonia, NC, in heptane or in ISOPAR® C, a proprietary isoparaffinic hydrocarbon offered by the Exxon Corporation, (U.S.A.). Other hydrocarbon-soluble dialkylmagnesium compounds, such as the butyl (ethyl)magnesium offered by Texas Alkyls, Inc., can be used with comparable success.



SCHEME 1

The attack of the magnesium at the C—H *ortho* to the SO_2 group (VI) was demonstrated by treatment with D_2O and the isolation of VII, whose mass spectrum showed it to be monodeuterated and whose IR spectrum displayed an intense band at 750 cm^{-1}, characteristic of an *o*-disubstituted benzene ring. In addition, as corroboration, the ^1H NMR spectrum of the deuterated diphenyl sulfone showed the appropriate decrease in the low-field *ortho*-proton multiplet. In a similar manner, methyl phenyl sulfone formed a complex with II and this complex reacted at 60—80°C to magnesiate the methyl group and to reduce the sulfone to a sulfide linkage (eq. 3).



$$Ph{-}\overset{O}{\underset{O}{S}}{-}CH_3 \xrightarrow{II} Ph{-}\overset{O}{\underset{O}{S}}{-}CH_n(MgBu)_{3-n} + Ph{-}S{-}CH_3 \quad (3)$$

From the isolation of sulfone complexes of IV and from the occurrence of magnesiation adjacent to the SO_2 group (α) in methyl phenyl sulfone (pK_a of 23) and *ortho* in diaryl sulfones (pK_a of $<$ 37)), it is clear that the course of such magnesiations is predetermined by complexation of the electrophilic Bu_2Mg at the oxygen of the sulfur group. Where such anchimeric assistance to electrophilic magnesiation is not available, no reaction with Bu_2Mg occurs. Thus, both toluene (pK_a of 35) and triphenylmethane (pK_a of 33) were not attacked by II.

These smooth and clean magnesiations of various carbon Brønsted acids by donor-free alkylmagnesiums make available novel unsolvated diorganomagnesium compounds, whose possible structures and chemical reactivity will surely excite the curiosity of organometallic chemists.

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