PREPARATION OF AN EXTREMELY ACTIVE MAGNESIUM SLURRY FOR GRIGNARD REAGENT PREPARATIONS BY METAL ATOM—SOLVENT COCONDENSATIONS

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Summary

Magnesium vapor (atoms) is cocondensed with solvents (THF or hexane) at —196°. Upon warming the magnesium agglomerates, and a Mg—solvent slurry is formed that is very active in Grignard reactions. Normally unreactive aryl halides react readily with this active Mg slurry. Low temperature Grignard formations can also be carried out easily with no problems with reaction initiation.

Recently, numerous publications concerned with the unusual activity and chemistry of clean high surface area metals have appeared [1—3]. These active metals have been produced by reduction of metal salts in solution. Also, as Rieke and Bales recently disclosed, in some cases simply adding metal salts can serve to activate a metal such as magnesium [1b]. These are very useful techniques. However, in some instances reactive metal surfaces (slurries in solution) are desirable in the pure form in the absence of metal salts. Our approach to the preparation of such slurries has been by the cocondensation of metal atoms with inert solvents at —196°, and then warm-up and isolation of the metal—solvent mixture. This slurry can then be manipulated in normal glassware under inert atmosphere. Thus, the overall technique is different from the normal metal atom reaction technique where the metal vapor and substrate are cocondensed [4,5].

Thus, by vaporizing nickel under vacuum and cocondensing the vapor with excess hexane or perfluorocyclobutane, we have produced a nickel film* that is quite reactive with organohalides. For example, allyl bromide readily reacts with this film at < 50° to yield propene and coupling products. Similarly, magnesium cocondensed with hexane or tetrahydrofuran (THF) followed by warming to

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* We do not detect products in these metal atom—solvent cocondensations as measured by GLPC techniques. Therefore, we consider these materials "inert" solvents. However, it is possible that the resultant metal surface in the slurry reacts with or at least strongly coordinates with these solvents when the matrix is warmed. Thus very small amounts of products may be formed, but not detected (private discussions with E.L. Muetterties).

TABLE 1

GRIGNARD REAGENT PREPARATION USING ACTIVE MAGNESIUM (UNDER ARGON)

Halide	Conditions	Time	Yield (%)	Method of determination
C_6H_5Br	THF, 25°	Very rapid		
C_6H_5Br	Et_2O, 25°	Very rapid		
C_6H_5Cl	THF, 25°	3 h	85	Methanol quenching, GLPC
o-$C_6H_4Cl(CH_2CH=CH_2)$	THF, 25°	23 h	80	Methanol quenching, GLPC
C_6F_5Br	THF, −30°	45 min	77	Cold I_2—THF solution used for quenching, GLPC
$CH_2=CHCH_2Br$	THF, −40°	30 min	61	Cold I_2—THF solution used for quenching, GLPC
CF_3Br	THF, −30°	50 min	1	Cold I_2—THF solution used for quenching, GLPC

room temperature produced a very active magnesium for Grignard preparations. It is interesting that the initial −196° matrix formed by Mg atom—THF vapor cocondensation is a dark blue color, apparently due to a charge-transfer complex similar to the complexes reported by Skell and Girard for Mg atoms with ammonia, water, and alkyl halides [6]. Upon slight warming our Mg—THF matrix turned black with the formation of a black Mg—THF slurry. The metal left after THF pump-off was black, pyrophoric in air, and extremely reactive with water. It could be stored under an argon atmosphere in the dry state or slurry state for weeks at a time without noticeable loss in activity. Manipulation of the Mg—THF slurry in normal glassware under a head of argon allowed the preparation of Grignard reagents from aryl halides normally considered quite unreactive*. Table 1 summarizes our results. Thus, chlorobenzene reacted readily at room temperature with this Mg—THF slurry. Reaction times of 3—4 h gave yields of 85% Grignard, whereas with several different forms of "normal" Mg no reaction occurred (these control experiments are discussed in more detail later). In another example, 2-chloroallylbenzene formed the Grignard reagent at room temperature with this Mg—THF slurry. With "normal" Mg, reflux for 24 h in THF gave only moderate yields of the reagent. Fluorobenzene, however, did not react with the Mg—THF slurry at room temperature or THF reflux. Bromobenzene, as would be expected, reacted extremely fast.

This active Mg—THF slurry was also useful for the preparation of Grignards at low temperature, and so valuable for preparing organomagnesium halides that are unstable at room temperature. No problems were encountered with reaction initiations at low temperatures. Thus, bromopentafluorobenzene in THF reacted at −30° to give a 77% yield of Grignard reagent in 45 min. This reaction started immediately at −30°, and even proceeded at as low as −45°. In a similar experiment, allyl bromide in THF was found to react at −40° in 30 min to yield 61% Grignard reagent. Complete reaction had taken place, the remainder of the Grignard formed the coupling product 1,5-hexadiene. Carrying out this reaction

* Atomic magnesium will also react with relatively unreactive halides to yield Grignard reagents (cf. ref.6).

in diethyl ether solvent yielded only poorer results in terms of ease of Grignard preparation and in terms of coupling. In another experiment designed to produce a Grignard reagent at low temperature (that is unstable at room temperature) we treated trifluoromethyl bromide in THF with the Mg—THF slurry at −30°. Reaction proceeded smoothly at this temperature, but polymeric material formed continuously, and only 1% Grignard reagent (CF_3MgBr) could be trapped by addition of iodine.

It should be pointed out that we have done a number of control experiments designed to show if normal Mg in various forms would react with the reported substrates. The rate of any Grignard reagent formation is, of course, dependent on the surface area of clean Mg available. Therefore, we attempted reactions of chlorobenzene with regular Mg chips, Mg powder, and Mg filings freshly prepared by filing a magnesium rod in an argon atmosphere. Also, reactions of 2-chloroallylbenzene with Mg chips and Mg powder were attempted. No reaction took place in any of these experiments at room temperature in THF. Thus, no initiation took place. So our Mg—THF slurry not only allows rapid Grignard preparations, but the advantage of immediate reaction initiation in every case. Immediate initiations at low temperature for the preparation of temperature-sensitive Grignards is also a big advantage.

It appears then, that our technique for the Mg—THF preparation allows the Mg to remain in an only moderately agglomerated and very clean state. Thus, the Mg surface is protected by the solvent. However, this surface protection by solvent works about equally well using hexane or THF as a codepositor with Mg atoms. This result was obtained by comparing the rates of Grignard formation with chlorobenzene with several types of active magnesium: (1) magnesium obtained from codeposition of Mg—THF and direct use of this slurry, (2) magnesium obtained from codeposition of Mg—THF followed by THF pump-off followed by THF readdition, and use of the resultant slurry, (3) magnesium obtained by codeposition of Mg—hexane followed by hexane pump-off followed by THF addition, and use of the resultant slurry. Interestingly, the results of these experiments showed that in each case the rate of Grignard formation was about the same. Thus, we conclude that the solvent codeposited with the Mg atoms can be either coordinating type (THF) or non-coordinating type (hexane) without significantly affecting the activity of the resultant magnesium. These experiments also showed that solvent pump-off followed by solvent readdition did not alter the Mg activity much as long as all manipulations were carried out in a rigorously inert atmosphere of argon. Slight exposure to air did cause deactivation.

It is likely that new forms of metals and metal surfaces will be quite important in the future for synthesis and catalysis [1—3,7]. This work points out a new approach to this area as well as another aspect of the advantages of using metal vapors in some schemes as synthetic reagents [4,5,8].

Experimental

All solvents in all operations were distilled from benzophenone ketal immediately prior to use. All manipulations were carried out under argon.

Active Mg preparation

In a typical active Mg preparation, 3.5 g Mg were vaporized in one hour from an aluminum oxide crucible in a tungsten wire heater (Mathis Co., C5 crucible, B 10 - 4x.030W heater) at 5.5 volts, 100 amps, connected to water cooled copper electrodes [5]. This apparatus was contained in a vacuum vessel (Kontes, 3000 ml, Kontes Glass Cat. No. K-612000 bottom, K-613200 top). During the Mg evaporation ca. 20 ml of THF (or hexane) was codeposited (vessel immersed in liquid nitrogen). Upon completion of the deposition the vessel was isolated from the vacuum pump and allowed to warm to room temperature. The Mg was isolated by surrounding the vessel with a polyethylene glove bag, argon flushing, filling the vessel with argon, and transfer of the Mg—THF to a weighed tube with a stopcock. The Mg—THF slurry could be used directly, or the THF could be pumped off leaving dry active Mg.

Manipulation of the active Mg under inert atmosphere

After preparation of the Mg—THF slurry, the THF could be pumped off. Then a desired portion of the dry active Mg could be transferred to a weighed reaction flask in an argon filled glove bag, followed by reweighing of the Grignard reaction flask to determine the charge of Mg.

In the cases where the Mg—THF slurry was used directly for Grignard preparations, it was only possible to make a rough estimate of the Mg transferred to the Grignard reaction flask. This was done by shaking the Mg—THF slurry vigorously and quickly pouring off a known volume (in an argon filled glove bag). Since the total Mg in the total Mg—THF slurry was known, and the total volume of the slurry was known, then the estimate could be made (with the assumption that the Mg was evenly dispersed after violent agitation).

The following section gives typical descriptions of Grignard reactions carried out.

Grignard reactions with active Mg

Bromopentafluorobenzene. In a typical Grignard reaction, 0.31 g (13 mmol) active Mg was transferred under argon to a one-necked 50-ml flask equipped with a serum cap for removal of liquid aliquots by syringe. After weighing, the flask was charged with 8 ml THF under argon. Then the flask, while under a head of argon, was cooled to $-30°$, and 1.78 g (7.2 mmol) bromopentafluorobenzene was syringed in. Aliquots (0.20 ml) were intermittently taken with a cold syringe and syringed into 0.5 ml THF samples at $-78°$ containing a few crystals of iodine. (Methanol quenching in some cases.) After warming and agitation, GLPC analyses on a 5' × 1/4" 20% SE-30 (silicon rubber) column (or 10' × 1/4" 20% Carbowax 20M) were carried out.

The preceding general technique was used for chlorobenzene, 2-chloroallylbenzene, allyl bromide, bromopentafluorobenzene, and trifluoromethyl bromide with the indicated reaction temperatures (Table 1).

Trifluoromethyl bromide. Dry active Mg (0.188 g, 7.7 mmol) was transferred as described above. The flask was connected to a vacuum system, evacuated, and 15 ml THF distilled in. The flask was cooled to $-70°$ with magnetic stirring, and then opened to a bulb of CF_3Br gas (5 mmol), most of which quickly condensed into the reactor flask. The pressure of the system was noted, and

then argon added until a pressure of 700 mm Hg was reached. Stirring was continued for one hour while samples were taken off by cold syringe and immediately quenched in a —78° I_2—THF mixture followed by GLPC analysis on a 15' × 1/4" SE-30 GLPC column at 28°. These analyses showed that no reaction occurred until the solution was allowed to warm to —30°, at which time reaction took place over a 50 min period with the precipitation of a blackish-red solid. Some perfluoroethane and ethylene was detected along with CF_3Br and CF_3I in the quenched samples. Approximately 95% of the CF_3Br had been consumed and a 1% yield of CF_3I was found by GLPC.

Acknowledgement

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