= CHEMISTRY ====

Synthesis of Phenylmagnesium Chloride in Hydrocarbons

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Received June 2, 2006

DOI: 10.1134/S0012500807010077

Phenylmagnesium halides are widely used for the introduction of phenyl groups into molecules of organic and organoelement compounds. In spite of the higher reactivity and the ease of preparation of phenylmagnesium bromide as compared with phenylmagnesium chloride, the use of the latter is much more preferable. This is due to the substantially lower cost and greater availability of the initial aryl halide and the lower propensity of phenylmagnesium chloride to undergo the Wurtz reaction.

Ether is the most widely used solvent for preparing Grignard reagents; however, the reaction of chlorobenzene with magnesium in this solvent proceeds so slowly that its use for preparation purposes is inexpedient. As a rule, the synthesis of phenylmagnesium chloride is carried out with the use of solvents with higher donor ability, tetrahydrofuran [1] and ethyl cellosolve [2]; however, their use is limited by their high cost, fire risk, and explosion hazard.

The method of synthesis of these Grignard reagents in hydrocarbons with addition of donor solvents is widely used, in particular, for preparing phenylmagnesium chloride in chlorobenzene with addition of tetrahydrofuran [3, 4]. However, in our opinion, such an approach is a certain compromise.

Phenylmagnesium chloride can be obtained by the reaction of magnesium with excess chlorobenzene in an autoclave at 160–170°C in about 70% yield; however, this method is poorly applicable in industry [5]. The synthesis of phenylmagnesium chloride was also facilitated by the assistance method when a mixture of chlorobenzene with ethyl bromide was used [6]; however, the yield of the compound was only 39%. Different additives have been used to promote the reaction:

iodine [7], metal alkoxides [8], and tetraethoxysilane [9]. However, until now, no reliable and industrially feasible method for preparing phenylmagnesium chloride in hydrocarbons has been available. At the same time, the preparation of aromatic Grignard reagents in hydrocarbons offers new possibilities for their commercial application taking into account the low cost, low hygroscopicity, and safety of these solvents [10].

The use of gallium trihalides as catalysts of different processes was proposed previously for preparing organometallic and organoelement compounds. Their catalytic activity was shown to be sharply different from the activity of similar aluminum and indium salts [11, 12]. Recently, Japanese researchers also demonstrated that gallium trichloride differs dramatically in reactivity and catalytic activity from aluminum trichloride [13]. Therefore, we studied the possibility of using gallium trihalides as catalysts for preparing phenylmagnesium chloride in a hydrocarbon medium. The addition of 10^{-4} mol % GaX₃ (X = Cl, I) into the reaction medium makes it possible to obtain phenylmagnesium chloride in aliphatic (nonane) and aromatic (xylene) hydrocarbons, narrow cuts of petroleum products (kerosene), and excess chlorobenzene. The reaction has a short induction period and starts at 120-125°C. The beginning of the reaction can easily be detected from a sharp change in the color of the reaction mixture from colorless to beige or bright yellow. The reaction is completed in 25-30 min on account of the inherent exothermic effect to result in complete magnesium dissolution. We did not determine directly the yield of the Grignard reagent. However, it is rather high because the addition of dimethyldichlorosilane to the reaction mixture leads to dimethyldiphenylsilane in 75–80% yield. Below, we describe a typical example of the reaction procedure.

A 12-g sample of magnesium (0.5 mol), 250 mL of chlorobenzene, and 10 mg of gallium trichloride were placed into a three-necked flask equipped with a mechanical stirrer, a dropping funnel, and a reflux condenser with a calcium chloride tube. The mixture was heated with stirring for 30 min at 130°C until the reaction began (the appearance of a yellow color); then the heating was turned off. After the reaction completed,

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25 g (0.2 mol) of dimethyldichlorosilane was added to the cold reaction mixture. Then, the mixture was heated for 8.5 h at 70°C. The precipitate was filtered off on a Buchner funnel and washed with chlorobenzene. The chlorobenzene was distilled off from the filtrate. The residue was distilled in a vacuum to give 31.8 g (75%) of dimethyldiphenylsilane, bp 128–130°C (5 mmHg). Literature data: bp 128°C (5 mmHg).

¹H NMR (δ , ppm): 0.6 (s, 6H, CH₃), 7.3–7.6 (m, 10H, C₆H₅).

¹H NMR spectra were recorded on a Bruker DPX-400 spectrometer operating at 400 MHz for 10% solutions in CDCl₃ with TMS as an internal reference.

The analysis of the reaction mixture by the GLC method was carried out on a Tsvet-500 chromatograph with a katharometer (3 m \times 4 mm glass columns with 10% PMS-1000 on 0.125–0.150 mm Inerton-super using helium as a carrier gas).

We found no marked influence of the nature of the halogen in gallium halide on the rate of magnesium dissolution. This indicates that GaBr₃ will show a similar catalytic effect. Thus, gallium halides can behave as efficient catalysts in the synthesis of Grignard reagents from unreactive halides.

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