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The Coupling Reaction of Phenylmagnesium Bromide with Mn(III) or Co(III) Tris(acetylacetonate)

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It is well known that aryl Grignard reagents give the corresponding diaryls with suitable metallic halides, such as $CoCl_2$, $CuCl_2$, $NiBr_2$, and AgBr.[1,2] However, no report has appeared concerning the coupling reaction of aryl Grignard reagents by means of the salts of Mn(III) or Co(III).

This note will deal with the coupling reaction of phenylmagenesium bromide with Mn(III) or Co(III) tris(acetylacetonate).

Results and Discussion

Into an ethereal solution of phenylmagnesium bromide under nitrogen we stirred, drop by drop, on cooling a dry benzene solution of a 0.8 molar equivalent of Mn(III) tris(acetylacetonate) to give mainly biphenyl, together with a small amount of acetophenone. The reaction conditions and yields are indicated in Table 1. During the course of the reaction, a precipitate was formed which had Mn(II) bis(acetylacetonate) as its main ingredient[3]; acetylacetone was never detected. When the mole ratio of Mn(III) tris (acetylacetonate) to phenylmagnesium bromide was decreased to 1:3, the relative yield of biphenyl was reduced, whereas that of acetophenone was considerably increased. The increasing yields of acetophenone were probably due to the reaction[4-6] of the excess of phenylmagnesium bromide with the acetylacetonate ion[5,7] liberated from Mn(III) tris(acetylacetonate) in the reaction mixture, though the exact reaction route remains obscure. When Mn(II) bis(acetylacetonate) was used as a coupling agent, only biphenyl was obtained in a low yield. A similar reaction using manganous chloride afforded a relatively high yield of biphenyl.[8]

TABLE 1. REACTIONS OF PHENYLMAGNESIUM BROMIDE WITH VARIOUS METAL SALTS IN THE PRESENCE AND ABSENCE OF α-METHYLSTYRENE

PhMgBr mol	Metal salt	mol	α-Methyl-styrene mol	Time min	Products: Biphenyl mmol (Yield, %)[a]	Products: Aceto-phenone mmol
0.025	$Mn(Acac)_3$	0.02	—	60	12.0 (98)	0.4
0.03	$Mn(Acac)_3$	0.01	—	60	7.0 (47)	6.9
0.03	$Mn(Acac)_3$	0.01	0.015	60	6.7 (45)	6.5
0.03	$Mn(Acac)_2$	0.01	—	60	2.3 (15)	0
0.03	$MnCl_2$	0.01	—	60	4.1 (27)	0
0.06	$Co(Acac)_3$	0.01	—	60	15.5 (52)	0
0.04	$Co(Acac)_2$	0.01	—	60	5.0 (25)	0

a) Based on reacted PhMgBr.

In order to obtain information concerning the nature of the coupling reaction by Mn(III) tris(acetylacetonate), the reaction was carried out in the presence of α-methylstyrene, which would be expected to be a radical acceptor.[9] As can be seen in Table 1, the presence of the radical acceptor does not affect the yields of the products. Accordingly, it may be said that the reaction does not involve free radical steps. The finding that Mn(II) bis(acetylacetonate) is relatively unreactive toward phenylmagnesium bromide may be ascribed to the fact that it is a stable metal complex.[3,10]

On the other hand, the slow addition of a suspension of Co(III) tris(acetylacetonate) in benzene to a ethereal solution of phenylmagnesium bromide gave the relatively good yield of biphenyl. No other products were detected. Thus, the result suggests a useful method for the coupling of aryl Grignard reagents. Co(II) bis(acetylacetonate) was similarly, but much less effective than Co(III) tris(actylacetonate).

Experimental

Reagent. The bromobenzene and α-methylstyrene were purified by distillation. The Co(II) bis(acetylacetonate), Co(III) tris(acetylacetonate), Mn(II) bis(acetylacetonate), and manganous chloride were of all of a special reagent grade and were used without further purification. The Mn-(III) tris(acetylacetonate) was prepared by the method of Charles.[11] The phenylmagnesium bromide solution was prepared according to the procedure of Kharasch and Fields.[12]

Small portions of the Grignard solution were taken out with a pipet, hydrolyzed by cold 1 N hydrochloric acid, and

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analysed with a Yanagimoto Model GCG-550-EP-type gas chromatograph, with columns packed with Silicone SE 30, in order to determine the quantity of biphenyl present in the Grignard solution.

General Procedure for the Reaction of Phenylmagnesium Bromide with Metal Salts. An outline of one reaction follows, while the general results are presented in Table 1. Into an anhydrous ethereal solution of 0.03 mol of phenylmagesium bromide, we stirred, drop by drop, and on cooling, 0.01 mol of Mn(III) tris(acetylacetonate) in a dry benzene solution, keeping the temperature at 10°C for 30 min. The reaction mixture was stirred at room temperature for another 30 min. The mixture was quickly filtered through a glass filter, and the precipitate was washed with benzene. The filtrate was hydrolysed by cold 1 N hydrochloric acid, and the hydrochloric acid layer was extracted with benzene. After separation, the combined organic layers were dried over sodium sulfate, and the solvent was removed under reduced pressure. The residue was submitted to gas-liquid partition chromatography (glpc). The yield data were obtained by glpc, with *n*-dodecane used as the internal standard. The products were identified by a comparison of their gas chromatograms and IR spectra with those of authentic samples obtained commercially.

The yields of biphenyl listed in Table 1 are freed from those formed in the preparation of the Grignard reagents.