Activated Metals. The Effect of Added Metal Salts on Magnesium Reactivity

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Summary Reduction of anhydrous magnesium chloride with potassium in refluxing THF in the presence of potassium iodide yields a black magnesium powder of exceptional reactivity, as demonstrated by its reaction with *p*-chlorotoluene, *p*-fluorotoluene, and other organic halides to give the corresponding Grignard reagents in high yields.

We recently reported[1,2] a new method for preparing magnesium and other metals in a very reactive state, using the combination $MgCl_2$–K–THF. We have since found that the addition of potassium iodide to a $MgCl_2$–K–THF mixture, prior to the reduction of the $MgCl_2$, results in magnesium much more active than that previously reported.[2] Table 1 shows the results for the preparation of the Grignard reagent of *p*-chlorotoluene (**1**), using commercial magnesium, our previous procedure, and the new procedure using potassium iodide.

The following procedure for the conversion of (**1**) into the Grignard reagent is representative of the general technique.

Table 1[a]

Magnesium source	Grignard yield (%) at reaction time (min) of 5	10	30	60
Commercial[b]	0	0	0	0
$MgCl_2$ + K[2]	0	0	14	50
$MgCl_2$ + KI + K[c] . .	84	94	97	100

[a] Grignard preparation of (**1**), Mg/(**1**) = 2, reaction run at room temperature. [b] 325 mesh magnesium, Poly Research. [c] KI/(**1**) = 1.

Freshly cut potassium (1·5 g, 38·4 mg atoms), anhydrous magnesium chloride (2·04 g, 21·4 mmol), oven-dried potassium iodide (1·6 g, 9·6 mmol), and freshly dried THF (50 ml, LAH distillation) were placed in a dry 100-ml round-bottomed flask equipped with septum inlet, magnetic stirring, nitrogen atmosphere, and condenser. The mixture was stirred and heated to reflux. Reflux times of 2—3 h. were employed, resulting in a viscous black mixture. The mixture was then cooled at room temperature for 0·5 h. **(1)** (1·22 g, 9·6 mmol) was injected, aliquots were periodically withdrawn from the stirred mixture and quenched in saturated NH_4Cl solution. Grignard yields were determined by v.p.c. measurement of toluene formed upon hydrolysis.

Table 2

Halide	Reaction time (min)	Grignard yield (%)[a] mono	di
(3)	15	100	100
(4)	15	100	10
	120	100	100
(5)	15	100	15
	120	100	30

[a] Yield obtained by hydrolysis and v.p.c. measurement of mono- and di-halides. Benzene was produced by hydrolysis in all reactions but was not measured.

Other salts have been studied, but at present none have been found which produce a more active magnesium than that obtained in the presence of potassium iodide. The ratio of magnesium to potassium iodide has been varied from 20 to 0·5, but little change was noted in magnesium reactivity. Optimum reactivity is, however, achieved when the potassium iodide is equivalent to the organic halide whose Grignard reagent is being prepared. It is interesting to note that if the potassium iodide is added to the reaction mixture after the reduction of $MgCl_2$ by K, there is no enhancement in the reactivity of the magnesium powder. Finally, the addition of potassium iodide to commercial magnesium resulted in a slower reaction with *p*-bromotoluene compared to the reaction using commercial magnesium by itself.

Further evidence of the higher reactivity of the metal compared to our normal procedure comes from the reaction of *p*-fluorotoluene **(2)** with potassium iodide activated magnesium. We recently reported[2] that refluxing fluorobenzene and the activated magnesium in diglyme for 1 h yielded 5—8% benzoic acid after treatment with CO_2.[2] Using the potassium iodide procedure (refluxing THF), and a magnesium/**(2)** ratio of 4, the yield of the Grignard reagent was 58% in 5 min and 70% in 1 h. The Grignard reagent was identified by its hydrolysis to toluene and its reaction with CO_2 to give *p*-toluic acid (65%).[3] 1-Chlorobicyclo-[2,2,1]heptane was converted into the Grignard reagent in 70% yield using the potassium iodide procedure followed by reaction with CO_2 to give 1-bicyclo[2,2,1]heptane carboxylic acid (63%).

Finally, Table 2 shows the results for the preparation of mono- and di-Grignard reagents of *p*-dibromobenzene **(3)**, *p*-bromochlorobenzene **(4)**, and *p*-dichlorobenzene **(5)** using our potassium iodide procedure. The reactions were run in THF at room temperature, using a magnesium/halogen ratio of 2 and a potassium iodide/halogen ratio of 1. The yields shown in Table 2 are vastly superior to previous preparations and attempted preparations of these di-Grignard reagents.[4]†

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† The active species could be Mg–K alloy, but the results using KI before and after the reduction of $MgCl_2$ by K seem to rule out this possibility. At present, the exact mode of action of KI is not known.

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[2] R. D. Rieke and P. M. Hudnall, *J. Amer. Chem. Soc.*, 1972, **94**, 7178.
[3] S. H. Yu and E. C. Ashby, *J. Org. Chem.*, 1971, **36**, 2123.
[4] For a summary of previous work see S. T. Ioffe and A. N. Nesmeyanov, 'Methods of Elemento-Organic Chemistry,' vol. 2, North-Holland, Amsterdam, 1967, p. 31.