

tation about the N-N bond²⁶⁻²⁹ inversion of the nitrogen atom,^{30,31} and the resonance effects of the non-

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bonded electrons of the nitrogen interacting with the fluoroformyl group resulting in hindered bond rotation about the carbonyl nitrogen bond.^{31,32} The number and location of the FCO group seem to determine the complexity of the variable temperature spectra; e.g., (CF₃)₄N₂ yields the simplest and CF₃(FCO)NNCF₃-(FCO) gave the most complex spectra of the entire hydrazine series. It should be noted that (CF₃C(O))₄N₂²⁶ and (CF₃FN)₂³² are reported to have incongruous nmr spectra.

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Activated Metals. IV. Preparation and Reactions of Highly Reactive Magnesium Metal¹

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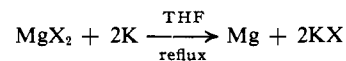
Abstract: The reduction of magnesium salts in ethereal solvents with potassium or sodium yields magnesium in the form of a fine black powder. This magnesium metal exhibits unusual reactivity toward alkyl and aryl halides. For example, bromobenzene reacts with the magnesium yielding phenylmagnesium bromide in a few minutes at -78°. The addition of potassium iodide and other inorganic salts prior to the reduction of the magnesium salt yields magnesium of even greater reactivity. Reactions of this magnesium with a variety of alkyl and aryl halides were studied as well as some of the physical properties of the black magnesium powders.

Grignard reagents represent one of the most important and versatile classes of organic intermediates known to the synthetic chemist. In spite of this, several types of Grignard reagents have not been readily available due to the lack of or slowness of reaction of certain types of halides with magnesium metal.

Previous to our studies, there were three basic modifications of the general procedure for the direct synthesis of difficultly formed Grignard reagents from the reaction of magnesium metal and an organic halide: (1) use of higher reaction temperatures by solvent variation, (2) use of a more strongly coordinating solvent, such as THF,³⁻⁷ and (3) activation of the magnesium metal.⁸⁻¹² The third method consists of activation of

the magnesium by reduction of the size of the metal particle¹¹ or by a chemical reaction. The Gilman catalyst,⁸ which involves the addition of iodine to activate the magnesium, is representative of this technique. Ethyl bromide and ethylene bromide have been employed in catalytic amounts to activate the metal surface and in molar quantities as entrainers.⁹ The use of certain transition metal halides has proven them to be useful catalysts.¹⁰ Ashby has recently combined the three techniques to prepare some alkylmagnesium fluorides.¹²

The initial studies of Rieke and Hudnall of the preparation of highly reactive magnesium metal have been reported.¹ We wish to report here further studies of activated magnesium prepared in a highly reactive state, finely divided, and free of metal oxides. The general technique is the reduction of a magnesium halide with alkali metal or other reducing agent, preferably in an ethereal solvent, and under an inert atmosphere. If



alkali metals are used, a solvent whose boiling point exceeds the melting point of the alkali metal is chosen. The reduction of magnesium halide yields a fine gray-black powder of magnesium metal. Usually, the Grignard reagents were prepared by simply adding the organic halide to the suspension of magnesium metal.

The studies reported here and preliminary investigations¹ show the reactivity of magnesium produced by our method is vastly superior to that of any of the methods described above.

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Results

Reaction with *p*-Bromotoluene (1). The reactions of activated magnesium with **1** under a variety of conditions are shown in Table I. Initially the system used

Table I. Reaction of *p*-Bromotoluene with Activated Magnesium^a

Reactn no.	Reflux time, hr MgCl ₂ + K ^b	Time at room temp, hr	Reactn temp, °C	Mg/ <i>p</i> -BrC ₆ H ₄ -CH ₃	% yield Grignard, 5 min reactn time
1	1	0.5	-78 ^c	1	87 ^d
2	2.5	0.5	-78	1	86
3	3.5	0.5	-78	1	84
4	3.5	93	-78	1	73
5	91	0.5	-78	1	63
6	2.5	0.5	25	1	84
7	2.5	0.5	25	2	100
8	2.5	0.5	-78	2	100

^a All reactions run in THF. ^b Magnesium source for all reactions was MgCl₂ + K. ^c Dry Ice-acetone bath. ^d All reactions were complete in 5 min or less, so yields at longer times are not given. Yields were obtained by hydrolysis and vpc measurement of toluene formed.

for magnesium preparation was MgCl₂-K-THF. The effects of reflux time, time at room temperature after reflux and prior to halide addition, and the ratio of magnesium to halide were studied. As the reflux time employed in the reduction of MgCl₂ was increased, the yield of Grignard reagent decreased (reactions 1-3 and 5). The reaction of K and MgCl₂ is exothermic, begins as soon as the K melts, and appears to be complete in 0.5 hr or less. Since little change in reactivity was noted for reflux times of 1-3.5 hr, subsequent reactions employed magnesium metal produced using reflux times of 2-3 hr. Also, an excess of MgCl₂ (10%) was usually run to prevent any problems with unreacted alkali metals.

The magnesium is also less reactive if it is prepared and then allowed to stand unstirred for periods longer than 0.5 hr (reactions 3 and 4). If the ratio of magnesium to **1** is 1, the maximum yield is in the range of 84-87%. This ratio assumes complete reduction of MgCl₂ by K, and these results indicate that all of the magnesium produced may not be in the same state of reactivity. From our studies with other metals, it is likely that part of the potassium metal is being consumed in cleavage of THF. This fact plus the fact that the system was probably not totally free of moisture and oxygen would lead to a less than quantitative conversion of magnesium salt to magnesium metal. No attempt was made to find the exact proportions of potassium to magnesium salts and ultimately to the organic halide which would yield exactly 100% conversion of **1** to the Grignard. In order to obtain complete conversion of the halide to Grignard, we simply used excess magnesium, as was done in reactions 7 and 8, using a magnesium/**1** ratio of 2. All of the reactions shown in Table I were complete in 5 min or less, so further studies normally used the less reactive halide *p*-chlorotoluene (**2**).

Effect of MgX₂. Several magnesium salts, MgX₂, were reduced in K-THF. The magnesium metal produced was then reacted with **2**. The results are shown in Table II. MgF₂ (reaction 9) and MgSO₄

Table II. Reaction of *p*-Chlorotoluene with Activated Magnesium Prepared from Various Magnesium Salts^a

Reactn no.	Magnesium salt MgX ₂	Reflux time, hr	Reactn temp, °C	Mg/KI ^b	% yield Grignard at reactn time (min) of 5 10 30 60 120
9	MgF ₂	10			MgF ₂ not reduced
10	MgCl ₂	3	25		0 0 14 50 75
11	MgBr ₂	4	25		0 0 21 47
12	MgI ₂	3	25		0 0 30 69 91
13	MgSO ₄	22			MgSO ₄ not reduced
14	MgCl ₂	3	0	2	26 46 73 85 91
15	MgBr ₂	5	0	2	0 0 0 10
16	MgI ₂	3	0	2	0 0 0 10 22

^a Mg/*p*-chlorotoluene = 2, reactions run in THF, using K. ^b KI added prior to MgX₂ reduction.

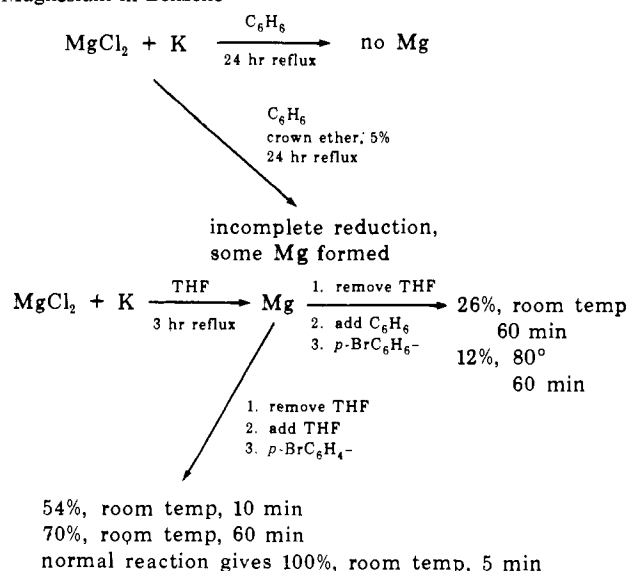
(reaction 13) gave very little or no magnesium metal during the reflux times shown, probably as a result of low solubility in THF. MgBr₂ was more difficult to reduce than MgCl₂, but gave essentially the same yield of Grignard (reactions 10 and 11). MgI₂ appeared to reduce as easily as MgCl₂, and the magnesium produced was slightly more reactive with **2** (reaction 12). On the basis of commercial cost and purity, MgCl₂ was used except when direct comparisons of magnesium halides were being run. Reactions 14-16 are discussed in another part of this report.

Effect of Solvent. MgCl₂ was reduced by K in the following solvents at their boiling point and the magnesium produced was then reacted with **1**: THF, DME, benzene, Et₃N, and diglyme. The ease of reduction of MgCl₂ in these solvents was: THF ≈ diglyme > DME > Et₃N > benzene. The reactivity of the magnesium produced was: THF > DME > diglyme (-78°); THF ≈ DME > diglyme (0°). Comparisons were not made for Et₃N and benzene since MgCl₂ reduction was incomplete in these solvents. In addition to these solvents, other alkali metal-solvent systems also work, such as Na-diglyme, but little research with these systems has been done. Except as noted, further work reported here employed the MgCl₂-K-THF system.

Reactions in Benzene. Several Grignard reagents have been formed in hydrocarbon solvents but usually the procedure is more difficult than using normal preparations in ethereal solvents. More vigorous conditions are utilized, and high yields in hydrocarbons require much greater attention to the experimental conditions than is required in conventional Grignard preparations.¹³ The results of our studies of benzene as a solvent for activated magnesium are summarized in Scheme I. Attempts to reduce MgCl₂ with K in benzene were unsuccessful, even after a reflux period of 24 hr. An attempt was made using the crown ether dicyclohexyl-18-crown-6 (5% based on K) to increase the solubility of the magnesium salts. Some reduction of the MgCl₂ occurred (solution became gray-black) but most of the potassium was unreacted after 24 hr of reflux.

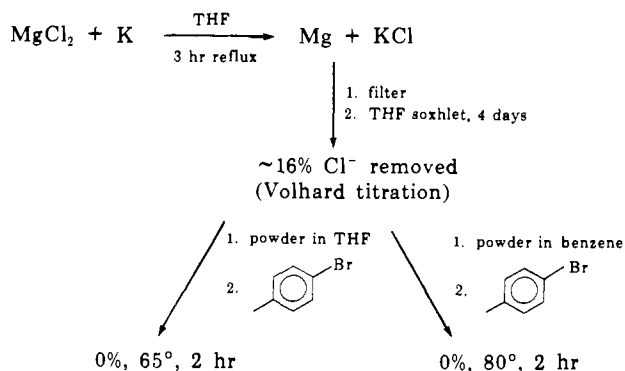
Magnesium metal was next produced by the normal procedure using MgCl₂-K-THF, THF was removed, and benzene was added to the magnesium powder, and the resulting benzene mixture was reacted with **1**. Several of these reactions were run, giving poor repro-

(13) For a review, see S. T. Ioffe and A. N. Nesmayanov, "Methods of Elemento-Organic Chemistry," Vol. 2, North Holland Publishing Co., Amsterdam, 1967, p 18.

Scheme I. Preparation and Reaction of Activated Magnesium in Benzene


ducibility. The best yield obtained was 26% of Grignard after 1 hr at room temperature. Running the reaction with **1** at 80° consistently gave lower yields than the room temperature reaction. The method of THF removal (distillation and vacuum or vacuum with no heat) did not affect the yield noticeably. Finally, removal of the THF followed by addition of fresh THF and reaction with **1** gave a 70% yield in 1 hr at room temperature, compared to a yield of 100% in 5 min by the normal procedure. At present, the reason for this deactivation of the magnesium by solvent removal is unknown. Possible explanations include an increase in particle coagulation and a change in the metal crystal structure.¹⁴

Soxhlet Experiments. In an attempt to remove the KCl produced in the reaction of MgCl₂ and K, the activated magnesium mixture was filtered through a soxhlet cup (nitrogen atmosphere) and then subjected to the normal soxhlet procedure using THF as solvent. The results of these experiments are shown in Scheme II.

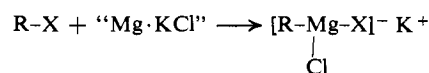
Scheme II. Soxhlet Experiments


After 4 days, an aliquot titrated by the Volhard method showed only 16% removal of chloride ion. The magnesium powder was then placed in a flask, benzene was added, and the mixture was reacted with **1**. No Grignard was formed after 2 hr at 80°. In another reaction, the magnesium powder was mixed with THF

(14) It is possible that the magnesium is reacting with the nitrogen atmosphere. This is being investigated.

as solvent, but again the powder was unreactive toward **1**, giving no Grignard after 2 hr at 65°. The reasons for the difficult removal of KCl and the resulting deactivation of the magnesium powder will be discussed later in this paper.

Effect of Added Metal Salts. In light of the soxhlet experiments and the apparent association of the KCl and magnesium metal, it was felt that possibly the reaction of organic halide and magnesium metal yielded an ate-complex. This would suggest that the alkali salts



might be an important factor in the high reactivity of the magnesium and therefore the reactivity might be increased more by varying the alkali metal salt. A series of reactions were run to assess the effect of adding excess salt to the activated magnesium mixture. Salts were added in various concentrations before and after the reduction of MgCl₂ by K. The results are summarized in Table III for the preparation of Grignard reagent from **2**.

Table III. Effect of Added Salt, MX, on the Reaction of *p*-Chlorotoluene and Activated Magnesium^a

Reactn no.	MX	Mg/MX	Reactn temp, °C	% yield Grignard at reactn time (min) of—				
				5	10	30	60	120
10	None		25	0	0	14	50	75
17	LiF	1	25	0	5	42	76	93
18	LiCl	1	25	0	7	47	74	88
19	NaF	1	25	0	0	30	64	87
20	NaCl	1	25	0	0	23	58	85
21	NaBr	1	25	0	0	13	54	84
22	NaI	1	25	89	93	98	99	100
23	KF	1	25	0	0	7	30	66
24	KCl	1	25	0	5	34	64	83
25 ^b	KCl	1	25	0	4	44	67	84
26	KBr	1	25	0	0	11	48	75
27 ^b	KBr	1	25	0	0	6	46	78
28	KI	1	25	87	93	98	99	100
29 ^b	KI	1	25	0	5	42	71	85
30 ^c	KI	1	25	43	66	92	97	100
31	KI	2	25	84	94	97	98	100
32	KI	20	25	51	76	94	97	100
33	KI	0.5	25	86	94	97	99	100
34	None		0	0	0	0	0	0
35	KI	10	0	8	17	55	75	85
36	KI	4	0	14	29	65	76	88
37	KI	2	0	26	46	73	85	91
38	KI	1	0	19	42	74	86	93
39	KI	0.5	0	25	45	74	85	93
40	LiI	2	0	0	0	0	0	11
41	NaI	2	0	0	6	21	49	70
42	CsI	2	0	6	12	41	73	89
43	I ₂	20	0	8	10	40	54	64
44	K ₂ SO ₄	1	25	13	33	69	87	95
45	K ₂ SO ₄	20	25	0	6	46	76	90
46	CuSO ₄	20	25	0	0	0	0	7
47	ZnBr ₂	20	25	0	16	31	64	86
48	MgCl ₂	0.5	25	0	0	9	22	48
49 ^b	MgCl ₂	0.5	25	0	0	0	0	0

^a Magnesium prepared from MgCl₂-K-THF, reflux 2-3 hr, Mg/*p*-chlorotoluene = 2, salt MX added prior to MgCl₂ reduction. ^b MX added after MgCl₂ reduction. ^c Concentration of all reactants halved.

The following salts resulted in a slight increase in reactivity of the activated magnesium compared to the reaction with no added salt (reaction 10): LiF, LiCl,

NaF, NaCl, and KCl (reactions 17–20 and 24). NaBr (reaction 21) and KBr (reaction 26) gave essentially the same results as the control reaction. KF (reaction 23) resulted in a slight decrease in reactivity. With NaI or KI, however, a remarkable increase was observed, resulting in an 87–89% yield of Grignard in 5 min (reactions 22 and 28). If KCl (reaction 25) or KBr (reaction 27) were added after the reduction of MgCl_2 , the results were essentially the same. However, KI addition after MgCl_2 reduction resulted in magnesium less reactive compared to that produced with prior addition (compare reactions 28 and 29).

When KI is added, the initial mixture prior to reduction is yellow. Upon reduction of MgCl_2 the resulting mixture is darker and more viscous than that produced normally using MgCl_2 -K-THF. Reducing the viscosity (reaction 30) resulted in a slight decrease in reactivity. Next, several reactions were run to determine the optimum amount of KI to use in the reaction. The ratio of magnesium to KI was varied from 20 to 0.5, and reactions were run at room temperature and 0° . The results (reactions 28 and 31–39) show that the various ratios had little effect after a reaction time of 30 min, indicating a catalytic effect for KI. The optimum ratio appears to be obtained when the KI added is equivalent to the organic halide whose Grignard is being prepared.

Reactions were run using LiI, NaI, and CsI at 0° for comparison to reaction 37 (reactions 40–42). None of these salts resulted in magnesium as reactive as that produced in the presence of KI, although all were superior to the normal procedure (reaction 34). Also, the addition of iodine (reaction 43) resulted in increased reactivity.

Other salts have been found which also result in a more reactive magnesium powder. For example, K_2SO_4 (reactions 44 and 45) and ZnBr_2 (reaction 47) accelerate the reaction with **2**, but CuSO_4 makes the magnesium less reactive (reaction 46). Finally, excess MgCl_2 was used, the ratio of MgCl_2 to magnesium produced being 2. Addition of MgCl_2 prior to reduction results in lower reactivity magnesium (reaction 48), while excess MgCl_2 added after reduction results in no Grignard being formed after a 2 hr reaction period (reaction 49).

In Table II reactions 14–16 show that the best magnesium halide to use with KI is MgCl_2 , since magnesium produced from MgBr_2 -KI-K or MgI_2 -KI-K resulted in substantially lower yields of Grignard when reacted with **2**.

Effect of MgCl_2 /K Ratio. Since a large excess of MgCl_2 resulted in lower reactivity (reaction 48) we decided to try other MgCl_2 /K ratios. The results are shown in Table IV. Using a stoichiometric amount of MgCl_2 or a 5% excess of K yielded magnesium more reactive than produced normally with 10% excess MgCl_2 (reactions 10, 50, and 51). However, when KI was used with the same ratios little difference in reactivity was observed (reactions 52–54). Excess K results in by-product formation, which was not observed otherwise. To avoid any excess K and retain high reactivity a MgCl_2 excess of 1–5% is recommended.

Use of Et_3N . In an attempt to extend this reaction to other solvent systems, several reactions were run using Et_3N and Et_3N -THF mixtures. The results are shown in Table V. Et_3N has been used previously for

Table IV. Effect of Various MgCl_2 /K Ratios on the Reaction of *p*-Chlorotoluene with Activated Magnesium^a

Reactn no.	MgCl_2 , % excess	K, % excess	Reactn temp, $^\circ\text{C}$	Mg/KI ^b	% yield Grignard at reactn time (min) of				
					5	10	30	60	120
10	10	0	25		0	0	14	50	75
50	0	0	25		0	14	62	82	94
51 ^c	0	5	25		20	44	77	80	84
52	10	0	0	2	26	46	73	85	91
53	0	0	0	2	22	44	83	93	97
54 ^c	0	5	0	2	10	22	56	68	73

^a MgCl_2 + K were refluxed 2–3 hr in THF, Mg/p -chlorotoluene = 2. ^b KI added prior to MgCl_2 reduction. ^c With excess K, the *p*-chlorotoluene reacted initially to give ca. 20% non-Grignard product, as measured by disappearance of starting material.

Table V. Reaction of *p*-Chlorotoluene with Activated Magnesium^a Prepared in THF- Et_3N ^a

Reactn no.	THF, ml	Et_3N , ml	MgCl_2 , % excess ^b	Reflux time, hr	Mg/KI	% yield Grignard ^b at reactn time (min) of				
						5	10	30	60	120
10	50	0	10	3		0	0	14	50	75
55	35	15	10	3		0	12	38	69	85
56	25	25	10	3			47	77	93	99
57	25	25	10	3	1	73	87	97	100	100
58	15	35	10	22		0	0	0	0	0
59	5	45	10	22		0	0	0	0	0
60	0	50	10	22		MgCl ₂ not reduced				
61	0	50	20	22		MgCl ₂ not reduced				
62 ^c	15	35	10	3		0	0	0	11	32

^a Magnesium prepared from MgCl_2 + K, *p*-chlorotoluene added to room temperature mixture, Mg/p -chlorotoluene = 2. ^b Excess based on potassium used. ^c MgCl_2 reduced in THF, followed by Et_3N addition.

Grignard preparations, notably by Ashby,¹⁶ who prepared Grignards using Et_3N and hydrocarbon solvent mixtures.

Using 35 ml of THF and 15 ml of Et_3N or 25 ml of each solvent results in a more reactive magnesium than normal (reactions 10, 55, and 56). However, increasing the amount of Et_3N resulted in slower reduction of MgCl_2 and no reactivity with **2** after 2 hr (reactions 58 and 59). In Et_3N only as solvent, MgCl_2 is not completely reduced after 22 hr reflux (K remains in mixture, reactions 60 and 61). When MgCl_2 was reduced in 15 ml of THF, followed by addition of 35 ml of Et_3N , some reaction with **2** occurred, but the yields were lower than those obtained in the 25 ml–25 ml solvent mixture (reaction 62).

Since the best results were obtained using a 25 ml–25 ml solvent mixture, this reaction was rerun using KI (reaction 57). A large increase in reactivity was observed, but the increase was no greater than observed in THF only using KI (reaction 28).

Comparisons to Commercial Magnesium. Comparisons were run using **1** and **2** and commercial magnesium (325 mesh, Poly Research). The results are shown in Table VI. The results show that commercial magnesium was much less reactive toward **1** and **2** than our activated magnesium. The addition of KCl, KI, and MgCl_2 to commercial magnesium retarded its reaction with **1** (reactions 64–66).

Reactions with Organic Fluorides. Activated mag-

(15) E. C. Ashby and R. Reed, *J. Org. Chem.*, 31, 971 (1966).

Table VI. Comparison of Activated Magnesium to Commercial Magnesium^a

Reactn no.	Mg source	Reactn Halide	temp, °C	Added salt MX ^b	% yield Grignard at reactn time (min) of			
					5	10	30	60
7	MgCl ₂ + K ^c	1	25		100	100	100	100
63	Comm ^d	1	25		21	69	93	100
64	Comm	1	25	KCl	5	12	75	100
65	Comm	1	25	KI	0	0	30	100
66	Comm	1	25	MgCl ₂	4	6	100	100
10	MgCl ₂ + K ^c	2	25		0	0	14	50
67	Comm	2	25		0	0	0	0
68	Comm	2	66		0	0	0	0

^a All reactions run in THF, Mg/*p*-tolyl halide = 2. ^b Mg/MX = 1, refluxed 3 hr prior to halide addition. ^c Refluxed 3 hr. ^d 325 mesh magnesium, Poly Research.

nesium was reacted with *p*-fluorotoluene (**3**) and 1-fluorohexane (**4**) under a variety of conditions. The results are shown in Table VII. Prior to our work, all

Table VII. Reaction of *p*-Fluorotoluene and 1-Fluorohexane with Activated Magnesium^a

Reactn no.	Fluoride	Mg/fluoride	Mg/KI	Reactn temp, °C	Solvent	% yield Grignard at reactn time (min) of			
						10	30	60	180
69 ^b	3	1		162	Diglyme		8	5	
70	3	2	2	66	THF		26	27	55
71	3	3	2	66	THF	40	53	59	58
72	3	4	2	66	THF	58	57	69	66
73	4	2		25	THF	10	26	27	54
74	4	2		66	THF	53	48	72	71
75	4	2	2	25	THF	38	53	73	89

^a Magnesium source for all reactions was MgCl₂ + K. ^b Refluxed 18 hr prior to fluoride addition. ^c All THF reactions refluxed 3 hr prior to fluoride.

efforts to prepare the Grignard reagent from fluoro-benzene and magnesium or **3** and magnesium had failed.¹² Using the MgCl₂-KI-K system, refluxing THF, and a Mg/**3** ratio of 4 gave a 69% yield of the fluoro Grignard in 1 hr (reaction 72). Quenching the Grignard with CO₂ gave a 63% yield of the expected *p*-toluic acid. Using a lower Mg/**3** ratio resulted in lower yields (reactions 70 and 71). Using diglyme but no KI gave only 8% yield after 1 hr at 162° (solvent refluxing). Continued refluxing in THF or diglyme for periods of 24–48 hr gave no appreciable increase in Grignard formation compared to reflux times of 2–3 hr.

Reaction with **4** using the normal procedure gave 54% yield in 3 hr at room temperature and 71% yield in 3 hr at 66° (reactions 73 and 74). When the KI procedure was employed, the yield was 89% after 3 hr at room temperature (reaction 75). Quenching the Grignard of **4** with CO₂ gave the expected heptanoic acid in 88% yield, based on Grignard. These results are superior to those obtained by Ashby for the preparation of the Grignard of **4**,¹² and provide further evidence for the high reactivity of magnesium prepared by our method.

Reactions with Other Halides. The reactions of activated magnesium with various halides and dihalides, some of which react with difficulty under the conditions of normal Grignard preparations, were investigated.

The results are summarized in Table VIII. The yields obtained by vpc after hydrolysis and the yields of carboxylic acids obtained after CO₂ quench are shown.

Previous efforts to prepare dimagnesium derivatives of benzene have been successful only with dibromo- or bromiodobenzene, required forcing conditions, and usually resulted in the monomagnesium derivative as the main product. This work has been surveyed by Ioffe and Nesmeyanov.¹³ Using the MgCl₂-KI-K-THF system, we have prepared the di-Grignard of *p*-dibromobenzene (**5**) in 100% yield in 15 min at room temperature (reaction 76). The yield was determined by vpc after hydrolysis and was based on the disappearance of starting material and bromobenzene and the formation of benzene. Yields at earlier reaction times were not determined. In earlier work, only one halogen atom of dichloro derivatives of benzene and naphthalene reacted with magnesium,^{16–19} and the chlorine of *p*-chlorobromobenzene (**6**) was found to be completely unreactive.²⁰ Using our method, we obtained a 100% yield of the mono-Grignard and a 10% yield of the di-Grignard of **6** in 15 min at room temperature (reaction 77). After 2 hr the yield of di-Grignard was 100%. With *p*-dichlorobenzene (**7**) the yield of di-Grignard was 30% in 2 hr (reaction 78). Using a lower Mg/halide ratio permitted the rapid and selective formation of the mono-Grignard of **7**, which was converted to 4-chlorobenzoic acid in 89% yield by CO₂ quench (reaction 79).

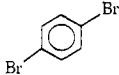
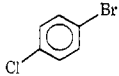
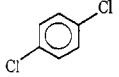
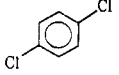





A primary halide, 1-bromooctane (**8**), reacted as expected to give 100% yield of the Grignard in 5 min at room temperature (reaction 80). CO₂ quench gave an 81% yield of nonanoic acid. The tertiary halide 2-methyl-2-chloropropane (**9**) gave a 100% yield in 10 min and was converted to pivalic acid in 52% yield after 1 hr of reaction (reaction 81). 1-Chlorobicyclo[2.2.1]heptane (**10**) reacted slowly at room temperature, so this was rerun in refluxing THF. Again, the Grignard preparation was slow, giving a 74% yield after 6 hr of reflux. The Grignard was then quenched with CO₂ to give 1-bicyclo[2.2.1]heptanecarboxylic acid (**11**) in 63% yield (reaction 82). Bixler and Niemann²¹ prepared **11** from **10** by conversion of **10** to the lithium salt, followed by CO₂ quench. Our method appears to be superior since it obviates the preparation of lithium sand used in the procedure of Bixler and Niemann.

An allyl halide, 3-chloro-2-methylpropene (**12**), was converted to 3-methyl-3-butenic acid (**13**) in 82% yield after 1 hr of reaction at room temperature (reaction 83). Wagner²² converted **12** to the Grignard in 81% yield after 10 hr at 14–16°, and obtained **13** from the Grignard in 40% yield after CO₂ quench.

Finally, the vinyl bromide 2-bromopropene (**14**) was converted to the Grignard in 100% yield in only 5 min at room temperature using our normal magnesium system, MgCl₂-K-THF. The Grignard of **14** was then converted to methacrylic acid (**15**) in 71% yield (reaction 84). Normant, in his pioneering work on vinyl Grignard preparations, has recommended a 40–50° range for halide addition to magnesium in THF,

(16) M. Gomberg and L. H. Cove, *Ber.*, **39**, 3274 (1906).(17) H. S. Pink, *J. Chem. Soc.*, **123**, 3418 (1923).(18) E. John and N. John, *Recl. Trav. Chim. Pays-Bas*, **55**, 585 (1936).(19) H. Normant, *C. R. Acad. Sci.*, **239**, 1510 (1954).(20) E. Krause and K. Weinberg, *Ber.*, **62**, 2235 (1929).(21) R. L. Bixler and C. Niemann, *J. Org. Chem.*, **23**, 742 (1958).(22) R. B. Wagner, *J. Amer. Chem. Soc.*, **71**, 3214 (1949).

Table VIII. Reactions of Activated Magnesium with Various Halides^a

Reactn no.	Halide	Mg/halide	Mg/KI	Reactn temp, °C	Reactn time, min	% yield Grignard ^b Mono	Di	% yield ^c -CO ₂ H
76		4	2	25	15		100	
77		4	2	25	15 60 120	100 100 100	10 57 100	
78		4	2	25	15 120	100 100	15 30	
79		2	2	25	5 60 180	70 86 90	0 0 0	89 ^d
80		2		25	5	100		81 ^e
81		2		25	10 60	100		52 ^e
82		1.7	2	66	15 90 360	11 42 74		63 ^d
83		2		25	60			82 ^e
84		2		25	5	100		71 ^e

^a Mg source was either MgCl₂ + K or MgCl₂ + KI + K, THF solvent, refluxed 2–3 hr prior to halide addition. ^b Yield by vpc after hydrolysis. ^c Yield of isolated carboxylic acid. ^d Yield based on Grignard. ^e Yield based on starting halide.

followed by heating for 0.5–1 hr at 70–80°. ²³ By this procedure he was able to obtain yields of 95–97% in the preparation of vinylmagnesium bromide. Our activated magnesium appears to be an improvement of Normant's method, since it allows the preparation of vinyl Grignards at room temperature or lower.

Reactions of Grignard Reagents. Grignard reagents prepared with our activated magnesium appear to react normally with various substrates. Reaction with H₂O gives the hydrocarbon and with CO₂ the carboxylic acid.

Bromobenzene (**16**) was converted to the Grignard with activated magnesium, and the Grignard was then reacted with benzophenone (**17**) in analogy with the procedure of Bachmann and Hetzner.²⁴ Triphenylmethanol (**18**) was obtained in 87% yield, compared to the literature²⁴ value of 89–93%. Next, the Grignard was prepared at –78° (Dry Ice–acetone bath) and reacted with **17** at –78°. Reaction for 2.5 hr yielded **18** in 28% yield, and the yield was raised to 73% after 17 hr reaction at –78°.

Discussion

The highly reactive magnesium described in this paper allows the ready preparation of many Grignard reagents which were heretofore not easily prepared or could not be prepared at all. One very important aspect of this work is that it permits the ready preparation of Grignard reagents at temperatures of –78° or even lower. This will allow the generation of Grignard

reagents of compounds which are stable only at low temperatures.

The origins of the unusual reactivity of the black metal powders can only be speculated about as our studies on the physical properties of these materials are only at a preliminary stage. We have referred throughout the paper to the black powders as magnesium metal. However, at this point we cannot rule out the possibility that we have prepared magnesium in the plus one oxidation state or that a magnesium–potassium alloy has been produced. Whereas we feel the experiments with the excess potassium support our contention that the powders do not contain an alloy, additional work needs to be done to clarify this point.

The soxhlet experiments clearly demonstrate that the magnesium metal is not a simple physical mixture of finely divided magnesium and precipitated alkali salt. In some manner, as the two materials are being formed and are precipitating out of solution, they are forming some composite material. Powder patterns and X-ray crystallographic data are being determined to help clear up this point. The soxhlet experiments also suggest that this material is formed in some metastable state, since prolonged refluxing decreases the reactivity of the magnesium.

Whatever the origins of the high reactivity (particle size, surface area, lack of oxide coating, high energy crystal packing, presence of alkali metal salt, or all of the above), we feel the procedures described in this paper will make the Grignard reagent an even more versatile reagent than it is now.

Experimental Section

Grignard reagents were analyzed by vpc, using a Hewlett-

(23) H. Normant, "Advances in Organic Chemistry," Vol. II, Interscience, New York, N. Y., 1960, pp 37–38.

(24) W. E. Bachmann and H. P. Hetzner, "Organic Syntheses," Collect. Vol. III, Wiley, New York, N. Y., 1955, p 839.

Packard 5750 research chromatograph and one of the following columns: 8 ft \times 0.25 in. 10% SE-30 on Chromosorb P, 6 ft \times 0.25 in. and 10 ft \times 0.25 in. 20% Carbowax 20M on Chromosorb W, or 6 ft \times $\frac{1}{8}$ in. 10% Ucon-W98 80-100 X. Aliquots of the reaction mixtures were hydrolyzed in saturated NH_4Cl solution and analyzed for starting material and hydrocarbon product, using either toluene or ethylbenzene as internal standard. Only reactions 51 and 54 (Table IV) resulted in detectable by-product formation during Grignard preparations. Ir spectra were recorded on Perkin-Elmer 421 and 257 spectrometers, using normal KBr pellet or liquid film techniques. Mass spectra were recorded on a Hitachi-Perkin-Elmer RMU-6E spectrometer. Melting points were determined on a Thomas Hoover capillary apparatus, and chloride ion determinations were by the Volhard method, using AgNO_3 and KCNS for back titration.

All operations concerning the preparation of activated magnesium and Grignard reagents were carried out in a nitrogen atmosphere either in a recirculating-equipped drybox (Fisher-Kewaunee) or on the bench using typical inert atmosphere and syringe techniques.²⁶ All compounds prepared were identified by comparison of melting points or boiling points and spectral characteristics to those of the authentic material.

Materials. The following organic halides were obtained commercially and used as supplied: **1**, **2**, **3**, **5**, **9**, **14** (Aldrich); **4**, **8**, **12** (Eastman); **7** and **16** (Allied); and **6** (Baker). Compound **10** was prepared by the literature²¹ procedure, and compound **17** was obtained from Aldrich.

Potassium (Baker purified) was cleaned under hexane or heptane prior to use. Commercial magnesium (325 mesh, 99.8%), used for comparison to our activated magnesium, was obtained from Poly Research. MgCl_2 (98%) was obtained from Alfa. MgF_2 (99.9%), MgBr_2 (99.9%), and MgI_2 (99%) were obtained from Poly Research. These MgX_2 compounds were stored in a desiccator over Drierite and used as supplied. MgSO_4 (Allied reagent, 98%) was oven-dried prior to use. THF (MCB), DME (Aldrich), diglyme (Aldrich), and benzene (Baker purified) were dried by distillation from LiAlH_4 prior to use. Et_3N (Aldrich) was distilled from NaAlH_4 .

The following inorganic compounds were obtained commercially and had listed purities of 99% or greater: NaBr , NaI , KF , KCl , KBr , KI (Allied); LiCl , NaF , NaCl , K_2SO_4 , I_2 (Baker); and LiF ,

ZnBr_2 (Fisher). These were ground to a fine powder and oven-dried prior to use. CuSO_4 was obtained by dehydration of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (Baker analyzed) under vacuum with heating. LiI and CsI were obtained from Alfa, stored in a desiccator over Drierite, and used as supplied.

General Procedure for the Preparation and Reaction of Activated Magnesium. Freshly cut potassium (1.5 g, 38.4 mg-atom), MgCl_2 (2.04 g, 21.4 mmol), the desired amount of inorganic salt, and THF (50 ml) were placed in an oven-dried 100-ml three-necked flask equipped with condenser, septum, heating mantle, magnetic stirring, and nitrogen atmosphere. The mixture was stirred and heated to reflux, where reduction of MgCl_2 occurred to give a dark gray mixture. Reduction in the presence of LiI , NaI , KI , or I_2 resulted in a mixture darker and more viscous than with other salts or in the absence of added salt. The mixture was normally refluxed for 2-3 hr to ensure complete reaction of potassium, and was then cooled at room temperature for 0.5 hr. The desired amount of organic halide was injected if liquid or added as a THF solution if solid. For reaction temperatures below room temperature, the mixture was cooled at room temperature for 0.5 hr and then placed in an ice bath (0°) or a Dry Ice-acetone bath (-78°) prior to halide addition. For reactions at solvent reflux temperatures, the halide was added to the magnesium mixture directly after the 2-3 hr reflux period, without an intervening period at room temperature. After halide addition, aliquots were periodically withdrawn from the stirred mixture and quenched in saturated NH_4Cl solution, followed by vpc analyses.

General Procedure for the Carbonation of Grignard Reagents. The reaction mixture was cooled to 0° (ice bath) and then quickly syringed onto a large excess of freshly crushed CO_2 powder in a flask equipped with stirring and nitrogen atmosphere. The resulting mixture was stirred vigorously until it reached room temperature and was then decomposed with 20% HCl solution. The resulting solution was extracted with ether, the ether was extracted with 10-20% NaOH solution, and the alkaline extract was acidified with concentrated HCl . The resulting aqueous solution was ether extracted, and the ether was dried (Na_2SO_4) and stripped under vacuum to yield the carboxylic acid, which was then purified.

Acknowledgment. Support of this research by the North Carolina Board of Science and Technology and by the Research Corporation is gratefully acknowledged. The authors thank Mr. G. Poindexter for the preparation of compound **10**.

(25) D. F. Shriver, "The Manipulation of Air-Sensitive Compounds," McGraw-Hill, New York, N. Y., 1969.