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The Preparation of Heavy Metal Hydride and Its Catalytic Activity. VIII.* Information on the Mechanism of Iron Hydride Formation**

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Some information on the mechanism of iron hydride formation in the reaction of iron(III) chloride with phenylmagnesium bromide under a hydrogen atmosphere has been presented. When the molar ratio ($C_6H_5MgBr/FeCl_3$) is larger than 5, 3—4 (mol./mol. $FeCl_3$) of hydrogen is absorbed during the synthesis of hydrides. The amounts of benzene, one of the by-products formed in the synthesis, have also been determined. The treatment of these hydrides with styrene under a nitrogen atmosphere has given ethylbenzene in amounts which correlate well with the amounts of hydrogen absorbed during the hydride synthesis. These observations can be taken as support for the formation of iron hydride. On the other hand, a mixture prepared by the reaction of iron(III) chloride with phenylmagnesium bromide under a nitrogen atmosphere evolved about 0.5 (mol./mol. $FeCl_3$) of hydrogen on hydrolysis. When the hydride prepared under a hydrogen atmosphere was hydrolyzed with dideuterosulfuric acid, D_2 as well as HD was evolved. These results seem to indicate that not only hydride sites but also metallic sites were formed during the iron hydride synthesis. On the basis of these observations, a possible mechanism for the formation of complex hydride containing iron and magnesium has been presented.

The formation of an iron hydride in the reaction of iron(III) chloride with phenylmagnesium bromide under a hydrogen atmosphere has been reported by several workers.[1-3] It was also demonstrated in our own earlier publications[4,5] that the iron hydride and several other transition metal hydrides were of interest for their high catalytic activities in the hydrogenation of olefins. Since the catalytic activity of the hydride is closely dependent on its composition (hydrogen content),[5] we investigated[6] the process of the iron hydride synthesis and found the following facts; 1) no hydrogen was absorbed so long as the ($C_6H_5MgBr/FeCl_3$) molar ratio was lower than 3; 2) a plot of the amounts of hydrogen absorbed during the hydride synthesis vs. the molar ratios was linear when the molar ratios were in the range from 3.5 to 7, and 3) about 4 mol. of hydrogen per mol. of iron(III) chloride was absorbed when the molar ratio was higher than 8. These observations suggested that the reaction scheme involved the following steps: 1) the formation of an intermediate; 2) the interaction of an excess of the Grignard reagent with the intermediate; 3) the replacement of phenyl groups with hydrogen atoms, and 4) the formation of a complex hydride.

$$FeCl_3 + 3C_6H_5MgBr \rightarrow Fe(C_6H_5)_3 + 3MgBrCl \quad (1)$$

$$Fe(C_6H_5)_3(C_6H_5MgBr)_{4/3} + H_2 \rightarrow FeH(C_6H_5)_2(C_6H_5MgBr)_{4/3} + C_6H_6 \quad (2)$$

$$FeH(C_6H_5)_2(C_6H_5MgBr)_{8/3} + H_2 \rightarrow FeH_2(C_6H_5)(C_6H_5MgBr)_{8/3} + C_6H_6 \quad (3)$$

$$FeH_2(C_6H_5)(C_6H_5MgBr)_4 + H_2 \rightarrow FeH_3(C_6H_5MgBr)_4 + C_6H_6 \quad (4)$$

$$FeH_3(C_6H_5MgBr)_{n>4} + C_6H_5MgBr + H_2 \rightarrow 1/2Mg(FeH_4)_2(C_6H_5MgBr)_{n>8} + 1/2MgBr_2 + C_6H_6 \quad (5)$$

However, in view of the instability of organo-iron compounds,[7] it appeared improbable that the $Fe(C_6H_5)_3$ could be an intermediate in the iron hydride synthesis. In this paper, several pieces of

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* Part VII: Y. Takegami, T. Ueno and T. Fujii, This Bulletin, **38**, 1279 (1965).

** Part of this work was reported at the 17th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1964.

[1] T. Weichselfelder, *Ann.*, **447**, 64 (1926).

[2] B. Sarry, *Z. anorg. u. allgem. Chem.*, **288**, 48 (1956).

[3] R. C. Ray and R. B. N. Sahai, *J. Indian Chem. Soc.*, **23**, 67 (1946).

[4] Y. Takegami and T. Fujimaki, *J. Chem. Soc. Japan, Ind. Chem. Sect. (Kogyo Kagaku Zasshi)*, **64**, 287 (1961).

[5] Y. Takegami, T. Ueno and K. Kawajiri, *Catalyst (Shokubai)*, **4**, 13 (1962).

[6] Y. Takegami, T. Ueno and K. Kawajiri, *J. Chem. Soc. Japan, Ind. Chem. Sect. (Kogyo Kagaku Zasshi)*, **66**, 1068 (1963).

[7] F. A. Cotton, *Chem. Revs.*, **55**, 571 (1955).

information about the intermediate will be presented, and a probable mechanism based on them will be discussed.

Experimental

Materials.—Phenylmagnesium bromide was prepared under nitrogen by the reaction of freshly-distilled phenylbromide with a 10% excess of magnesium in dry tetrahydrofuran (THF) or diethyl ether. The Grignard reagent was filtered, and the concentration of the stock solution (0.6—0.9 mol./l.) was determined, prior to use, according to Gilman's method.[8] The solvent, tetrahydrofuran or diethyl ether, was dried over sodium and freshly distilled just before use.

The Preparation and Hydrolysis of Iron Hydride.—Since in all cases the hydrides were sensitive to air and moisture, all operations were carried out in a nitrogen or hydrogen atmosphere. The apparatus for the preparation of hydrides consisted of a four-necked flask equipped with a stirrer, a dropping funnel (60 ml.) and a thermometer; this was connected to a gas buret through a silica gel tube. Before the reaction, the apparatus was flushed with hydrogen. A solution of 70 ml. of tetrahydrofuran containing 0.005 mol. of iron(III) chloride was stirred at the reaction temperature for 40 min. To this solution a desired amount of the phenylmagnesium bromide solution (in THF) was then added through the dropping funnel. The solution immediately turned black, and a hydrogen absorption took place. The mixture was then stirred for 5 hr. or more, until the hydrogen absorption ceased. Then the hydride was hydrolyzed by the addition of 20 ml. of 15% aqueous hydrochloric acid, and the amount of hydrogen evolved was measured.

The Reaction of Iron Hydrides with Styrene under a Nitrogen Atomosphere.—The iron hydride was prepared at 0°C. The hydrogen gas in the system was exchanged with nitrogen, and then 5 ml. (0.0435 mol.) of styrene was added to the iron hydride solution. The mixture was stirred for 5 hr. at 0°C (styrene treatment). The mixture was hydrolyzed by the addition of aqueous hydrochloric acid, and the amount of hydrogen evolved was measured. The addition of ether produced two layers. The organic layer was separated, washed with water, concentrated by the evaporation of ether, and analyzed by gas chromatography.

The Determination of the Amounts of Benzene Produced during the Iron Hydride Synthesis.—Two variations of the determination procedure were used. In one method (procedure A), the iron hydride was prepared under hydrogen at 0°C, using ether as the solvent. At the end of the preparation, the stirrer was quickly replaced with a short distilling head, and the solvent, containing a small amount of benzene, was distilled under reduced pressure (10 mmHg) and at room temperature. The distillate collected in a dry ice trap was analyzed by gas chromatography, using cyclohexane as an internal reference. In order to check the validity of this method, another procedure (procedure B) was also employed. To the iron hydride prepared as above, 5 ml. of diethylketone was added, and the solution was stirred for 2 hr. at 0°C. The solution was then hydrolyzed and analyzed by gas chromatography, using cyclohexane as an internal reference. As a small amount of benzene was produced by the same treatment of Grignard reagent alone, it was necessary to correct the observed amount of benzene in gas chromatography in order to determine the true amount of benzene produced by the iron hydride synthesis.

The Hydrolysis of the Iron Hydride with Dideuterosulfuric Acid.—Dideuterosulfuric acid was prepared by the reaction of deuterium oxide with the sulfur trioxide which evolved from warm 30% fuming sulfuric acid. Several iron hydrides were hydrolyzed with dideuterosulfuric acid (30% D_2SO_4 in D_2O). The gas evolved during the hydrolysis was washed with concentrated sulfuric acid and analyzed by mass spectrography.

The Reaction of Iron(III) Chloride with 2, 4, 6-Trideuterophenylmagnesium Bromide.—2,4,6-Trideuterophenylmagnesium bromide was prepared by the reaction of 2,4,6-trideuterophenyl bromide with magnesium in THF. 2,4,6-Trideuterophenyl bromide was prepared by the reaction of phenyl bromide with dideuterosulfuric acid (50 mol.% D_2SO_4 in D_2O) according to Wilson's method.[9] The reaction of iron(III) chloride with the 2, 4, 6-trideuterophenylmagnesium bromide was carried out in THF at 25°C under a nitrogen atomosphere. The reaction mixture was then hydrolyzed by the addition of aqueous hydrochloric acid, and the gas evolved during the hydrolysis was analyzed by mass spectrography.

Results

The Synthesis of Iron Hydrides under a Hydrogen Atmosphere at Various Reaction Temperatures.—In order to elucidate the course of the iron hydride synthesis, reactions of iron(III) chloride with Grignard reagents were carried out at different molar ratios and at several reaction temperatures. The results are given in Tables I

Table I. Synthesis and hydrolysis of iron hydrides*

$FeCl_3$ mmol.	Molar ratio $C_6H_5MgBr/FeCl_3$	H_2 absorbed	H_2 evolved on hydrolysis mol./mol.$FeCl_3$
		(at −20°C)	
5.55	2.99	0.09	0.37
4.95	3.96	1.04	—
5.23	4.88	2.27	2.46
4.80	5.72	2.70	—
4.95	6.10	2.50	2.74
5.28	8.04	1.63	1.80
5.18	8.20	1.35	1.52
5.14	12.2	1.88	2.06
		(at −40°C)	
5.73	3.59	(0.65)	0.83
6.71	4.90	(1.70)	—
		(at −70°C)	
5.39	6.06	0	0.20

* Solvent: THF, about 100 ml.

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[8] H. Gilman, E. A. Zoellner and J. B. Dickey, *J. Am. Chem. Soc.*, **51**, 1576 (1929).

[9] A. P. Best and C. L. Wilson, *J. Chem. Soc.*, **1946**, 239.

TABLE II. SYNTHESIS OF IRON HYDRIDES AT 0°C AND THEIR STYRENE TREATMENT*

$FeCl_3$ mmol.	Molar ratio $C_6H_5MgBr/FeCl_3$	H_2 absorbed	H_2 evolved**	Ethylbenzene	
		mol./mol.$FeCl_3$		%	mol./mol.$FeCl_3$
5.31	3.77	0.96	0.81	4.6	0.38
5.56	3.96	1.14	0.79	6.7	0.52
5.32	4.46	1.89	0.59	17.0	1.39
5.16	5.36	2.79	0.52	27.6	2.33
5.12	6.96	3.61	0.63	37.6	3.19
4.82	8.49	3.79	0.61	37.7	3.40
3.89	11.42	3.90	0.58	29.6	3.31
5.31	15.10	3.72	0.49	42.1	3.45

* Styrene treatment: at 0°C for 5 ml. (43.5 mmol.) of styrene. Solvent: THF, about 100 ml.

** Amounts of hydrogen evolved on the hydrolysis subsequent to the styrene treatment.

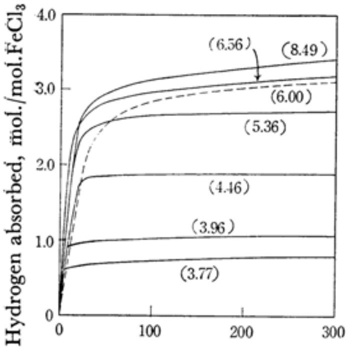

Fig. 1. Hydrogen absorption curves in the reactions carried out at 0°C.
Numerals in parentheses represent the molar ratios ($C_6H_5MgBr/FeCl_3$). Dotted line shows the results of the reaction of ($FeCl_3 + 1/4\ LiAlH_4$) with 6 C_6H_5MgBr.

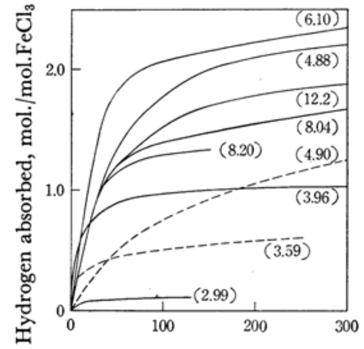

Fig. 2. Hydrogen absorption curves in the reactions carried out −20°C and −40°C.
Solid lines: at −20°C Dotted lines: at −40°C
Others are same in Fig. 1.

and II. The hydrogen absorption curves obatined from the reaction carried out at 0°C are shown in Fig. 1. At the relatively low molar ratios of 3 and 4, the total amount of hydrogen absorbed was small, though the initial rate of the hydrogen absorption was high. At relatively high molar ratios between 6 and 12, the hydrogen absorption proceeded rapidly up to about 3 (mol./mol. iron(III) chloride) but there followed a sluggish hydrogen absorption; the total amount of hydrogen absorbed reached about 4 (mol./mol. iron(III) chloride). This correlation between the hydrogen absorption curves and the molar ratios is almost the same as that observed in the reactions carried out at 35°C.⁶⁾

The experiments performed at lower temperatures (Fig. 2) show that the rates of hydrogen absorption slowed down as the reaction temperature was lowered. At −40°C, the rate was very slow and, therefore, no end point of the hydrogen absorption was detected exactly. At −70°C, no hydrogen absorption was observed, and the reaction mixture did not turn black.

The amount of hydrogen absorbed during the hydride synthesis is closely dependent on the molar ratio. The amounts of hydrogen absorbed plotted against the molar ratios (Fig. 3) show that the amounts of hydrogen absorbed at 0°C are more dependent on the molar ratio than those absorbed at 35°C. At −20°C, the amount of hydrogen absorbed reaches a maximum when the molar ratio is 6.10, decreasing with any further increase

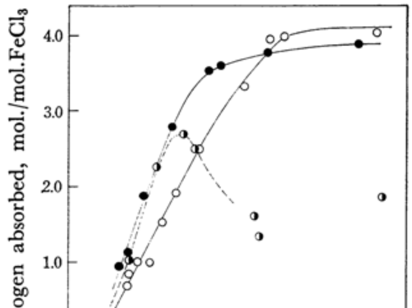

Fig. 3. Molar ratios vs. amounts of hydrogen absorbed.
-○-: At 35°C
-●-: At 0°C
-◑-: At −20°C

in the molar ratio. Evidently, this dependence of the amount of absorbed hydrogen on the molar ratio is different from those observed at 0°C and 35°C. When the iron hydride was prepared at −20°C in the molar ratio of 6, and when phenylmagnesium bromide was added to the reaction mixture at the same temperature, no hydrogen evolution was observed, even though the molar ratio was as high as 12. It now seems impossible to find any probable interpretation for this decrease in the amount of hydrogen absorbed with the increase in the molar ratio.

On the hydrolysis of the hydrides prepared above, a hydrogen evolution was observed. The amounts of hydrogen evolved are given in the last column of Table I. They are somewhat larger than those absorbed during the hydride synthesis.

The Styrene Treatment of the Iron Hydrides.—Ethylbenzene was produced by the reaction of the iron hydride with styrene under a nitrogen atmosphere. The amounts of ethylbenzene produced are given in Table II. They are also shown graphically in Fig. 4 as a function of the amounts of hydrogen absorbed during the hydride synthesis. As may be seen in Fig. 4, a linear relationship is observed between the amounts of ethylbenzene produced during the styrene treatment and the amounts of hydrogen absorbed during the hydride synthesis.

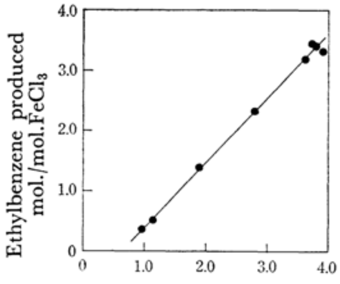

Fig. 4. Amounts of hydrogen absorbed during hydride synthesis vs. amounts of ethylbenzene produced during styrene treatment.

The Determination of the Amounts of Benzene Produced during the Iron Hydride Synthesis.—One mole of benzene should be produced per mole of hydrogen absorbed so long as the iron hydride formation proceeds according to Eqs. 1—5. Therefore, the amounts of benzene produced during the iron hydride synthesis were determined in order to check the scheme. As may be seen in Fig. 5, plots of the amounts of benzene produced against the amounts of hydrogen absorbed during the hydride synthesis gave a straight line, with a slope of 1.0. These results show that one mole of benzene is produced per mole of hydrogen absorbed. However, when the data are extrapolated to zero hydrogen absorbed, about 0.6 (mol./mol. iron(III) chloride) of benzene is to be produced.

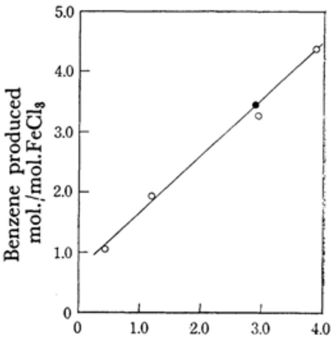

Fig. 5. Amounts of hydrogen absorbed during hydride synthesis vs. amounts of benzene produced.
○: Procedure A
●: Procedure B (See Experimental)

The Reaction of Iron(III) Chloride with a Grignard Reagent under a Nitrogen Atmosphere,—Even when the reaction of iron(III) chloride with a Grignard reagent was carried out under a nitrogen atmosphere, a black solution was produced and about 0.5 mol. of hydrogen per mole of iron(III) cholride was evolved on the hydrolysis, as is shown in Table III. The amount of hydrogen evolved increased steadily as the molar ratio increased from 3 to 5, and then it reached a plateau. It was also observed that the amount of hydrogen evolved on the hydrolysis of the nickel (II) chloride - Grignard reagent system was somewhat larger than that evolved from the iron(III) chloride - Grignard reagent system.

TABLE III. HYDROLYSIS OF REACTION MIXTURES PREPARED UNDER A NITROGEN ATMOSPHERE*

MX_n mmol.	Molar ratio C_6H_5MgBr/MX_n	H_2 evolved on hydrolysis mol./mol.MX_n
	($FeCl_3$-Grignard reagent)	
5.53	1.99	0.11
5.42	2.93	0.36
4.93	4.03	0.51
5.18	5.12	0.55
5.38	6.45	0.49
5.02	7.98	0.46
	($NiCl_2$-Grignard reagent)	
5.37	2.94	0.62
5.23	5.88	0.77

* Metal halides was treated with phenylmagnesium bromide at 0°C for 2 hr. prior to the hydrolysis. Solvent: THF, about 100 ml.

Figure 6 shows that, in the styrene treatment of the reaction mixture prepared under a nitrogen atmosphere, the ethylbenzene produced and the hydrogen evolved on the hydrolysis subsequent to

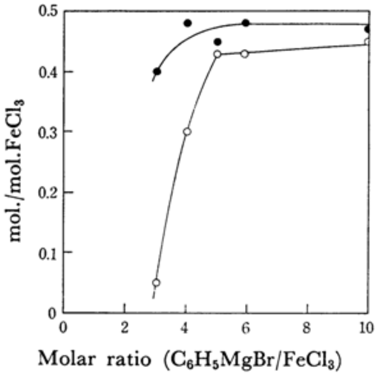

Fig. 6. Styrene treatment of reaction mixture prepared under a nitrogen atmosphere.
○: Amounts of ethylbenzene produced.
●: Amounts of hydrogen evolved on the hydrolysis subsequent to the styrene treatment.

the styrene treatment was about 0.5 (mol./mol. iron(III) chloride) when the molar ratio was higher than 5.

Hydrogen Absorption Subsequent to the Reaction Carried Out under a Nitrogen Atmosphere.—The reaction of iron(III) chloride with the Grignard reagent was carried out under a nitrogen atmosphere (the first step), and then under a hydrogen atmosphere (the second step).*[1] The amount of hydrogen absorbed was measured in the course of the second step. The hydrogen absorption curves are shown in Fig. 7. A comparison between Fig. 1 and Fig. 7 shows that the hydrogen absorption rate and the amounts of hydrogen absorbed are quite the same as those in the one-step reactions. As is shown in Table IV, the amounts of hydrogen evolved during the hydrolysis subsequent to the hydrogen absorption are larger by 0.3—0.4 than the amounts of hydrogen absorbed in the second step as expressed by the mol. hydrogen/mol. iron(III) cholride ratio. In the cases of the nickel(II) chloride - Grignard reagent system, these increments in the amount of hydrogen evolved on the hydrolysis amounted to 0.6—1.0. The increase in the amount of hydrogen seemingly comes from the hydrogen which the reaction product of the first step evolves in the hydrolysis.

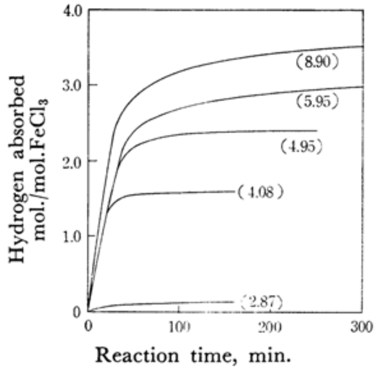

Fig. 7. Hydrogen absorption curves in the second-step reactions.
Numerals in parentheses represent the molar ratios ($C_6H_5MgBr/FeCl_3$).

TABLE IV. AMOUNT OF HYDROGEN ABSORBED IN THE SECOND STEP AND EVOLVED ON HYDROLYSIS OF THE PRODUCT FROM TWO-STEP REACTION*

MX_n mmol.	Molar ratio C_6H_5MgBr/MX_n	H_2 absorbed	H_2 evolved on hydrolysis
		mol./mol.MX_n	
	($FeCl_3$-Grignard reagent)		
5.22	2.87	0.14	0.40
5.62	4.08	1.60	1.63
5.25	4.95	2.43	2.81
6.39	5.86	2.57**	2.91
5.04	5.95	3.32	3.63
5.52	8.90	4.00	3.96
	($NiCl_2$-Grignard reagent)		
5.49	1.91	0.29	0.91
5.82	3.04	0.83	1.66
5.86	4.12	1.23	2.22
5.08	7.19	1.63	2.41

* Metal halide was treated with phenylmagnesium bromide at 0°C for 2 hr. under a nitrogen atmosphere prior to the hydrogen absorption. Solvent: THF, about 100 ml.

** The first-step reaction was conducted under nitrogen atmosphere for 48 hr. and then the second-step reaction under hydrogen atmosphere.

The Hydrolysis of Iron Hydrides with Dideuterosulfuric Acid.—It has been assumed that the hydrogen evolved on the hydrolysis should be attributed to the hydride. However, there is still another possibility, that a metallic compound which evolves hydrogen on the hydrolysis may be included in the reaction system. Therefore, several reaction products of the reaction of iron(III) chloride with phenylmagnesium bromide were hydrolyzed with dideuterosulfuric acid, and the gas evolved, a mixture of D_2, HD and H_2, was analyzed by mass spectrography. Although the mechanism of the evolution of D_2, HD and H_2 has not yet been constructed, we assume that the amount of D_2 evolved can be an index of the amount of the free metal and/or the reaction product not containing hydrogen as a constituent, and that the amount of HD evolved can be an index of the amount of hydride. The results are listed in Table V. The D-purity of the dideuterosulfuric acid was about 92% as determined by the hydrolysis of iron metal (Run 1).

The agreement between the compositions of the

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*[1] The preparation of hydride which takes two steps (first and second steps) will be described as "two-step reaction," while the preparation carried out under a hydrogen atmosphere from the beginning of the reaction will be described as "one-step reaction" in the discussion below.

TABLE V. HYDROLYSIS OF IRON HYDRIDE WITH DIDEUTEROSULFURIC ACID

Run	Sample	Acid	Mass number, %		
			2	3	4
1	Fe-metal	D_2SO_4	2	13	85
2	PhMgBr-$FeCl_3$ in N_2	D_2SO_4	5	16	79
3	PhMgBr-$FeCl_3$, $N_2 \rightarrow H_2$*	D_2SO_4	26	45	29
4	PhMgBr-$FeCl_3$ in H_2**	D_2SO_4	20	43	37
5	$C_6H_2D_3MgBr$-$FeCl_3$ in N_2	HCl	>99	<1	—

* Prepared by the two-step reaction: the amount of hydrogen absorbed was 3.2 mol./mol.$FeCl_3$.

** Prepared by the one-step reaction: the amount of hydrogen absorbed was 3.2 mol./mol.$FeCl_3$.

gas evolved in Runs 1 and 2 demonstrates that the major product in the reaction of iron(III) chloride with phenylmagnesium bromide under a nitrogen atmosphere is indeed the free metal and/or the reaction product not containing hydrogen as a constituent. In the cases of the hydrides which absorbed hydrogen, the gas evolved was about 45% (1.6 mol./mol. iron(III) chloride) HD, which can be taken as further support for the presence of the iron hydride. On the other hand, there was about 30% (1.4 mol./mol. iron(III) chloride) D_2; this can not be explained by Eqs. 1—5. About 20% (1.0 mol./mol. iron(III) chloride) of H_2 was also evolved.[*2]

As may be seen in Run 5, no appreciable D-fraction was detected in the gas evolved during the hydrochloric acid hydrolysis of the product of the reaction of ferric chloride with 2, 4, 6-trideutero phenylmagnesium bromide.

Discussion

The linear relationship between the amounts of hydrogen absorbed during the hydride synthesis and the amounts of ethylbenzene produced during the styrene treatment of the hydrides (Fig. 4) indicates that the hydrogen absorbed during the synthesis was consumed in the formation of the hydride. The evolution of HD during the hydrolysis with dideuterosulfuric acid subsequent to the hydrogen absorption (Table V) is conceivably due to the presence of the hydride.

The facts that one mole of benzene was produced per mole of hydrogen absorbed during the iron hydride synthesis and that plots of the amounts of hydrogen absorbed against the molar ratios were linear in the reaction carried out at 0°C, as well as at 35°C, can be taken as further confirmations of the proposed scheme, Eqs. 1—5.

However, there are several facts that can not be explained by the proposed scheme. About 0.5 mol. of hydrogen per mole of iron(III) chloride was evolved during the hydrolysis of the reaction mixture produced under a nitrogen atmosphere (Table III). Since 0.5 mol. of ethylbenzene per mole iron(III) chloride was produced when this reaction mixture was treated with styrene under a nitrogen atmosphere (Fig. 6), it seems plausible that a small amount of hydride was formed under a nitrogen atmosphere by the elimination of FeH from the intermediate, $Fe(C_6H_5)_3$.[*3] This view, however, is discarded by the fact that no appreciable deuterium fraction was detected in the gas evolved on the hydrolysis, with hydrochloric acid, of the reaction mixture prepared by the reaction of iron(III) chloride with 2, 4, 6-trideuterophenylmagnesium bromide under a nitrogen atmosphere. The mass spectral data also show that the reaction mixture produced by the reaction of iron(III) chloride with phenylmagnesium bromide under nitrogen does not contain hydrogen as a constituent. This compound absorbs hydrogen to give the nearly same amount of the hydride as that formed in the one-step reaction under a hydrogen atmosphere. A reasonable scheme must be proposed for the hydrogen absorption in the two-step reaction.

The $Fe(C_6H_5)_3$ intermediate has been considered to be formed in the reaction of iron(III) chloride with phenylmagnesium bromide. This intermediate, however, does not evolve hydrogen in the hydrolysis, and it is improbable that the intermediate is left intact for 2 hr. or more. Therefore, the intermediate in the two-step reaction is considered to be one of the decomposition products of $Fe(C_6H_5)_3$,[*4] i. e., $Fe(C_6H_5)_2$, $Fe(C_6H_5)$ or Fe. If Fe is the intermediate, 1.0 mole. of hydrogen should be evolved on the hydrolysis, while no hydrogen evolution should be observed if $Fe(C_6H_5)_2$ is the intermediate. Thus, $Fe(C_6H_5)$

[*2] Three points can be considered as the source of this H_2; 1) the H-fraction in the dideuterosulfuric acid used in the hydrolysis; 2) the hydrolysis of iron hydride which contains a relatively large amount of hydrogen (for example, $FeH_3 + 2D_2SO_4 \rightarrow FeSO_4 + 2HD + 1/2\ H_2$), and 3) hydrogen which is adsorbed on the metal surface. We now consider that 1) and 2) contribute greatly to the H_2-evolution.

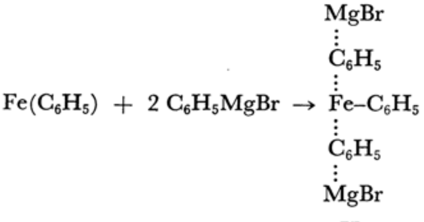
[*3] When cyclohexylmagnesium bromide is used instead of phenylmagnesium bromide, 1.4 mol. of hydrogen per mole of iron(III) chloride is evolved on the hydrolysis of the reaction mixture prepared under a nitrogen atmosphere, presumably indicating the formation of iron hydride through cyclohexene-elimination from the iron-cyclohexyl intermediate; Y. Takegami, T. Ueno, K. Shinoki and T. Sakata, *J. Chem. Soc. Japan, Ind. Chem. Sect.* (*Kogyo Kagaku Zasshi*), **67**, 316 (1964).

[*4] Kharasch and his co-workers (*J. Am. Chem. Soc.*, **83**, 3229 (1961)) reported, in their study of the modification of the Grignard reaction in the presence of a small amount of iron(III) chloride serving as a catalyst, that phenylmagnesium bromide combines with iron(III) chloride to produce an unstable organo-iron compound, which then decomposes to give a biphenyl and a reduced iron salt in the following way: $2C_6H_5MgBr + FeCl_3 \rightarrow (C_6H_5)_2FeCl + 2MgBrCl$, $(C_6H_5)_2FeCl \rightarrow FeCl + C_6H_5$-$C_6H_5$. Our assumption of $Fe(C_6H_5)_3$ as an unstabe intermediate in place of $Fe(C_6H_6)Cl$ is based on the fact that hydrogen is absorbed only when the molar ratio is higher than 3 (Fig. 3), indicating that 3 mol. of Grignard reagent has been consumed before the hydrogen absorption takes place in the reaction.

appears to be the best choice as the intermediate which evolves 0.5 mol. of hydrogen in the hydrolysis.*5 The fact that the product in the reaction of iron(II) chloride, as well as iron(III) chloride, with the Grignard reagent under a nitrogen atmosphere evolved about 0.5 mol. of hydrogen per mole of iron(III) chloride is also in agreement with the prediction of such an intermediate as $\mathrm{Fe(C_6H_5)}$.

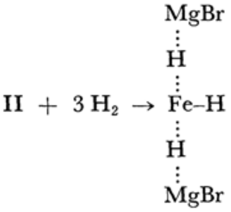
As may be seen in Table III, 4—8 mol. of the Grignard reagent per mole of iron(III) chloride is necessary for the hydrogen absorption. The effect of the excess Grignard reagent appears quite similar to that considered in Eqs. 1—5. Therefore, the hydrogen absorption in the two-step reaction is assumed to be initiated by the interaction of the Grignard reagent with $\mathrm{Fe(C_6H_5)}$ to form an iron subphenyl-Grignard reagent complex such as II, followed by the replacement of phenyl groups with hydrogen atoms by the attack of hydrogen molecule. Thus, a complex hydride such as III should be produced when 3 mol. of hydrogen per mole of iron(III) chloride is absorbed. On the hydrolysis of III, 3.5 mole. of hydrogen per mole of iron(III) chloride should be evolved. Since this corresponds to the results presented above, the shceme I→II→III can be assumed in the two-step reaction:

$$\mathrm{FeCl_3} + 3\,\mathrm{C_6H_5MgBr} \rightarrow$$
$$\mathrm{Fe(C_6H_5)_3} + 3\,\mathrm{MgBrCl}$$
$$\mathrm{Fe(C_6H_5)_3} \rightarrow \underset{\mathrm{I}}{\mathrm{Fe(C_6H_5)}} + \mathrm{C_6H_5{-}C_6H_5}^{*6} \qquad (6)$$



$$\mathrm{Fe(C_6H_5)} + 2\,\mathrm{C_6H_5MgBr} \rightarrow \begin{array}{l} \mathrm{MgBr}\\ \vdots\\ \mathrm{C_6H_5}\\ \vdots\\ \mathrm{Fe{-}C_6H_5}\\ \vdots\\ \mathrm{C_6H_5}\\ \vdots\\ \mathrm{MgBr}\end{array} \qquad (7)$$

II



$$\mathrm{II} + 3\,\mathrm{H_2} \rightarrow \begin{array}{l} \mathrm{MgBr}\\ \vdots\\ \mathrm{H}\\ \vdots\\ \mathrm{Fe{-}H}\\ \vdots\\ \mathrm{H}\\ \vdots\\ \mathrm{MgBr}\end{array} \qquad (8)$$

III

Although this new scheme is proposed for the formation of the iron hydride in the two-step reaction, it seems almost certain that this scheme also contributes greatly to the iron hydride formation in the one-step reaction under hydrogen. If this is the case, the following experimental results in the one-step reaction, which can not be explained by the earlier scheme, can be explained: 1) the rate of the absorption and the amount of hydrogen absorbed are nearly the same in the one-tsep reaction as in the two-step reaction (Fig. 1 vs. Fig. 7); 2) the amounts of hydrogen evolved in the hydrolysis are somewhat larger than those absorbed during the hydride synthesis (Table II); 3) the composition of the gas evolved in the hydrolysis with dideuterosulfuric acid is nearly the same as that in the two-step reaction (Table V); 4) about 5 mol. of Grignard reagent per mole of iron(III) chloride is needed to absorb 3 mol. of hydrogen in the iron hydride synthesis (the reaction carried out at 0°C, in Fig. 3), and 5) almost the same results were obtained when iron(III) chloride was used instead of iron(III) chloride (Fig. 1).

It can be reasonably concluded, therefore, that the scheme I→II→III is also valid in the one-step reaction. A more detailed discussion of this hypothesis must, however, await the accumulation of additional data on the composition of the gas evolved by the hydrolysis of hydrides of various hydrogen contents with dideuterosulfuric acid, as well as on other reaction parameters. These data are now being gathered.

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*5 $\mathrm{Fe(C_6H_6)} + 2\,\mathrm{HCl} \rightarrow \mathrm{FeCl_2} + \mathrm{C_6H_6} + 1/2\,\mathrm{H_2}$. This intermediate is being studied by means of electron-spin resonance.

*6 Like Kharasch, we assume a production of one mole of biphenyl. However, a small amount of phenyl radicals may also be produced, which then abstracts the hydrogen atom from the solvent to give benzene. This hypothesis may explain the production of about 0.6 mol. of benzene when the amount of hydrogen absorbed during the iron hydride synthesis is zero (Fig. 5).