

IRON CATALYSIS IN THE REACTION OF GRIGNARD REAGENTS WITH ALKYL HALIDES

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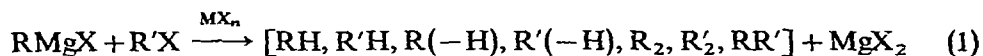
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SUMMARY

The stoichiometry and kinetics of the reaction between various Grignard reagents and alkyl halides with an iron catalyst have been examined in tetrahydrofuran solutions. The catalytic iron species is produced *in situ* by the reduction of iron-(II) and -(III) halides by Grignard reagent. The activity of the catalyst is dependent on the solvent and deactivation by ageing is attributed to aggregation of the catalytic iron species. The catalytic process is postulated to occur via a redox cycle, in which the oxidative addition of alkyl halide to a reduced form of iron is followed by disproportionation of the alkyliron intermediates to regenerate the iron catalyst. Alkyl radicals are formed in the step involving oxidative addition. Thus, styrene preferentially scavenges only that alkyl moiety derived from the alkyl halide. Side reactions involving the catalytic exchange of Grignard reagent with alkene and alkyl halide are also described.

INTRODUCTION

The reactions of a variety of Grignard reagents with alkyl halides are readily induced under mild conditions by catalytic amounts of transition metal complexes¹. These catalytic reactions, commonly known and generally described as the Kharasch reaction, produce alkane, alkene and alkyl dimers in varying but not necessarily stoichiometric amounts depending on the metal. In most studies carried out heretofore, diethyl ether has usually been the medium of choice and products derived from attack on the solvent have also been detected.

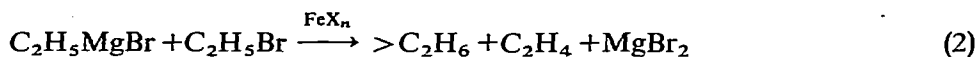


The mechanism of these facile processes bears on the important question of the role of metal complexes in catalytic processes and has been the subject of extensive investigations²⁻¹². Its complexity, however, has precluded a general description of the elementary steps involved in the catalytic processes. Thus, the roles which metal catalysts play, the reactions of metastable organometallic intermediates and the presence of transient alkyl radicals have remained unclear.

We have examined the mechanisms of the reactions between aliphatic Grignard reagents and alkyl halides in tetrahydrofuran (THF) solutions. As a solvent, THF has a number of advantages over diethyl ether¹³. A systematic study of various metal systems has led us to categorize them into three mechanistic groups according to their ability to promote specific functions: (a) silver, (b) copper, and (c) manganese, cobalt, nickel, palladium and iron¹⁴⁻¹⁵. In this report we wish to present some of our studies with iron as a catalyst generally representing the last group of metals.

RESULTS

A representative reaction between ethylmagnesium bromide and ethyl bromide was initially examined under standard conditions with iron halides. Two procedures were followed in which either (a) catalytic amounts of iron halide were exposed to the Grignard reagent first and followed later by reaction with ethyl bromide or (b) the ethylmagnesium bromide was the last component added. Ethane and ethylene were produced by either procedure and the stoichiometry of the reaction was represented by eqn. 2.



As shown in Fig. 1, iron in concentrations as low as 10^{-5} M was an efficient catalyst for the reaction between ethylmagnesium bromide and ethyl bromide at 2° in THF solutions. The separation of iron as a different phase was not apparent at the low levels of metal used in these studies. No sedimentation occurred even after prolonged standing or centrifugation and a significant fraction, if not all, of the iron species was apparently in solution. At this juncture, we felt that a superficial examination of the existence possibly of colloidal iron particles (*e.g.*, by light scattering) could lead to little additional insight into the catalytic species and was not pursued.

The stoichiometric requirements for the reduction of ferric and ferrous

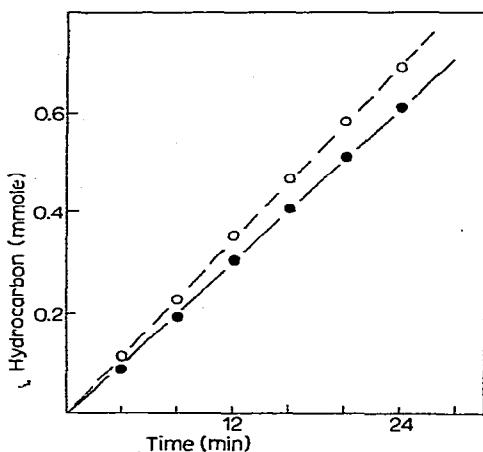
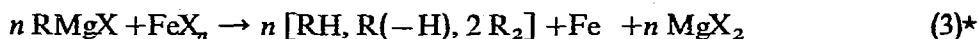


Fig. 1. Kinetics (initial rate) of the iron-catalyzed reaction of 0.16 M ethylmagnesium bromide and 0.48 M ethyl bromide at 2° in THF using 3×10^{-6} M ferric chloride: ○ ethane (2.30×10^{-5} M/sec) and ● ethylene (2.02×10^{-5} M/sec).

chloride by various Grignard reagents was defined by $Q(R)$ in eqn. 4. The value of



$Q(R)$ was generally equal to the oxidation state (n) of iron in the metal salt used (see

$$Q(R) = \frac{\text{RH} + \text{R}(-\text{H}) + 2 \text{R}_2}{\text{FeX}_n} = n \quad (4)$$

experimental section). Detailed examination of the reduced iron species is under investigation.

Kinetics of the Kharasch reaction catalyzed by iron

The reaction between ethylmagnesium bromide and ethyl bromide in the presence of iron was followed by direct and continual sampling and analysis of the gaseous products. An empirical rate expression was obtained by systematically varying the concentration of each component, and was applied to the first 10% of the reaction (Table 1). An extensive kinetic treatment was not attempted since kinetics cannot be rigorously established for a system consisting of a number of side reactions of varying importance.

The rate of reaction given by eqn. (5) represented the sum of the rates of formation of ethane and ethylene. Butane was neglected in most cases since it was a minor product usually formed in less than 1% yield.

$$\frac{d\Sigma\text{Et}}{dt} = k \cdot [\text{FeCl}_3]^{1.0} \cdot [\text{EtMgBr}]^{0.0} \cdot [\text{EtBr}]^{0.8} \quad (5)$$

Several features of the kinetic results were noteworthy. Thus, the total rate of

TABLE 1

THE RATES OF REACTION OF ETHYLMAGNESIUM BROMIDE AND ETHYL BROMIDE IN THE PRESENCE OF IRON^a

Run	FeCl ₃ (10 ⁻⁵ M)	EtMgBr (M)	EtBr (M)	Temp. (°C)	Rates of product formation ^b		R(C ₂ H ₄) + R(C ₂ H ₆)	R(C ₂ H ₆) / R(C ₂ H ₄)
					R(C ₂ H ₄)	R(C ₂ H ₆)		
1	0.12	0.157	0.161	2.0	0.26	0.34	0.60	1.31
2	0.30	0.157	0.161	2.0	0.87	1.03	1.90	1.18
3	0.60	0.157	0.161	2.0	1.96	2.04	4.00	1.04
4	1.20	0.157	0.161	2.0	3.85	3.87	7.72	1.00
5	0.30	0.079	0.161	2.0	0.93	1.04	1.97	1.12
6	0.30	0.314	0.161	2.0	0.77	0.90	1.67	1.17
7	0.30	0.157	0.064	2.0	0.41	0.48	0.89	1.17
8	0.30	0.157	0.322	2.0	1.54	1.77	3.31	1.15
9	0.30	0.157	0.483	2.0	2.02	2.30	4.32	1.14
10	0.30	0.157	0.161	9.2	1.18	1.42	2.60	1.20
11	0.30	0.157	0.161	22.2	0.89	1.23	2.12	1.39
12	6.00	0.157	0.161	23.0	^c	^c	^c	1.13

^a In THF solutions. Rate of formation of n-butane was negligibly small in all runs. ^b R(C₂H₄) and R(C₂H₆) are rates of formation of ethylene and ethane, respectively, in 10⁵ M/sec. ^c Not determined.

* All of the coordination around the metal is not specified here or in the following unless required for the discussion.

TABLE 2. THE KIHARASCH REACTION INDUCED BY FERRIC CHLORIDE^a

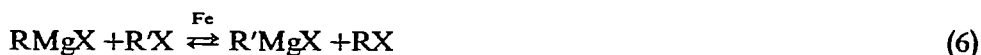
Run	RMgBr	R ^b /Br	FeCl ₃ (10 ⁻⁵ M)	Temp. (°C)	Period (min)	Products (mmole)				R(-H)/ RH	R'(-H)/ R'H	Relative rate ^c
						R(-H)	RH	R'(-H)	R'H			
13	Me	Pr	240	2.0	420	1.54	1.54	1.54	0	0.20	0	∞
14	Me	Pr	1.2	25	420	0.68	0.61	0.61	0.06	0.24 ^d	0	10
15	Me	i-Pr	240	25	15	1.26	1.05	1.05	0	0.40	0	∞
16	Me	i-Pr	1.2	25	180	0.86	0.78	0.78	0.05	0.32 ^d	0	16
17	Et	Pr	240	2.0	2.5	1.07	1.69	1.62	1.24	0	0.63	1.31
18	Et	Pr	1.2	2.0	27	0.69	0.50	0.05	0.34	0	0.56	1.38
19	Et	Pr	0.12	2.0	180	0.36	0.32	0	0.30	0	0.12	1.12
20	Et	i-Pr	240	2.0	2.5	1.01	1.81	1.78	0.95	0	0.56	1.88
21	Et	i-Pr	6.0	2.0	10	0.18	0.53	0.50	0.14	0	0.03	3.57
22	Et	i-Pr	0.3	2.0	60	0.07	0.29	0.26	0.06	0	0.01	4.33
23	Et	i-Pr	0.3	25	60	0.21	0.44	0.29	0.21	0	0.02	1.38
24	Et	Et	1.2	2.0	31	1.40	1.40	1.40	1.40	0	1.0	1.0
25	Et	t-Bu	24	2.0	10	1.36	1.46	1.55	1.45	0	0.93	1.07
26	Et	neo-Pent	240	25	20	1.55	1.75	1.75	1.60	0 ^{e,f}	0.89	0
27	Et	neo-Pent	1.2	25	45	0.43	0.47	0.47	0.49	0 ^{e,f}	0.03	0
28	Pr	Me	1.2	2.0	20	0.91	0.68	0.68	0.29	0.13 ^h	1.39	0
29	Pr	Et	1.2	2.0	45	0.23	0.50	0.29	0.08	0	0.14	0.46
30	Pr	Pr	1.2	2.0	55	0.45	0.50	0.50	0.08	0	0.90	3.63
31	i-Pr	Et	0.3	2.0	240	0.26	0.31	0	0.11	0	0.24	0.84
32	neo-Pent	Et	240	25	10	1.82	2.20	2.20	0	0.30	0	∞
33	neo-Pent	Et	1.2	25	240	0.64	0.64	0.08	0.56	0.03	0	0.14
34	Ph	Et	240	25	5	1.12	0.45 ⁱ	0.45 ⁱ	0.71	0.45 ⁱ	0	1.58
35	Ph	Et	1.2	25	1440	0.01	0.01	0.01	0.15	0.01 ^j	0	0.07
36	PhCH ₂	Et	240	25	60	0.98	0.98	0.98	0.51	0.09 ^k	0	1.92

^a In 21 ml THF containing 2.1–4.2 mmole RMgBr and 6.2 mmole R^bBr. ^b Additional alkane liberated after hydrolysis with dilute sulfuric acid. ^c Combined yield of products divided by time and FeCl₃ concentration (arbitrary units) at temperature cited. ^d Ethane 0.03. ^e 0.37. ^f 2,2,5,5-Tetramethylhexane. ^g 0.12. ^h Ethane 0.01. ⁱ Biphenyl 0.55, butane 0.11. ^j Biphenyl 0.20. ^k Biphenyl 0.35, butane 0.11.

reaction showed first-order dependence on the concentrations of iron and ethyl bromide. The rate was independent of the concentration of ethylmagnesium bromide, but varied with the structure of the Grignard reagent (*vide infra*). Between 2° and 25° the rate was rather insensitive to temperature and may even have decreased slightly at higher temperatures (*cf.* runs 10 and 11). Ethane was formed faster than ethylene at low concentrations of iron, but these rates became equal at higher concentrations (runs 1–4). Increasing the temperature had a similar effect of favoring the formation of ethane relative to ethylene (runs 3, 10 and 11), but the effect could be partially offset by increasing the iron concentration (runs 3 and 12). Finally, the relative rates of formation of ethane and ethylene were not affected by variations in the concentration of ethylmagnesium bromide and ethyl bromide (runs 2, 5–9).

The reactions of Grignard reagents and alkyl bromides catalyzed by iron

The products of the iron-catalyzed reactions of various Grignard reagents and alkyl halides are given in Table 2. Significant amounts of coupled products were obtained only when the alkyl group was methyl, neopentyl, phenyl or benzyl which have no readily available β -hydrogens. In other cases, disproportionation was the predominant reaction. The disproportionation between dissimilar alkyl groups was dependent on the concentration of iron. Thus, in the reaction between ethylmagnesium bromide and n-propyl bromide, the ratio of propene to propane decreased and the ratio of ethylene to ethane increased as the iron concentration was lowered (runs 17–19). On the other hand, the opposite trend was observed between ethylmagnesium bromide and isopropyl bromide (runs 20–22). Equivalent results were not obtained when alkyl groups attached to the Grignard reagent and the organic halide were interchanged. The interpretation of these results was somewhat complicated by the iron-catalyzed exchange of alkyl groups between reactants. Hydrolysis after partial reaction indicated, however, that it contributed to less than 10% scrambling in most cases (*exp. section, Table 10*).



The reactivities of various Grignard reagents listed in Table 2 can be placed qualitatively in the following sequence: ethyl > n-propyl > isopropyl > neopentyl > methyl > benzyl > phenyl. The same sequence of reactivities was previously found in the silver-catalyzed coupling of Grignard reagents with alkyl bromides^{14,15}. The reactivities of some of the alkyl bromides are also shown in Table 2. Quantitative comparisons are not possible since the reactions were not studied under the same experimental conditions, the problems of which are mostly due to uncertainties regarding the concentration of active iron species. Qualitatively, however, the reactivities of alkyl bromides decreased in the order tert-butyl > isopropyl > n-propyl.

The effect of styrene on the Kharasch reaction

The catalyzed reaction of ethylmagnesium bromide and tert-butyl bromide produced only ethane, ethylene, isobutane and isobutene. Coupled products such as butane, 2,2-dimethylbutane and 2,2,3,3-tetramethylbutane were absent. Alkyl exchange in this system was negligibly slow. The stoichiometry of the reaction and the rates of formation of ethane and ethylene derived from the Grignard reagent (ΣEt)

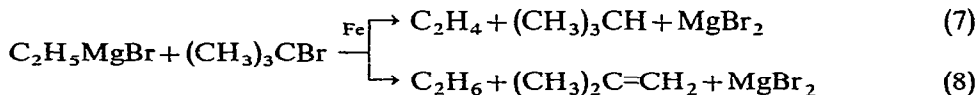
TABLE 3

EFFECT OF STYRENE ON THE KHARASCH REACTION BETWEEN ETHYLMAGNESIUM BROMIDE AND tert-BUTYL BROMIDE^a

Additive (0.415 M)	Products (mmole)				R(Σ Et) ^{c,d}	R(Σ t-Bu) ^{c,e}	R(Σ t-Bu)/ R(Σ Et)
	C ₂ H ₄	C ₂ H ₆	i-C ₄ H ₈	i-C ₄ H ₁₀			
None	1.36	1.46	1.55	1.45	820	860	1.0
Styrene	0.65	0.61	0.02	0.00 ^b	360	6	0.0
PPh ₃	0.76	1.13	1.15	0.85	540	572	1.1

^a In 21 ml THF containing 2.4×10^{-4} M ferric chloride, 0.18 M ethylmagnesium bromide and 0.30 M tert-butyl bromide at 2° for 10 min. Preformed solution of iron added to reaction mixture. ^b Ethylbenzene analyzed after hydrolysis, 0.17 mmole. ^c Rate of formation of products (2.8×10^{-7} moles/sec). ^d Ethane plus ethylene. ^e Isobutane plus isobutene.

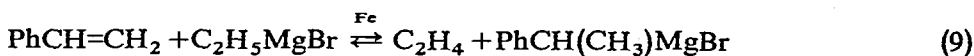
and isobutane and isobutene from the alkyl halide (Σ t-Bu) given in Table 3 were consistent with eqns. (7) and (8).



The catalyzed reaction between ethylmagnesium bromide and tert-butyl bromide was repeated in the presence of 0.4 M styrene to act as a scavenger of alkyl radicals. The decrease in the relative rates of Σ t-Bu/ Σ Et to zero in the presence of styrene indicated that it was the tert-butyl group which was preferentially scavenged. Polymers containing the tert-butyl moiety (absorption at 1375 and 1385 cm^{-1}) were isolated but not identified quantitatively. Styrene also caused a small decrease in the absolute rates of formation of ethylene and ethane, but it is not certain whether the retardation was due to trapping of any ethyl radicals. The retardation may have been due to the formation of less active π -complexes of the catalytic iron species with styrene, since the π -bonding ligand triphenylphosphine had a similar effect. As expected, triphenylphosphine did not affect the relative rates of Σ t-Bu/ Σ Et.

Trapping experiments using the reverse combination of tert-butylmagnesium bromide and ethyl bromide could not be studied meaningfully due to extensive alkyl exchange (eqn. 6) between the reactants catalyzed by iron. Under these conditions, however, selective trapping of the alkyl group from the alkyl bromide is not restricted to the tert-butyl radical since essentially the same results were also obtained from the study of ethylmagnesium bromide and n-propyl bromide in the presence of styrene (Table 8, experimental section).

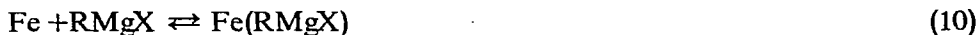
Styrene in these catalytic systems was also involved in a capacity other than as a radical trap since ethylbenzene could be isolated from the reaction mixture. The reduction of styrene and other alkenes has been previously observed under similar conditions and has been attributed to a catalyzed exchange with Grignard reagent (eqn. 9) or catalytic hydrogenation accompanying decomposition of the organometallic intermediates¹⁴⁻¹⁷. (See the experimental section for a further discussion of this catalyzed exchange.)



Under these experimental conditions there was no reaction between Grignard reagent and most of the alkyl bromides in the absence of iron. However, coupling of Grignard reagents with the more reactive allyl and benzyl bromides was observed in the absence of metal catalyst (see Table 5, experimental section). The cross-coupled product was a major, but not exclusive, component of the reaction mixture. Significant amounts of disproportionation and homo-coupling indicated that these halides induced other processes as well. The latter are probably related to electron transfer reactions observed widely in the interaction of alkyllithium and some Grignard reagents with alkyl halides, particularly iodides¹⁸⁻²³.

The catalytic iron species

Ferric and ferrous halides were readily reduced under the conditions of the Kharasch reaction. The same catalytic species of iron could be prepared by prior reduction of ferric and ferrous halides by three and two moles, respectively, of Grignard reagent. The visible absorption spectrum of the reduced iron species in THF showed no definite maximum, and the extinction coefficient diminished gradually from the ultraviolet into the visible region beyond 600 nm. A large excess of Grignard reagent was generally present relative to iron during the Kharasch reaction. However, the catalytic activity of the iron species was rather insensitive to the Grignard reagent provided a large excess was present. We infer that the catalytic species was an iron species complexed with Grignard reagent, similar to those isolated from the reduction of cobaltous complexes^{2,8,24} (cf. also ref. 25).



The catalytic activity of this iron species was markedly dependent on the time elapsed between its preparation and its subsequent use. The catalytic reaction between ethylmagnesium bromide and ethyl bromide in diethyl ether is illustrated in Fig. 2. If the iron species were generated by reduction of ferric chloride with ethylmagnesium bromide directly in the presence of ethyl bromide, the catalytic activity was high. However, if the reduced species of iron was allowed to age for 90 minutes prior to the addition of ethyl bromide there was a marked decrease in the rate shown in Fig. 2. There was, however, an apparent *autocatalysis* which was more marked for the "aged" catalyst whose activity eventually approached that of the iron generated directly, *i.e.*, the catalytic activity once degraded by ageing was recovered during the reaction. Autocatalysis was much less pronounced in THF solution. Significantly, the deactivation of the catalyst with ageing was quite severe with cobalt species and showed no evidence of recovery during the course of reaction. Furthermore, the onset of deactivation as shown in Fig. 2, occurred immediately after preparation of the cobalt catalyst.

Iron species which differed only in the extent of ageing were employed as catalysts for the reaction between ethylmagnesium bromide and ethyl bromide under a standard set of experimental conditions. The rates of formation of ethane and ethylene given in Table 4 showed that most of the deactivation occurred within 5 minutes after preparation of the catalyst (runs 53, 54). Moreover, the production of ethane was proportionally less affected than that of ethylene by ageing the catalyst,

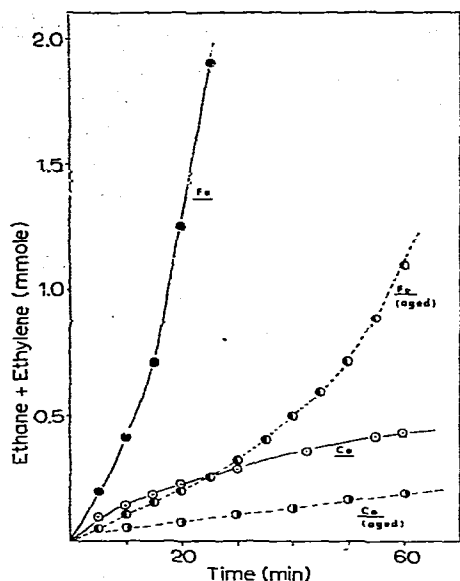


Fig. 2. The effect of ageing the catalyst on the catalyzed reaction of 0.18 *M* ethylmagnesium bromide and 0.16 *M* ethyl bromide at 2°: ● 2.4 × 10⁻⁴ *M* Fe in diethyl ether, no ageing; ○ 2.4 × 10⁻⁴ *M* Fe in diethyl ether, aged for 90 min at 2°; ⊙ 4.8 × 10⁻⁵ *M* Co in THF, no ageing; ⊚ 4.8 × 10⁻⁵ *M* Co in THF, aged for 90 min at 25°.

TABLE 4

EFFECT OF CATALYST AGEING ON THE RATE OF REACTION^a

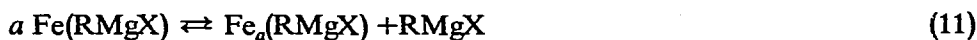
Run	RMgBr		Ageing conditions ^b		Rates of product formation ^c			$R(C_2H_6)/R(C_2H_4)$
	R	(<i>M</i>)	Temp. (°C)	Period (min)	$R(C_2H_4)$	$R(C_2H_6)$	$R(\Sigma)$	
53	Et	0.18	No ageing		>12.6	>13.6 ^d	27.2	1.08
54	Et	0.18	25	5.0	2.38	3.10	5.48	1.30
55	Et	0.18	25	15.0	1.52	2.28	3.80	1.50
56	Et	0.18	25	120	1.07	1.59 ^e	2.74	1.49
57	Et	0.090	25	15.0	0.69	1.13	1.82	1.64
58	Et	0.045	25	15.0	0.50	0.93	1.43	1.84
59	Me	0.18	No ageing		1.28	0.05 ^f	3.11	0.04
60	Me	0.18	25	120	0.14	0.07 ^g	0.43	0.50
61	Me	0.18	2.0	120	0.32	0.07 ^h	0.85	0.22

^a In 21 ml THF containing 0.16 *M* ethyl bromide and 1.2 × 10⁻⁵ *M* and 2.4 × 10⁻⁴ *M* ferric chloride for EtMgBr and MeMgBr, respectively. ^b Ageing represented by time elapsed between mixing of FeCl₃ and Grignard reagent and addition of EtBr. ^c From initial rates (2.8 × 10⁻⁷ moles/sec), less than 25% conversion. $R(C_2H_4)$, $R(C_2H_6)$ and $R(\Sigma)$ represents rate of formation of ethylene, ethane and combined ethylene, ethane plus 2 × butane, respectively. ^d Butane < 0.5. ^e Butane 0.04. ^f Methane 1.32 and propane 0.23. ^g Methane 0.20 and propane 0.01. ^h Methane 0.40 and propane 0.03.

an effect which could also be achieved at lower concentrations of Grignard reagent with the same degree of ageing (runs 55, 57, 58). The ratio of ethane to ethylene generally increased with decreasing activity of the catalyst or when the rates were slower. The rate

of formation of ethylene was also affected more than ethane when the catalyst was aged at a higher temperature (runs 59, 60). An inverse relationship was generally observed between the catalytic activity and the ratio of ethane to ethylene produced. Coordination by triphenylphosphine could also be employed to modify the iron species.

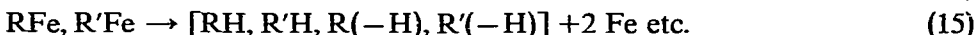
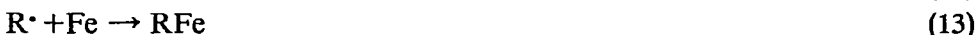
Aggregation of the active iron species may be responsible for the deactivation observed on ageing the catalyst. A simplified scheme consistent with the data is presented below. In this formulation, $\text{Fe}(\text{RMgX})$ as the ethereal complexes, represents



the most active catalytic species. Aggregation to the less active polynuclear iron species is represented by eqn. (11) and is accelerated by temperature. The formation of iron aggregates apparently occurred with the liberation of Grignard reagent and ethereal ligands. Thus, deactivation was retarded by Grignard reagent and was more severe with diethyl ether than THF in accordance with their ability to coordinate with iron²⁶⁻²⁸. Triphenylphosphine probably served a similar function, although deactivation of the iron catalyst was observed at high concentrations of triphenylphosphine.

DISCUSSION

The kinetic results show that the iron-catalyzed reaction of Grignard reagents and alkyl halides is largely independent of the concentration of the alkylmagnesium halide. The rate is roughly first-order in alkyl halide and iron catalyst. Moreover, only that alkyl moiety derived from the alkyl halide is trapped by styrene. We wish to propose tentatively the following catalytic cycle to account for these observations and to form the basis for further study.

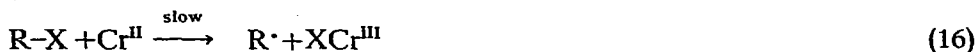


The catalytic amounts of iron required for the facile disproportionation of Grignard reagents with alkyl halides according to this mechanism are continually recycled between several oxidation states. If reactions (12) and (13) provide the route for the oxidation of iron, the decomposition of an alkyliron species according to eqn. (15) would provide the path for its regeneration. The aspects of this working hypothesis which require further elaboration are (a) the oxidation of the iron species by alkyl halides, (b) the regeneration of the catalyst by decomposition of alkyliron intermediates and (c) the role of alkyl radicals in the chain process.

Oxidation of the catalytic iron species by alkyl halides

Alkyl halides react with a variety of transition metal complexes particularly with those in their low oxidation states. Thus, processes in which displacement of halide ion by the metal nucleophile with inversion, oxidative addition particularly

of d^8 systems with retention, and ligand transfer of halogen to the metal reductant with racemization have all been described²⁹⁻³³. Displacement and addition are *formally* heterolytic processes, whereas ligand transfer proceeds via free alkyl radicals as discrete intermediates³². The formation of alkylchromium ion from alkyl halide and chromium(II) is such a two-step process³⁴.



Since alkyl radicals readily add to styrene and 1,3-butadiene, the latter can be used as effective probes for homolytic processes. Thus, only the alkyl group derived from the alkyl halide was selectively trapped by styrene during the iron-catalyzed reaction of tert-butyl or n-propyl bromide with ethylmagnesium bromide, (*cf.* Tables 3 and 8). These observations lend support to a homolytic mechanism for the reduction of alkyl halide by iron species given by eqns. (12) and (13). The qualitative reactivities of alkyl bromides in the sequence: tert-butyl > isopropyl > n-propyl is also in accord with analogous ligand transfer reduction of alkyl halides by chromium(II), tin(III) and cobalt(II) complexes³⁴⁻⁴⁰.

The kinetics support oxidative addition of alkyl halide to iron (eqn. 12) as the rate-limiting step in the catalytic process. Accordingly, reaction occurs most readily with the mononuclear iron species and to a lesser degree with iron aggregates. The extent to which the latter are involved will affect the apparent first-order dependence on the iron halide charged. Nonetheless, regeneration of the catalyst deactivated by ageing no doubt is associated with such a process, *e.g.*:



Decomposition of alkyliron intermediates

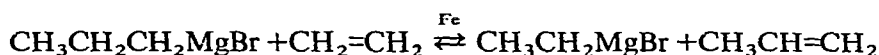
Metastable alkyliron intermediates are invoked as the species responsible for the regeneration of the reduced form of iron. Alkenes and alkanes are formed in the decomposition, although not necessarily in equimolar amounts. Alkyliron species



such as RFe are too labile to examine directly. However, the somewhat related dialkylmanganese and alkylcopper can be generated from the Grignard reagents and manganous or cuprous chlorides under similar conditions^{14,15}. Both organometals on decomposition also afford alkene and alkane in addition to reduced forms of manganese and copper, and mechanisms for these processes have been proposed.

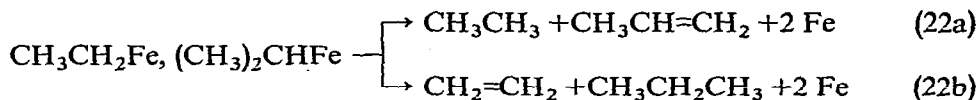


The yields of alkenes and alkanes, however, do not directly reflect only the decomposition of alkyliron species. The formation of ethylbenzene from styrene, for example, indicates that olefin-alkyl exchange, occurred during reaction. Similar exchanges may occur with alkenes formed as a result of disproportionation. The



exchange, however, is temperature and solvent dependent and is generally slow in THF at 2° (see Table 8). Finally, cognizance should be taken of the possibility of the decomposition of hydridoiron species followed by hydrogenation of alkene, by a process similar to that described for the decomposition of alkylmanganese species¹⁵.

Mixtures of alkanes and alkenes result from the simultaneous decomposition (for example, eqns. 22) of alkyliron intermediates formed both by metathesis of the alkylmagnesium halide (eqn. 14) and oxidative addition of the alkyl halide (eqn. 13).



Further studies on the decomposition of alkyliron species delineating their role in these reactions are in progress.

Alkyl radicals as intermediates in the Kharasch reaction

There are extensive and varied indications for the presence of alkyl radicals as intermediates in the Kharasch reaction²⁻¹². The extant literature, which has recently been summarized², is somewhat contradictory. One of the prime sources of confusion lies in the homolysis of alkylmetallic intermediates:



Bond dissociation energies for organometals of the transition series are generally undetermined. Judging from the trend in the values known for the homolysis of various alkylmetals, particularly of the Main group elements as far as the sixth period (Hg, Tl, Pb)⁴¹⁻⁴⁴, however, one would not expect homolysis to contribute substantially to a facile catalytic process. The tendency for organometals with methyl and alkyl derivatives containing no available β -hydrogens (including benzyl) to be more stable than other alkyl analogues is not consistent with a facile homolysis^{14,15}. Thus, the simple (trimethylsilyl)methyl derivatives of iron(II) and -(III) as well as those of the related transition metal ions have been prepared⁴⁵⁻⁴⁷ despite the fact that the (trimethylsilyl)methyl radical is appreciably stable and readily formed⁴⁸. Furthermore, the stabilizing influence usually exerted by π -bonding ligands is due less to the strengthening of the metal-alkyl bond than occupation of the coordination sites necessary for elimination since a variety of alkyl derivatives of substitution-inert chromium(III) and cobalt(III) are known³³⁻³⁷.

As yet we find little direct evidence for homolytic scission of the metal-alkyl bond taking place to any significant extent under the mild experimental conditions employed in these studies. That is not to preclude their occurrence at higher temperatures which have been employed in the past (particularly with cobalt catalysts). Thus, it is likely that the stoichiometric reduction of iron(II) and -(III) halides by Grignard reagent as presented in eqn. (3), proceeded via some of the same organoiron intermediates involved in the catalytic disproportionation of Grignard reagent with alkyl halides. Detection of alkyl radicals during such a reduction would provide support for bond homolyses and we are presently carrying out electron spin resonance and chemically induced dynamic polarization studies to probe this point. Chemical studies with styrene as a radical scavenger are not truly indicative due to complications from olefin-alkyl exchange catalyzed by iron (*vide infra*). Ferric chloride itself

is a rather efficient oxidant toward alkyl radicals^{32,49-52}, and should be investigated as a radical trap for alkyl radicals as possible intermediates.



Indirect evidence for homolysis may be gleaned from the data. Thus, in the iron-catalyzed disproportionation of Grignard reagents with alkyl halides the yields of alkenes were generally equal to alkanes as demanded by the stoichiometry. However, at very low concentrations of iron the yields of alkanes (runs 19, 23, 33) and the rates of formation of alkanes and alkenes varied accordingly (runs 1-3, 53-58). The excess of hydrogen in the material balance was more severe in diethyl ether than in THF (see experimental section, runs 49 and 51, Table 8) and at higher temperatures (run 11). No doubt, the extra hydrogen under these conditions was derived from solvent. It is tempting to suggest that alkyl radicals formed by homolysis abstracted hydrogen from solvent. However, homolytic processes were not necessarily involved since dehydrogenation of the ethereal solvent by the active metal catalyst is possible¹⁵. If homolysis of the organometallic intermediate occurred it would generally be at higher temperatures and with alkyl groups containing no available β -hydrogens. Our studies^{14,15} indicate that disproportionation represents the energetically most favorable route for decomposition, and the prime source of alkyl radicals in the Kharasch reaction lies in oxidative addition of alkyl halide to iron (eqn. 12). The alkyl group derived from the Grignard reagent is not directly involved in homolytic processes during the catalytic disproportionation of Grignard reagents and alkyl halide. However, metathesis of the Grignard reagent and the alkyl halide is also induced by the iron species during catalytic disproportionation. Alkyl exchange was most severe with primary alkyl halides (Table 2) and could obscure the source from which the alkenes and alkanes were derived. Finally, alkyl iodides and allylic as



well as benzylic halides are not desirable models to probe for homolytic mechanisms due to the facility of the Wurtz reaction^{18-23,53-58}.

CONCLUSION

The Kharasch reaction between Grignard reagents and alkyl halides is catalyzed by reduced iron species. A chain reaction is proposed in which the iron species are recycled between several oxidation states, involving reduction by decomposition of metastable alkyliron intermediates (eqn. 15) and oxidation by ligand transfer with alkyl halide (eqn. 12). Trapping experiments with styrene are consistent with alkyl radicals formed principally from the alkyl halide as a result of the ligand transfer step. The activity of the iron catalyst is sensitive to ageing. A number of side reactions involving alkyl exchange between Grignard reagent and alkyl halide as well as exchange and reduction of the product (alkene) are also catalyzed by the iron species extant in solution. The latter complicate the quantitative comparison of the structural effects of the Grignard reagents and the alkyl halides. Thus, the products as well as the rates of the reactions between a given alkylmagnesium halide and an alkyl halide may not be the same as the reverse combination in which the alkyl groups are interchanged (*cf.* Table 2).

EXPERIMENTAL SECTION

Materials

A billet of triply sublimed magnesium was obtained from Dow Chemical Co. (spectrographic analysis: Cu, < 0.001; Fe, < 0.0003; Mn, < 0.001; Ni, < 0.0005; Pb, < 0.003; Co, < 0.005; Cr, < 0.005; Ag, < 0.001; Rh, < 0.005; Pd, < 0.001; Mo, < 0.005; Ti, < 0.005%). Anhydrous nickel chloride was prepared from the reaction of its hexahydrate and thionyl chloride. Anhydrous ferrous chloride was prepared by disproportionation of iron and anhydrous ferric chloride in tetrahydrofuran. Anhydrous manganese chloride was prepared from its tetrahydrate by treating at 150° for 50 h *in vacuo*. Anhydrous ferric chloride, palladium chloride, cobalt bromide, cuprous chloride, cupric chloride, silver bromide and lithium nitrate were commercial grade and were used without further purification. Neopentyl bromide was prepared from the reaction of neopentyl alcohol and tri-*n*-butylphosphine dibromide. Triphenylphosphine was commercial grade and was used without further purification. Styrene and all organic halides were purified by distillation before use.

Preparation of Grignard reagent

Grignard reagents were prepared as usual except for the use of 1.5 times excess metallic magnesium and low temperatures (5~25°). After filtration under nitrogen, all Grignard reagent solutions (0.5~2.0 M) were almost colorless. Determination of the concentration of each Grignard reagent was made by back-titration with base and measurement of the amount of hydrocarbon after acidic hydrolysis.

The reaction of ethylmagnesium bromide and ethyl bromide induced by ferric chloride (typical example)

A 250 ml round bottomed flask was equipped with magnetic stirrer bar and a rubber serum cap placed at the top of flask. The atmosphere was replaced with helium and 18.5 ml of tetrahydrofuran, 2.0 ml of ethylmagnesium bromide (3.3 mmole, 0.157 M solution) and 0.25 ml of ethyl bromide (0.16 M solution) were added with hypodermic syringes. After the flask was immersed in a dry ice-acetone bath, 25 ml of methane and 25 ml of isobutane (both markers) were added with syringes. The flask was then transferred to an ice-water bath. After 5 min agitation, 0.25 ml of solution of ferric chloride in THF (0.60×10^{-5} M) was added to the solution with stirring. The color of the solution was colorless to pale yellow. At 5 min intervals, a small portion of gas phase was removed with a hypodermic syringe and analyzed by gas chromatography. The amounts of ethylene, ethane and *n*-butane (trace) at each 5 min intervals were plotted against time. From the slope of the resulting line, the rate of formation of each product was calculated (initial rate). In the cases of liquid products (*e.g.* Table 2), the reaction was quenched by the addition of dilute aqueous sulfuric acid at the appropriate time and each product (except gases) was analyzed by gas chromatography. The apparent rate of formation of each product was calculated by assuming that the rate of formation of each product was linear, at least in the initial stages of the reaction. All subsequent reactions were also carried out in a similar manner.

The gaseous hydrocarbons were analyzed by sampling the gas phase directly. Quantitative analysis was carried out by the internal standard method. Calibration curves were constructed at various concentrations of the components under carefully

TABLE 5

REACTIVITY OF ALLYLIC AND BENZYLIC SYSTEMS^a

RMgBr	R'Br	Styrene (mmole)	Period (min)	Products (mmole)					
				R(-H)	RH	RR	RR'	R'H	R'R'
Et	CH ₂ =CHCH ₂ ^b	0	15	0	0.13	0.21	2.41	0	0.20
Et	CH ₂ =CHCH ₂	0	5	0.04	0.18	0.21	2.66	0.02	0.17
Et	CH ₂ =CHCH ₂	26.1	5	0.05	0.09	0.17	2.59	0.02	0.13
Et	PhCH ₂ ^b	0	10	0.06	0.11	0.22	0.41	^c	0.43
Et	PhCH ₂	0	10	1.71	1.76	0.09	0.13	^c	1.02
Et	PhCH ₂	26.1	5	1.89	1.96	0.11	0.05	^c	0.70
PhCH ₂	Et	0	30	^c	0.35	0.09	0.51 ^d	^c	0.11
PhCH ₂	Et	26.1	30	^c	0.02	0.16	0.07 ^e	^c	0.02

^a In 21 ml THF at 2° containing 1.2×10^{-5} M ferric chloride, 3.40 mmole Grignard reagent and 3.35 mmole alkyl halide. ^b No ferric chloride. ^c Not determined. ^d Ethylene (0.98 mmole) also formed. ^e Ethylene (0.15 mmole) also formed.

TABLE 6

REDUCTION OF IRON HALIDES BY GRIGNARD REAGENTS^a

MCl _n (mmole)	RMgBr (mmole)	Styrene (mmole)	Q(R)	Products (mole%)		
				RH	R(-H)	RR
FeCl ₃	(1.0) Me	(5.7)	0	3.0	30	67 ^b
FeCl ₂	(1.0) Me	(5.7)	0	2.0	68	27 ^c
FeCl ₃	(1.0) neo-Pent	(2.3)	0	2.3	62	38
FeCl ₃	(1.0) Et	(8.8)	0	3.7	60	22
FeCl ₂	(1.0) Et	(8.8)	0	2.1	68	26
FeCl ₃	(1.0) ^d Et	(5.7)	0	3.5	45	41
FeCl ₃	(1.0) ^d Et	(5.7)	26.1	3.9	26	63
FeCl ₂	(1.0) ^d Et	(5.7)	0	2.0	51	41
FeCl ₂	(1.0) ^d Et	(5.7)	26.1	4.2	19	78

^a In 21 ml THF at 2°. ^b Ethylene (3 mole%) also present. ^c Ethylene (5 mole%) also formed. ^d In diethyl ether. ^e Ethylbenzene before hydrolysis, 1.05 mmole; after hydrolysis, 1.88 mmole. ^f Ethylbenzene (2.53 mmole) after hydrolysis.

controlled conditions which reproduced the reaction mixture.

The stoichiometric reduction of iron halides were carried out by suspending them in a degassed solution of THF at 2° and adding excess Grignard reagent with rapid stirring. The gaseous products were analyzed in the usual manner.

Diethyl ether and THF as solvents

The iron-catalyzed reaction between ethylmagnesium bromide and n-propyl bromide was approximately 15 times faster in THF than in diethyl ether at 2°. The material balance between alkane (ethane plus propane) and alkene (ethylene plus propene) in Table 8 indicated that substantially more alkane was formed in diethyl ether than could be accounted for simply by a disproportionation process. Dehydrogenation of diethyl ether was also indicated by the formation of substantial

TABLE 7

CONDITIONS OF GAS CHROMATOGRAPHY

Compound	Column	Temp. (°C)	Internal standard
Methane	2 ft-Porapak Q	R.T.	C ₂ H ₄ or C ₂ H ₆
Ethylene	2 ft-Porapak Q	R.T.	CH ₄
Ethane	2 ft-Porapak Q	R.T.	CH ₄
Propene	15 ft-Dowtherm	R.T.	i-C ₄ H ₈
Propane	15 ft-Dowtherm	R.T.	i-C ₄ H ₈
Isobutene	15 ft-Dowtherm	R.T.	i-C ₄ H ₈
n-Butane	15 ft-Dowtherm	R.T.	i-C ₄ H ₈
Isobutene	15 ft-Dowtherm	R.T.	n-C ₄ H ₁₀
Isobutane	15 ft-Dowtherm	R.T.	n-C ₄ H ₁₀
cis-2-Butene	15 ft-Dowtherm	R.T.	n-C ₄ H ₁₀
trans-2-Butene	15 ft-Dowtherm	R.T.	n-C ₄ H ₁₀
Ethyl chloride	12 ft-SF96	30	n-C ₄ H ₁₀
n-Pentane	15 ft-FFAP	65	n-C ₇ H ₁₆
n-Hexane	15 ft-FFAP	65	n-C ₇ H ₁₆
Ethyl bromide	15 ft-FFAP	65	PrBr
Ethylbenzene	15 ft-FFAP	135	PhMe

TABLE 8

SOLVENT DEPENDENCE OF THE CATALYZED REACTION OF ETHYLMAGNESIUM BROMIDE AND n-PROPYL BROMIDE^a

Run	Solvent	Products ^b (mmole)				After hydrolysis ^c		$\frac{\Sigma n\text{-Pr}}{\Sigma \text{Et}^d}$
		C ₂ H ₄	C ₂ H ₆	C ₃ H ₆	C ₃ H ₈	EtPh	C ₃ H ₈	
49	Et ₂ O ^e	0.57	0.56	0.14	0.41		0.21	0.49
50	Et ₂ O ^{e,f}	1.14	0.69	0.02	0.03	0.22	0.01	0.03
51	THF ^g	2.00	1.48	0.81	1.36		0.42	0.62
52	THF ^h	0.68	0.65	0.02	0.09	< 0.02	0.27	0.08

^a In 21 ml THF or ether containing 2.4×10^{-4} M ferric chloride, 0.18 M ethylmagnesium bromide and 0.16 M n-propyl bromide at 2°. ^b Yield of butane, pentane and hexane negligibly small in all runs. ^c Hydrocarbon liberated after hydrolysis (mmole). ^d $\Sigma \text{Pr} = \text{C}_3\text{H}_8 + \text{C}_3\text{H}_6$; $\Sigma \text{Et} = \text{C}_2\text{H}_4 + \text{C}_2\text{H}_6$. ^e Analysis after 45 min. ^f Styrene 26.1 mmole present. ^g Reaction almost complete after 10 min. ^h Analysis after 20 min, 26.1 mmole styrene present.

amounts of ethylbenzene when reactions were carried out in diethyl ether containing styrene (Table 8).

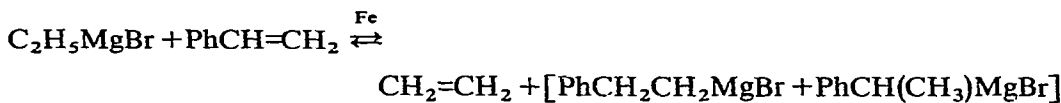
Catalytic exchange of alkenes and Grignard reagents

Exchange between alkene and Grignard reagent could be induced by catalytic amounts of iron in THF solutions. Thus, ethylmagnesium bromide and styrene did not react until 2×10^{-4} M ferric chloride was added (Table 9). Ethylene was evolved and after hydrolysis equivalent amounts of ethylbenzene were found. Labelling with deuterium oxide followed by mass spectroscopic analysis indicated that α - and β -phenethylmagnesium bromide were formed in a ratio of approximately 15/1. Insignificant amounts of ethylbenzene were found when methylmagnesium bromide

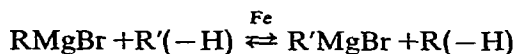
TABLE 9
CATALYZED EXCHANGE OF GRIGNARD REAGENTS WITH ALKENES^a

RMgBr	R'(-H)	Solvent	Temp. (°C)	Products (mmole) ^b	
				R(-H)	R'H
Et ^c	Sty. ^d	Et ₂ O	2.0	0.57	0.60 ^e
Et ^{c,f}	Sty. ^d	Et ₂ O	25	0.06	0.06 ^g
Et ^{c,f}	Sty. ^d	THF	2.0	0.05	0.03 ^h
Et ^{c,f}	Sty. ^d	THF	25	0.61	0.59 ⁱ
Me ^{c,f}	Sty. ^d	Et ₂ O	2.0		0.04 ^j
Et	C ₃ H ₆	THF	25	0.03	0.03
Et	C ₃ H ₆	Et ₂ O	2.0	< 0.01	< 0.01
Pr	C ₂ H ₄	THF	25	0.68	0.70
Pr	C ₂ H ₄	Et ₂ O	2.0	0.45	0.45
i-Pr	C ₂ H ₄	THF	25	1.20	1.33
i-Pr	C ₂ H ₄	Et ₂ O	2.0	0.31	0.33
t-Bu	C ₂ H ₄	THF	25	0.15	0.16

^a In 21 ml solvent, 3.0 mmole Grignard reagent, 2.0 mmole alkene and 0.025 mmole ferric chloride. ^b Analysis after 60 min, liquid products after acidic hydrolysis. ^c 3.8 mmole. ^d 26.1 mmole styrene. ^e PhCHD-CH₃ (71%), PhCH₂CH₂D (5%), PhCH₂CH₃ (24%) analyzed 90 min after quenching with D₂O. ^f 0.0050 mmole ferric chloride. ^g Analysis after 90 min. ^h Analysis after 100 min. ⁱ Analysis after 60 min. ^j Analysis after 480 min.



was treated under similar conditions. The exchanges between various Grignard reagents and other alkenes are given in Table 9 which also shows that exchange was more facile in diethyl ether than THF at 2°, but reversed at 25°.



The exchange between Grignard reagent and alkene can obscure the stoichiometry of the reduction of iron(II) and -(III) halides and the disproportionation with alkyl halides. Thus, in the presence of excess Grignard reagent the value of $Q(\text{R})$ in eqn. (4) was equal to n (see Table 6, 2.0 for ferrous and 3.0 for ferric) when exchange was not possible ($\text{R} = \text{methyl}$). However, the value of $Q(\text{Et})$ under similar conditions was larger. In diethyl ether it was 3.5 and increased to 3.9 in the presence of styrene. Similarly, in the catalytic disproportionations between Grignard reagents and alkyl halides the rates and yields of alkene relative to alkane were usually higher in the presence of styrene (Tables 3 and 8).

The facile exchanges between alkenes and Grignard reagents catalyzed by iron are similar to those previously observed with titanium and nickel^{16,17}. The catalytic species of iron was readily deactivated by ageing and triphenylphosphine (Fig. 3) in a manner reminiscent of the catalyst responsible for the disproportionation of Grignard reagents and alkyl halides (*cf.* Fig. 2). It should be pointed out, moreover, that oxidative addition of the reduced iron species by alkyl halides in the disproportionation reaction (eqn. 18) allows for the regeneration of the deactivated iron ag-

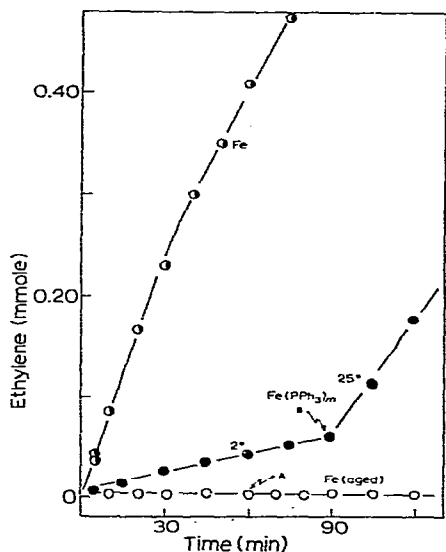
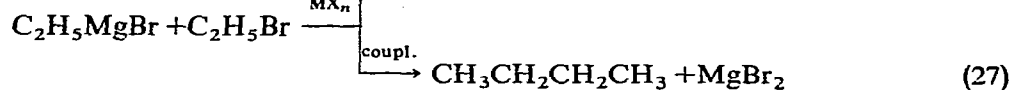
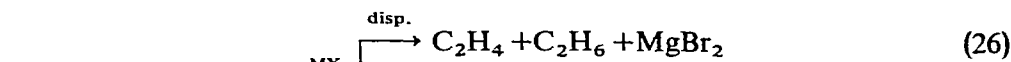


Fig. 3. Catalyzed exchange of 1.24 *M* styrene and 0.18 *M* ethylmagnesium bromide at 2° in diethyl ether using 2.4×10^{-4} *M* ferric chloride; ● no ageing; ○ aged for 60 min and styrene added at point A; ● in the presence of 0.18 *M* triphenylphosphine, no ageing, temperature raised to 25° at point B.

gregates, a route which is not necessarily available in the exchange process.

Comparative activities of transition metals as catalysts

The typical reaction between ethylmagnesium bromide and ethyl bromide was also examined under standard conditions with a representative group of transition metal salts. Various amounts of ethane, ethylene and *n*-butane were formed by disproportionation (eqn. 26) and coupling (eqn. 27). The results of the catalyzed



reaction between ethylmagnesium bromide and ethyl bromide are given in Table 10. All of the yields were corrected, as a first approximation, for the amounts of hydrocarbon formed by the reduction of the transition metal salt by ethylmagnesium bromide in the absence of ethyl bromide (see Table 6). The last column of Table 10 indicates that the stoichiometric requirements were invariant despite the varying



extent to which disproportionation and combination were promoted by different metal catalysts. The latter fell into three categories listed earlier. Alkylmanganese species were appreciably more stable than the other organometals and required relatively elevated temperatures for decomposition^{14,15}. Iron, cobalt, and nickel promoted disproportionation. Ethane and ethylene were not always formed in equimolar

TABLE 10

REACTION OF ETHYLMAGNESIUM BROMIDE AND ETHYL BROMIDE INDUCED BY TRANSITION METAL HALIDES^a

Metal halide	Method ^b	EtMgBr (mmole)	Products ^c (mole%)			$\Sigma\text{Et}/\text{EtBr}^d$
			C ₂ H ₄	C ₂ H ₆	n-C ₄ H ₁₀	
FeCl ₂	B	8.75	49.5	50.5	0.0	1.8
FeCl ₃	B	8.75	45.1	54.9	0.0	1.9
CoBr ₂	A	8.75	38.3	55.7	6.0	1.9
NiCl ₂	A	8.75	41.6	52.4	6.0	2.0
PdCl ₂	A	7.00	47.5	47.8	4.7	2.0
PdCl ₂	B	7.00	44.0	50.3	5.7	1.9
MnCl ₂	A ^e	8.75	49.4	50.6	0.0	1.9
CuCl	B	7.00	15.8	17.5	66.7	1.8
CuCl ₂	A	7.00	51.3	48.7	0.0	2.0
CuCl ₂	B ^f	7.00	0.3	2.2	97.5	2.1
AgBr	A	7.00	1.3	2.9	95.8	1.9
AgBr	B	7.00	1.3	2.5	96.2	1.9

^a In 21 ml THF containing 1.30 mmole ethyl bromide and 1.0 mmole metal halide at 2° for 60 min.^b Method A: ethyl bromide added after reaction of metal halide and ethylmagnesium bromide completed (60 min). B: ethyl bromide added before ethylmagnesium bromide. ^c All products produced from reaction of metal halide and ethylmagnesium bromide were subtracted as a blank. ^d $\Sigma\text{Et} = \text{C}_2\text{H}_4 + \text{C}_2\text{H}_6 + 2\text{C}_4\text{H}_{10}$. ^e At 30°. ^f For 120 min.

amounts as may be implied unintentionally by the term disproportionation or by eqn. (26).

Silver was unique among the metals listed in Table 10 in favoring the coupling reaction under both experimental conditions. On the other hand, copper in two oxidation states were both catalytically involved in the reaction of Grignard reagent with alkyl halide, and the relative amounts of disproportionation and coupling could be deliberately altered by adjusting conditions, as clearly indicated in Table 10. The mechanism of the catalyses by silver and copper and the decomposition of alkylmanganese species have been described previously^{14,15}.

The catalytic activity shown by transition metals is qualitatively compared in Fig. 4. In these studies the metal catalysts were prepared by the prior reduction of *catalytic* amounts of the metal halide with an excess of ethylmagnesium bromide and then followed by the addition of ethyl bromide. The most important feature of this figure is the high catalytic activity *maintained* by iron to beyond 50% conversion of ethyl bromide. In contrast, the pronounced curvature shown in the figure by cobalt, nickel and palladium indicated rapid deterioration of the catalytic activity at an early stage of the reaction. The deactivation of the catalyst is ascribed to varying degrees (and rates) of aggregation of the active metal species and will be discussed further. Although cobalt(II) halides have been extensively used in the Kharasch reaction, this variation in the activity of the catalytic species obviated their use for further kinetic studies.

Alkyl exchange between Grignard reagent and alkyl halide catalyzed by iron

The iron-catalyzed exchange between alkyl groups during reaction of alkylmagnesium bromide and alkyl bromide under Kharasch conditions was studied by

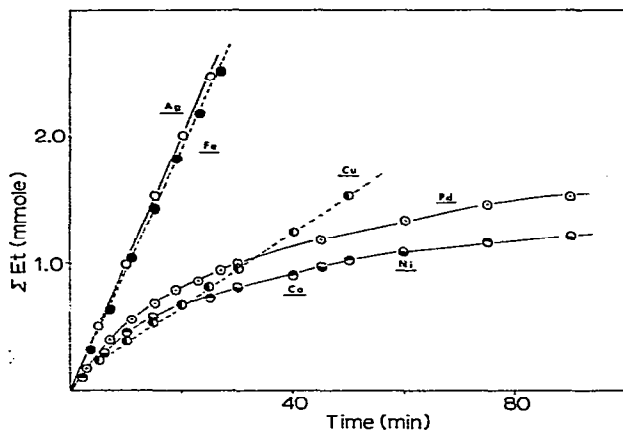


Fig. 4. Comparative activities of transition metals as catalysts in the reaction of 0.18 *M* ethylmagnesium bromide and 0.30 *M* ethyl bromide at 2° in THF; ○ 5.7×10^{-3} *M* Ag, ● 1.2×10^{-3} *M* Fe, ● 1.2×10^{-4} *M* Cu, ○ 2.2×10^{-4} *M* Pd, ● 5.7×10^{-4} *M* Co and ● 2.2×10^{-4} *M* Ni.

quenching the reaction with water at intermediate stages of the reaction. The extent of exchange was determined as shown in the last column of Table 11 by measuring



the amount of extra alkane liberated after hydrolysis. The alkane (derived from the alkyl bromide) formed under these conditions qualitatively represented the exchange reaction (eqn. 29). The results show that alkyl exchange occurred generally most rapidly with primary alkyl bromides and slowly with tertiary alkyl bromides. It was

TABLE 11

ALKYL EXCHANGE BETWEEN GRIGNARD REAGENT AND ALKYL HALIDE INDUCED BY IRON^a

Run	RMgBr	R'Br	FeCl ₃ (10 ⁵ M)	Temp. (°C)	Period (min)	R'H ^b (mmole)
13	Me	Pr	240	2.0	420	0
15	Me	i-Pr	240	25	15	0
18	Et	Pr	1.2	2.0	27	0.56
19	Et	Pr	0.12	2.0	180	0.12
21	Et	i-Pr	6.0	2.0	10	0.03
22	Et	i-Pr	0.3	2.0	60	0.01
23	Et	i-Pr	0.3	25	60	0.02
25	Et	t-Bu	24	2.0	10	0
27	Et	neo-Pent	1.2	25	45	0.03
28	Pr	Me	1.2	2.0	20	1.39
29	Pr	Et	1.2	2.0	45	0.14
31	i-Pr	Et	0.3	2.0	240	0.24
32	neo-Pent	Et	240	25	10	0
35	Ph	Et	1.2	25	1440	0
36	PhCH ₂	Et	240	25	60	0

^a In 21 ml THF containing 2.1–4.2 mmole RMgBr and 6.3 mmole R'Br entries correspond to those given in Table 2. ^b Additional alkane liberated after hydrolysis with dilute sulfuric acid after period specified. For other products see Table 2.

also a more serious complication with secondary Grignard reagents compared to their primary analogues.

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