Journal of Organometallic Chemistry, 225 (1982) 279—299
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

IRON CATALYSIS OF GRIGNARD REDUCTIONS. MECHANISM OF 1,3-REDUCTIVE ELIMINATIONS FROM γ-PROPYL HALIDES *

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(Received May 28th, 1981)

Summary

The iron-catalyzed reduction of various 3-substituted propyl bromides by Grignard reagents affords propylene and cyclopropane. The reduction to propylene is particularly noteworthy since it formally represents a 1,2-hydrogen shift. Two key intermediates have been identified in propylene formation, in which 3-methoxypropyl bromide is first catalytically reduced to the magnesium derivative by Grignard reagent. The iron-catalyzed β-elimination of the 3-methoxypropylmagnesium intermediate affords allyl methyl ether, which is then reductively cleaved to propylene. Extensive studies of deuterium labeling in the reactants, as well as in both intermediates, allow the course of the hydrogen shift to be followed unequivocally. The mechanism of iron catalysis is proposed in Schemes 2 and 3, representing the first and second stages of the reduction to propylene.

Introduction

Transition metal catalysis of the reduction of a variety of organic halides by Grignard reagents is generally described as the Kharasch reaction [1—6]. Organotransition metal species play an important role in the catalytic cycle, which derives its high efficiency from the rapid rates of formation and decomposition of these transient intermediates [7]. Indeed, the very evanescent nature of the organotransition metal intermediates by itself poses an inviting mechanistic challenge in the elucidation of the Kharasch reactions.

Iron complexes are especially effective in the Kharasch reaction, as shown by the catalytic disproportionation in eq. 1, in which the Grignard reagent is

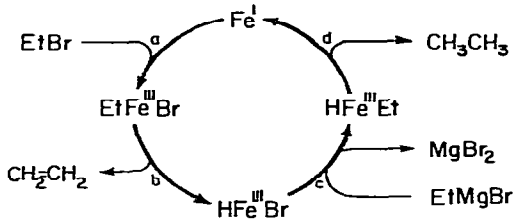
* Dedicated to Professor Henry Gilman whose pioneering research led to the flowering of organometallic chemistry.

0022-328X/82/0000—0000/$02.75

formally oxidized and the alkyl halide reduced, i.e.,

$$CH_3CH_2MgBr + CH_3CH_2Br \xrightarrow{[Fe]} CH_3CH_3 + CH_2{=}CH_2 + MgBr_2 \quad (1)$$

The role of the iron catalyst is to mediate the oxidation-reduction via the ethyl-iron intermediates in the simplified catalytic cycle shown below [8] *..



SCHEME 1

A similar catalytic cycle has been proposed in the iron-catalyzed cross coupling reaction of Grignard reagents with vinylic halides [9]. The catalytic mechanism in each of these processes is characterized by an organoiron intermediate which decomposes by β-elimination (as in step b) or reductive elimination (as in step d), without the intermediacy of alkyl(ethyl) radicals. The latter bears importantly on the intriguing transformation of 3-substituted propyl halides during the Kharasch reaction, e.g.,

$$CH_3OCH_2CH_2\dot{C}H_2Br + PhMgBr \xrightarrow{[Fe]} CH_2{=}CHCH_3 + [Ph] + MgBr_2 \quad (2)$$

in which the propylene was considered to arise via a 1,2-shift of a hydrogen atom in a 3-methoxypropyl radical intermediate [10]. [Note, eq. 2 is not balanced.]

Our interest in the reductive elimination in eq. 2, with its concurrent 1,2-hydrogen shift, is to demonstrate how this rearrangement represents a natural consequence of the mechanism of iron catalysis (as in Scheme 1), and does not proceed via an unprecedented 1,2-hydrogen atom shift in an alkyl radical.

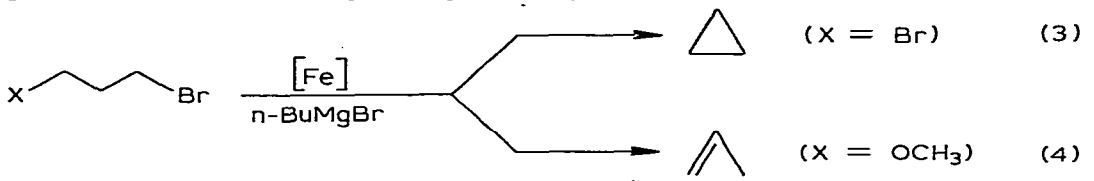
Results

We proceed in the mechanistic study by demonstrating the presence of four discrete processes in the catalysis, viz., (i) the reduction of the iron(III) precursor to an active iron catalyst, (ii) the catalytic conversion of 3-methoxypropyl bromide to the magnesium derivative by the Grignard reagent, (iii) catalytic decomposition of 3-methoxypropylmagnesium to allyl methyl ether, followed by (iv) the catalytic reductive cleavage of allyl methyl ether to propylene. Before doing so, however, we first show how the reduction products of the various 3-substituted propyl bromides are determined by the γ-substituent.

* Hereinafter, only those ligands required for the discussion are included in the mechanistic schemes. The specification of the oxidation states is intended solely for electron bookkeeping purposes, and not to establish identity.

I. Effect of the γ-substituent on the Kharasch reaction of propyl bromides

The reduction of the 3-substituted propyl bromides was carried out with n-butylmagnesium bromide and catalytic amounts of iron(III) in tetrahydrofuran (THF) solutions at both 0°C and ambient temperatures. The results in Table 1 show that either propylene or cyclopropane (or a mixture) is the major product of reduction, depending on the γ-substituent.



Since 3-methoxypropyl bromide afforded the highest yields of propylene, all subsequent studies were carried out with this derivative. Furthermore, the results in Table 1 show that high yields of propylene are derived from the iron-catalyzed reduction of allyl methyl ether with the same Grignard reagent, i.e.,

High yields of propylene are also generated simply when a catalytic amount of iron(III) is added to 3-methoxypropylmagnesium bromide.

II. Formation of the active catalyst by the Grignard reduction of iron(III)

A yellow THF solution of ferric chloride is rapidly reduced by n-butylmagne-

TABLE 1

IRON-CATALYZED REDUCTION OF 3-SUBSTITUTED PROPYL BROMIDES BY GRIGNARD REAGENT [a]

$XCH_2CH_2CH_2Br$	Iron(III)	Temp. (°C)	Yield (%) [b]			C_3H_7X
			△	⫽	○	
Bromo	$Fe(DBM)_3$	0	2	3	68	
		22	13	7	78	<5
	$FeCl_3(THF)$	0	3	3	72	
		22	19	7	79	<5
Chloro	$Fe(DBM)_3$	23	2	6	59	22
	$FeCl_3(THF)$	23	1	6	55	11
Methoxy	$Fe(DBM)_3$	0	<0.5	73	<0.5	21 [c]
	$FeCl_3(THF)$	0	<0.5	73	<0.5	
Phenoxy	$Fe(DBM)_3$	0	0	14	4	50 [d]
		23	1	19	9	56
	$FeCl_3(THF)$	0	1	28	3	44 [d]
		23	1	19	7	62
$MeO(CH_2)_3MgBr$	$Fe(DBM)_3$	0	<0.5	71	<0.5	24
Allyl methyl ether	$Fe(DBM)_3$	0	<0.5	63	<0.5	<1 [e]
	$FeCl_3(THF)$	24	<0.5	68	<0.5	<1 [f]

[a] In THF solution containing 0.1 *M* n-BuMgBr and 0.04 *M* $X(CH_2)_3Br$ in 10 ml. Solution of iron(III) added incrementally (1%) every 5 min. [b] Based on $X(CH_2)_3Br$. [c] Methyl heptyl ether (1%), 1,6-dimethoxyhexane (1%), biallyl (<1%) not detected. [d] Isolated yields. [e] Heptene (8%) and biallyl (18%). [f] Heptene (5%) and biallyl (20%).

sium bromide to afford a dark brown, but apparently homogeneous system. Figure 1 shows that the limiting amounts of butane and butene are obtained in a molar ratio of 1 : 2 with about 4 equivalents of n-BuMgBr. Moreover, the catalytically active iron species is only formed after more than 3 equivalents

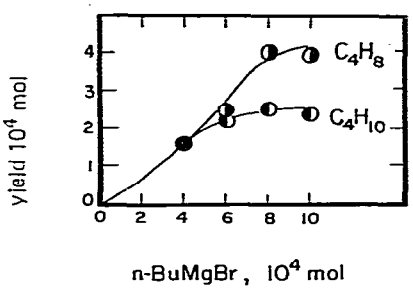


Fig. 1. Formation of butane (●) and butene (◑) attendant upon the reduction of 2.0 × 10^{-4} mol $FeCl_3$-(THF) by n-BuMgBr in 10 ml THF at 0°C.

of n-BuMgBr are added, as shown by the complete recovery of 3-methoxypropyl bromide in Table 2. We infer from this stoichiometry that iron(III) is reduced to a hydridoiron species, e.g.,

$$3\ n\text{-}C_4H_9MgBr + FeCl_3 \rightarrow 2\ C_4H_8 + C_4H_{10} + HFe^I + 3\ MgBrCl \qquad (7)$$

In accord with this formulation, acidolysis of the reduced iron solution yields 1 mole of dihydrogen. Furthermore, the use of the deuterium-labeled Grignard reagent derived from n-decyl-β,β-d_2 bromide, afforded large amounts of HD (see Experimental Section). Pending further studies, we tentatively ascribe the catalyst to a hydridoiron(I) species, hereafter referred to as Fe^I.

III. Iron-catalyzed conversion of 3-methoxypropyl bromide to the magnesium derivative

A solution of 3-methoxypropyl bromide and n-BuMgBr is stable indefinitely at room temperature. However, the addition of small amounts of iron(III) is

TABLE 2

GRIGNARD REQUIREMENT FOR IRON CATALYSIS OF PROPYLENE FORMATION FROM 3-METHOXYPROPYL BROMIDE [a]

n-BuMgBr [b]	Iron(III) [b]	[b]	/\ [b]	BuH [b, c]	Bu(—H) [b]	CH_3O-$(CH_2)_3Br$ recovered (%)
4.0	$Fe(DBM)_3$	2.0	<0.04	2.0	2.0	100
	$FeCl_3$(THF)	2.0	<0.04	1.5	1.3	100
6.0	$Fe(DBM)_3$	2.0	<0.04	2.3	2.4	85
	$FeCl_3$(THF)	2.0	<0.04	2.8	2.4	100
8.0	$Fe(DBM)_3$	2.0	0.13	3.1	3.6	50
	$FeCl_3$(THF)	2.0	0.91	4.0	3.2	29

[a] With 2.0 × 10^{-4} mol 3-methoxypropyl bromide in 10 ml THF at 0°C. [b] In units of 10^{-4} mol. [c] n-Octane (6—10%) also formed.

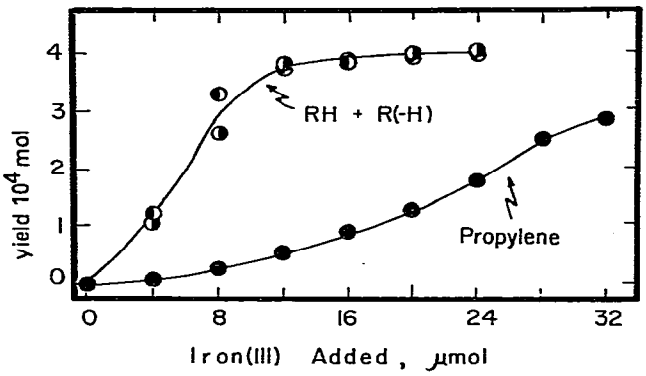
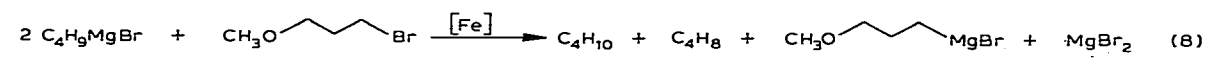


Fig. 2. The reduction of 0.08 *M* 3-methoxypropyl bromide by 0.18 *M* n-BuMgBr in two stages. Initial evolution of n-butane (○) and 1-butene (◑) from 5 ml THF at 0°C, followed by the subsequent reduction to propylene (●), as indicated by the incremental addition of $Fe(DBM)_3$.

accompanied by the spontaneous evolution of an equimolar mixture of butane and butene, even at 0°C. Essentially no propylene is evolved until incrementally more iron(III) is added, as shown in Fig. 2. Halogen—metal interconversion did not occur under these conditions, since no n-butyl bromide was formed. Instead, the formation of a 3-methoxypropylmagnesium intermediate is readily shown by quenching experiments. Thus the addition of either acetic acid or carbon dioxide after the first stage leads to high yields of methyl propyl ether or 4-methoxybutyric acid, respectively. The stoichiometric relationship among these products is given in Table 3, from which a turnover number of about 25 is obtained for the catalytic conversion of 3-methoxypropyl bromide to the magnesium derivative.



(8)

Deuterium labeling studies show that the alkane and alkene are derived in eq. 8 by hydrogen transfer specifically from the β-position of the Grignard reagent. Thus the iron-catalyzed reduction of 3-methoxypropyl bromide by

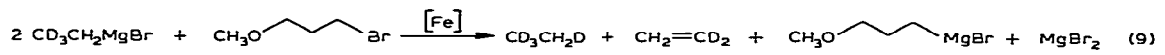
TABLE 3

IRON-CATALYZED CONVERSION OF 3-METHOXYPROPYL BROMIDE TO THE MAGNESIUM DERIVATIVE WITH GRIGNARD REAGENT [a]

Iron(III) added (%) [b]	⩓ (10^4 mol)	Bu(—H) (10^4 mol)	BuH (10^4 mol)	$PrOCH_3$ (10^4 mol)	CH_3O-$(CH_2)_3MgBr$ (%) [b, c]	$CH_3O(CH_2)_3Br$ recovered (%) [b]
0.5	0.05	0.60	0.80	0.14	25	73
1.0	0.24	1.1	1.5	0.29	35	50
1.5	0.36	2.0	2.0	0.61	48	22
2.0	0.42	2.1	2.3	0.64	55	18
2.5	0.51	2.2	2.2	0.98	50	5
3.0	0.69	2.9	2.9	0.92	43	7

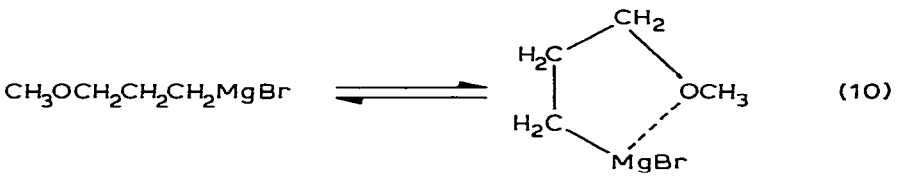
[a] With 9.0×10^{-4} mol n-BuMgBr and 4.0×10^{-4} mol $Br(CH_2)_3OCH_3$ in 5 ml THF at 0°C for 30 min. [b] Based on $Br(CH_2)_3OCH_3$. [c] Determined by quenching with carbon dioxide.

β,β,β-trideuterioethylmagnesium bromide yields ethane-d_4 and ethylene-d_2.



No deuterium is incorporated into the 3-methoxypropylmagnesium derivative.

It is important to note that the iron-catalyzed Grignard formation is rather specific to 3-methoxypropyl bromide. For example, simple alkyl halides are converted in less than 20% yields to the corresponding magnesium derivative under equivalent conditions. Furthermore, the higher methoxy homologues in Table 4 [11] behave as simple alkyl halides, and only afford low yields of the ω-methoxyalkylmagnesium derivatives. As expected, 2-methoxyethyl bromide was converted to ethylene [12]. We tentatively ascribe the unique behavior of 3-methoxypropyl bromide to intramolecular stabilization of the magnesium derivative, e.g.,



Indeed, competition experiments, in which an equimolar mixture of 3-methoxypropyl bromide and n-propyl bromide was treated with an insufficiency of EtMgBr, showed that 3.4 times more $CH_3O(CH_2)_3MgBr$ was formed than n-PrMgBr.

IV. Allyl methyl ether as the intermediate in the iron-catalyzed conversion of 3-methoxypropylmagnesium to propylene

The iron-catalyzed conversion of 3-methoxypropylmagnesium to propylene shown in eq. 6 is tantamount to a 1,2-shift of hydrogen concurrent with the elimination of CH_3OMgBr. Deuterium labeling studies shed considerable light on this unique transformation. Thus, the results in Table 5 show that 3-methoxy-

TABLE 4

IRON-CATALYZED CONVERSION OF VARIOUS ALKYL HALIDES TO THE MAGNESIUM DERIVATIVE WITH EtMgBr [a]

Alkyl bromide RBr	EtH	Et(—H)	RH	R(—H) [b]	RMgBr (%) [c]
$CH_3O(CH_2)_3$	3.95	3.05	0.14	0	92
$CH_3O(CH_2)_4$	2.59	2.26	1.95	0.26	18
$CH_3O(CH_2)_5$	2.58	2.40	1.69	0.33	20
$CH_3O(CH_2)_6$	2.89	2.55	1.81	0.38	25
$CH_3O(CH_2)_2$	3.75	6.71			0
$CH_3CH_2CH_2$	2.71	2.28	1.85	0.36	15
$CH_3(CH_2)_5$	2.40	2.24	1.98	0.18	20

[a] With 2.0 × 10^{-3} mol EtMgBr and 4.0 × 10^{-4} mol RBr in 10 ml THF at 0°C containing 1.2 × 10^{-5} mol $Fe(DBM)_3$ for 60 min. All products expressed in units of 10^{-4} mol. Data based on studies by P.O. Nubel. [b] Terminal alkene only. [c] Based on RBr added.

propylmagnesium bromide, which is specifically labeled at C(2), yields propylene-2,3-d_2, i.e.,

$$CH_3OCH_2\underset{\displaystyle D}{\overset{\displaystyle D}{C}}CH_2MgBr \xrightarrow{[Fe]} CH_2=\underset{\displaystyle D}{C}-CH_2 + CH_3OMgBr \qquad (11)$$

The deuterium labeling in the propylene fraction can be readily ascertained from the ^2H NMR spectrum, as described in the Experimental Section. The presence of small amounts (2%) of allyl methyl ether specifically labeled at C(2) (i.e., $CH_2=CDCH_2OCH_3$) suggests that it is an intermediate in propylene formation. Indeed, if an equimolar amount of unlabeled allyl methyl ether is deliberately added in the iron-catalyzed conversion of the labeled 3-methoxypropylmagnesium bromide, more than 30% of the mono-deuteriated $CH_2=CDCH_2OCH_3$ is observed in the recovered allyl methyl ether. Furthermore, the evolved propylene consists of a mixture of di- and mono-deuteriated species, i.e., $CH_2=CDCH_2D$ and $CH_2=CHCH_2D$, the amount of the latter corresponding roughly to the reisolated mono-deuteriated $CH_2=CDCH_2OCH_3$. The mono-deuteriated propylene becomes dominant in the presence of a 5-fold excess of unlabeled allyl methyl ether according to the stoichiometry:

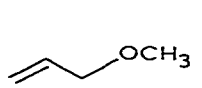
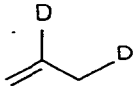
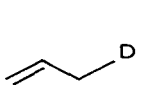
$$CH_3OCH_2\underset{\displaystyle D}{\overset{\displaystyle D}{C}}CH_2MgBr + CH_2=CHCH_2OCH_3 \xrightarrow{[Fe]}$$

$$CH_3OCH_2\underset{\displaystyle D}{C}=CH_2 + CH_2=\underset{\displaystyle D}{CH}CH_2 + CH_3OMgBr \qquad (12)$$

These deuterium labeling experiments demonstrate two important facets: (a) the

TABLE 5

IRON-CATALYZED CONVERSION OF 2,2-DIDEUTERIO-3-METHOXYPROPYLMAGNESIUM BROMIDE [a]. EFFECT OF ADDED ALLYL METHYL ETHER ON THE DEUTERIUM LABEL IN PROPYLENE

	D-label [b]				
(10^4 mol)	C≡C—C			(%) [c]	(%) [c]
0	0.08	0.84	0.66	80	*d*
4.0	<0.02	0.24	0.48	48	52
20	<0.02	0.04	0.53	8	92

[a] With 4.0 × 10^{-4} mol $CH_3OCH_2CD_2CH_2MgBr$ (85% D-incorporation) in 10 ml THF with 4 × 10^{-5} mol $Fe(DBM)_3$ added at 22°C. [b] Expressed as fraction D. [c] Determined by ^2H NMR, ±10%. [d] 2-Deuteriopropylene (~10%) and 1,2-dideuteriopropylene (~10%) also found. See Experimental Section.

apparent 1,2-hydrogen shift in the conversion of $CH_3OCH_2CD_2CH_2MgBr$ is actually an intermolecular process, and (b) it stems from the specific transfer of the β-hydrogen (deuterium) at C(2) to allyl methyl ether. Formally, such a two-step process is equivalent to the prior decomposition of $CH_3OCH_2CD_2CH_2$-MgBr to allyl methyl ether and DMgBr, followed by a metathetical exchange, i.e.,

$$[CH_3OCH_2CD_2CH_2MgBr \xrightarrow{a}$$

$$CH_3OCH_2CD{=}CH_2 + DMgBr \xrightarrow{b} DCH_2CD{=}CH_2 + CH_3OMgBr] \qquad (13)$$

Thus the added, unlabeled allyl methyl ether competes with that ($CH_3OCH_2CD{=}CH_2$) formed in eq. 13a to afford the deuterium distribution observed in eq. 12. This 2-step process also accounts for the actual isolation of allyl methyl ether in ~20% yields, when excess (0.24 *M*) 3-methoxypropyl bromide is present during its catalytic reduction with 0.08 *M* EtMgBr. In other words, when 3-methoxypropyl bromide is present in excess, it is capable of competing with allyl methyl ether in eq. 13b. Furthermore, the viability of allyl methyl ether as an intermediate in eq. 5 can be demonstrated separately, by showing that it is readily reduced to propylene by n-BuMgBr under catalytic conditions (see Table 1). Allyl methyl ether is not converted to 3-methoxypropylmagnesium under these conditions.

V. The iron-catalyzed reduction of allyl methyl ether to propylene

The iron-catalyzed reduction of allyl methyl ether by the deuterium-labeled CD_3CH_2MgBr affords only propylene-d_1, which is specifically labeled on the methyl group, i.e.,

$$CH_3OCH_2CH{=}CH_2 + DCH_2CH_2MgBr \xrightarrow{[Fe]} CH_2CH{=}CH_2 + \begin{matrix} D \\ D \end{matrix}\!\!>\!C{=}CH_2 + CH_3OMgBr \qquad (14)$$

This labeling experiment, however, does not reveal how the allyl group is reductively cleaved. Such information is obtained from the reduction of the deuterium-labeled allyl ether in Table 6, which is summarized as:

$$CH_3OCHCH{=}CH_2 + n\text{-}C_{10}H_{21}MgBr \xrightarrow[THF]{[Fe]}$$

$$[HCHCH{=}CH_2 + \begin{matrix} D \\ D \end{matrix}\!\!>\!C{=}CHCH_3] + C_{10}H_{20} + CH_3OMgBr \qquad (15)$$

The same results are obtained in the iron-catalyzed reduction of 3-methoxypropyl bromide using the substrate with deuterium labeling at each end, viz., $CH_3OCD_2CH_2CH_2Br$ and $CH_3OCH_2CH_2CD_2Br$. Both isomers gave essentially the

ABLE 6

ERMINAL DEUTERIUM LABELING OF ALLYL METHYL ETHER AND 3-METHOXYPROPYL ROMIDE [a]

ubstrate	Iron(III)	$D_2C{=}CHCH_3$ (%) [b]	$H_2C{=}CHCD_2H$ (%) [b]
$H_2C{=}C(D)COCH_3$ (D)	$Fe(DBM)_3$	52	48
	$FeCl_3$(THF)	55	45
$BrCH_2CH_2C(D)(D)COCH_3$	$Fe(DBM)_3$	52	48 [c, d]
	$FeCl_3$(THF)	56	44 [c, d]
$BrC(D)(D)CH_2CH_2OCH_3$	$Fe(DBM)_3$	40	60 [c, e]
	$FeCl_3$(THF)	44	56 [c, e]

Reactions carried out at 25°C using 5 ml of THF containing 9×10^{-4} mol n-$C_{10}H_{21}MgBr$ and 4×10^{-4} ubstrate. A solution of iron(III) added incrementally over 5 min to total 10% of the substrate. [b] Mol ercent determined directly by ^2H NMR, ±10%. [c] 2-deuteriopropylene (≤3%) also detected. [d] Unrearanged $CH_3OCD_2CH_2CH_3$ formed. [e] Unrearranged $CH_3OCH_2CH_2CD_2H$ formed.

ame equimolar mixture of propylene-d_2 shown in eq. 15. Furthermore, all the leuterium atoms retain their geminal relationship in the propylene product hown below.

$$CH_3OCH_2CH_2C(D)(D)Br \xrightarrow[RMgBr]{[Fe]} [CH_3CH{=}C(D)(D) + CH_2{=}CHC(D)H] \xrightarrow[RMgBr]{[Fe]} CH_3OC(D)(D)CH_2CH_2Br \quad (16)$$

TABLE 7

SOLVENTS EFFECTS ON ALLYL EQUILIBRATION [a]

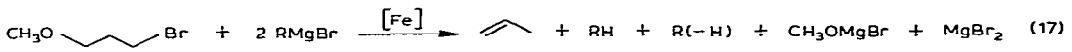
Substrate	Solvent	Iron(III)	Propylene (10^4 mol)	$D_2C{=}CHCH_3$ (%) [b]	$H_2C{=}CHCD_2H$ (%) [b]
$H_2C{=}C(D)COCH_3$ (D)	C_6H_6	$Fe(DBM)_3$	2.1	68	32
	n-Bu_2O	$Fe(DBM)_3$	2.6	68	32
$BrC(D)(D)CH_2CH_2OCH_3$	n-C_6H_{14} [c]	$Fe(DBM)_3$	0.2	27	73
	C_6H_6	$Fe(DBM)_3$	1.8	25	75
	n-Bu_2O	$Fe(DBM)_3$	1.4	29	71
	n-Bu_2O	$FeCl_3$(THF)	3.4	30	70
	$(MeOCH_2)_2$	$Fe(DBM)_3$	2.1	36	64
$BrCH_2CH_2C(D)(D)COCH_3$	n-Bu_2O	$FeCl_3$(THF)	1.2	70	30
	$(MeOCH_2)_2$	$Fe(DBM)_3$	2.4	57	43

[a] Reactions carried out at 25°C in 5 ml solvent with 9×10^{-4} mol n-$C_{10}H_{21}MgBr$ and 4×10^{-4} mol substrate. Iron(III) solution (total of 10%) added incrementally over 5 min. [b] Determined directly by ^2H NMR, ±10%. 2-Deuteriopropylene (≤3%) also detected. Deuterium label in methyl ether unrearranged. [c] Heterogeneous.

These experiments show that the allyl methyl ether is converted to a symmetrical allyl intermediate during the iron-catalyzed reduction in eq. 14. The same is true in the catalytic reaction starting with 3-methoxypropyl bromide in eq. 16. However, complete equilibration of the allyl moiety is not a general phenomenon, since the variation of the solvent from THF to 1,2-dimethoxyethane, di-n-butyl ether and benzene or hexane leads to an increasing imbalance between the pair of unsymmetrically labeled propylenes in eq. 16, as shown in Table 7.

Discussion

The fascinating reduction of 3-methoxypropyl bromide to propylene by Grignard reagents is efficienctly catalyzed by iron complexes. Despite the myriad side products which accompany the formation of propylene, the essential stoichiometry is given by eq. 17,

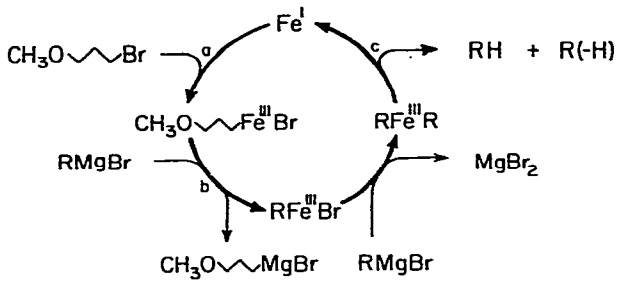


where R = C_2H_5, n-C_4H_9, n-$C_{10}H_{21}$, etc. Deuterium labeling studies have helped in unequivocally establishing the presence of two important intermediates, viz., 3-methoxypropylmagnesium (bromide) and allyl methyl ether. Consequently, the reduction of 3-methoxypropyl bromide can be formulated as three discrete processes, involving (i) its conversion to 3-methoxypropylmagnesium in eq. 8, which (ii) undergoes β-elimination to allyl methyl ether in eq. 12, followed by (iii) reductive cleavage to propylene in eq. 14. The sequence of changes in (i), (ii), and (iii) represents a series of oxidation-reduction processes formally involving 2*e* reduction, 2*e* oxidation, 2*e* reduction, respectively, for an overall 2*e* reduction. The latter is provided by the concomitant 2*e* oxidation of the Grignard reagent. Thus the role of the iron catalyst is to facilitate each of these redox changes.

I. Mechanism of the iron catalysis

We draw now on the previous studies [8,9] of the Kharasch reaction to provide a mechanistic basis for the iron catalysis. According to Scheme 1 (see Introduction), the iron catalyst mediates each of the redox changes by reactions which are well documented in organometallic chemistry, viz., oxidative addition, β-elimination, ligand substitution, and reductive elimination [13]. As applied to the reduction of 3-methoxypropyl bromide to propylene, two catalytic cycles must be constructed, which correspond to the two stages of the reaction described by Fig. 2. Scheme 2 represents the first stage, in which 3-methoxypropyl bromide is reduced to the magnesium derivative.

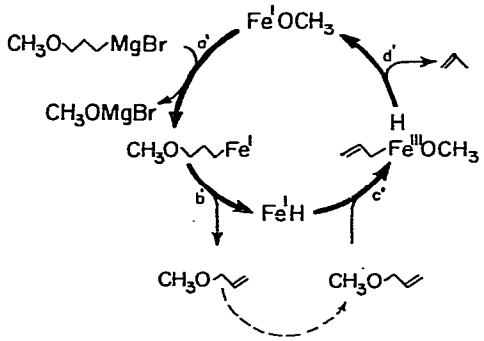
Step a′ corresponds to the oxidative addition in Scheme 1. Step b′ is simply a metathetical exchange, the equilibrium position of which is determined by the relative stabilities of RMgBr and $CH_3OCH_2CH_2CH_2MgBr$ (see the discussion of eq. 10) [14]. The reductive elimination in step c represents the disproportionation of alkyl ligands. The specific transfer of the β-deuterium label from one alkyl group to another in eq. 9 is in accord with previous studies of such reductive disproportionation processes [15]. The overall process in Scheme 2



SCHEME 2

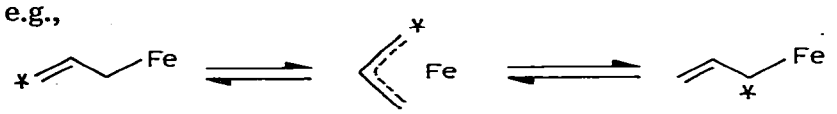
represents the stoichiometry in eq. 8.

Scheme 3 represents the catalytic cycle for the second stage, in which 3-methoxypropylmagnesium bromide is converted to propylene via allyl methyl ether.



SCHEME 3

Methoxypropylmagnesium enters the second catalytic cycle in step a′ via an unexceptional metathetical exchange. The resulting β-elimination of the methoxypropyl ligand in step b′ accords with the transfer of the deuterium label reported in eq. 12, and is tantamount to eq. 13a. The concomitant formation of a hydridoiron species has ample precedent [16]. The oxidative addition of allyl methyl ether in step c′ is related to that of a variety of allylic derivatives with reduced metal species [17]. Furthermore, the complete scrambling of the deuterium label at the termini of the allyl group is readily accommodated by the facile σ—π rearrangement, which is a characteristic of this ligand [18], e.g.,



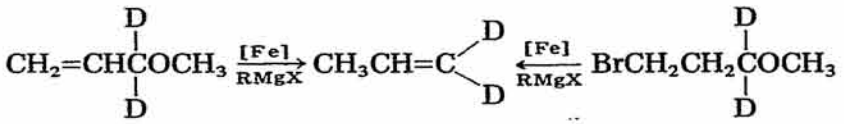
(18)

Finally the reductive elimination of propylene in step d′ accounts for the specific intermolecular transfer of deuterium in the labeling experiments described in eqs. 12 and 14. Reductive elimination of alkylmetal hydrides is known to occur readily [19]. The overall process in Scheme 3 corresponds to the stoichiometry in eq. 6 or 11. Finally, Schemes 2 and 3 together represent the overall stoichiometry in eq. 17.

II. Some fine points of the mechanism

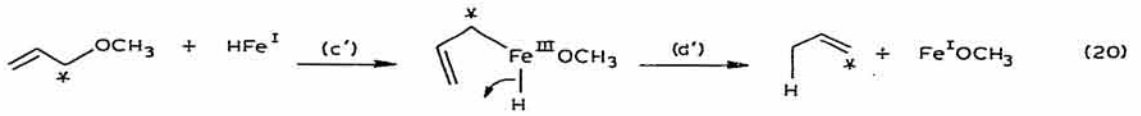
The dashed arrow in Scheme 3 represents the liberation and reincorporation of allyl methyl ether into the catalytic cycle. On the other hand, if the allyl ether remains π-bonded to iron, it must be readily replaced by any added (i.e., external) allyl methyl ether, as demonstrated by the deuterium labeling in eq. 12.

The oxidative addition of allyl methyl ether in step c′ of Scheme 3 is apparently not a straightforward process, since the solvent studies reported in Table 7 indicate that hydrogen transfer to allyl methyl ether preferentially occurs at the vinyl terminus, particularly in noncoordinating solvents such as benzene, i.e,,



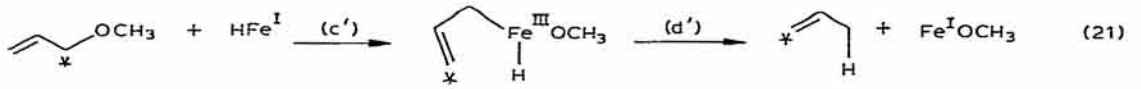
(19)

Such regiochemistry can obtain in either of two ways: (a) direct oxidative addition in step c′ followed by a reductive elimination in step d′ at the remote center, i.e.,



(20)

or the reverse:



(21)

We hope that further studies of the oxidative addition will resolve this ambiguity.

Free alkyl radicals per se are not important intermediates in the catalytic reduction of 3-methoxypropyl bromide. Thus, side products derived from alkyl coupling of either the organic halide, the Grignard component, or both, never exceed a few percent. (Alkyl groups with no available β-hydrogens are the exception [20].) However, there is CIDNP evidence which suggests that oxidative addition in step a of Scheme 1 is a two-step process involving a caged radical pair [21]. Although diffusive separation could lead to some free 3-methoxypropyl radicals, the 1,2-hydrogen shift as originally proposed cannot pertain to propylene formation, since deuterium labeling in eq. 12 has conclusively demonstrated it to be an intermolecular process. Methyl propyl ether, which is the principal byproduct of the reduction, may derive in part from such radicals by attack on the solvent.

A variety of evidence including stoichiometry, electron spin resonance spectroscopy, and quenching studies suggests that iron(III) complexes are easily reduced to highly labile hydridoiron(I) species by Grignard reagents, especially those containing available β-hydrogens [22]. However, the catalytic activity of this reduced iron is dependent on the presence of excess Grignard reagent, as well as the time elapsed between its preparation and its subsequent use. Thus, it is not easily proved which species actually initiates the catalytic

process. For example, a stable hydridoiron complex of the stoichiometry $FeH_6Mg_4Br_{3.5}Cl_{0.5}(THF)_8$ has been isolated from the reaction of ferric chloride with excess dihydrogen and phenylmagnesium bromide [23], which is somewhat reminiscent of the Kharasch reaction. A subsequent X-ray crystallographic investigation showed it to consist of molecular units of octahedral FeH_6^{4-} covalently bound to four $MgX(THF)_2$ units, where X = Br or Cl [24]. It is unlikely, however, that this iron hydride is directly involved in the catalytic cycle, since it is known that the catalytic species is rapidly deactivated in situ, simply on ageing for even 5 minutes [8]. For this reason, the optimum conditions for catalyst longevity require the presence of organic halide for the reoxidation of the deactivated species. The absence of a definitive identification of the catalytically active species in step a of Scheme 1 fortunately does not affect the principal conclusions of this study.

III. Formation of cyclopropane

The iron-catalyzed reduction of 3-substituted propyl bromides with Grignard reagents can also lead to cyclopropane as well as propylene. The results in Table 1 show that cyclopropane formation is dominant with 3-bromopropyl bromide, less so with 3-chloropropyl bromide, and minor with 3-phenoxypropyl bromide [25]. The catalytic cycles similar to those in Schemes 2 and 3 readily accommodate the formation of cyclopropane as a competitive process in the decomposition of the organoiron intermediates, i.e.,

(22)

Such a γ-elimination has been established in a series of organochromium deriactives, and it is highly dependent on leaving-group properties of the γ-substituent [26]. Accordingly, the formation of cyclopropane and propylene in eqs. 3 and 4 represents competitive processes in the reductions of various 3-substituted propyl bromides in Table 1. The relative amounts of cyclopropane and propylene thus relate to the facility of the two modes of decomposition of the organoiron intermediate in eq. 22 and in step b′ of Scheme 3, respectively.

Conclusion

The principal features of the mechanism of iron catalysis in Schemes 2 and 3 are the extensive shuttling among various Fe^{III} and Fe^{I} species, which mediate the redox changes in the formation and decomposition of the prime intermediates — 3-methoxypropylmagnesium and allyl methyl ether. The remarkably clean separation of the two stages in the reaction (as observed in Fig. 2 and described by Schemes 2 and 3) is largely responsible for the relatively high yields of propylene obtainable in this complex catalytic process. Indeed, the extent of crossover between these catalytic cycles is determined by ligand substitution, and it leads to the byproducts usually found in this system. Schemes 2 and 3 portray the types of organometallic reactions involved in the Kharasch reduction. The catalytic cycles are not intended to delineate the actual sequence of all the steps, which is difficult if not impossible to establish rigorously in any catalytic process [27].

Experimental section

Materials

Magnesium was kindly supplied by Dow Chemical Co. as triply sublimed metal. Tetrahydrofuran was provided in generous quantity by E.I. DuPont Co., and repurified by first treating it with potassium benzophenone and then transferring it from the dark blue solution in vacuo to a flame-dried Schlenk flask and stored under argon. Benzene and n-hexane were distilled under argon from Na/K alloy [28]. Di-n-butyl ether was refluxed over CaH_2, distilled from it, and redistilled from Na/K alloy. Dimethoxyethane was initially dried over CaH_2, stirred with Na/K alloy at 0°C until the blue solution persisted, and then vacuum transferred to a flame-dried Schlenk flask and stored under argon. The alkyl halides were obtained as described previously [8].

Grignard reagents ($\leqslant 0.2\ M$) were prepared under argon from the appropriate alkyl halide and magnesium in THF, and stirred for at least 4 h at room temperature. This solution was discarded, and the preparation repeated. An aliquot of the resulting colorless solution was withdrawn under argon pressure with a hypodermic syringe, and titrated with 2-butanol and xylene using 1,10-phenanthroline as the indicator [29]. 3-Bromopropyl phenyl ether (Eastman) was purified by fractional distillation at reduced pressure, b.p.$_{10}$ 117—117.5°C. 3-Bromopropanol was synthesized according to the method of Bogert and Slocum [30] from 76 g (1 mol) 1,3-propanediol (Eastman). Yield 101 g (72%); b.p.$_3$ 48—53°C. 3-Bromopropyl methyl ether was prepared by converting 35 g (0.25 mol) 3-bromopropyl alcohol to the alkoxide with NaH, followed by the addition of 28 ml (0.3 mol) dimethyl sulfate. Yield 30 g (77%); b.p.$_{760}$ 131—132°C. Allyl methyl ether was obtained from allyl bromide (0.4 mol) and 0.5 mol $NaOCH_3$ in methanol in 80% yield (23 g); b.p.$_{760}$ 41—42°C. Methyl 3-methoxypropionate was prepared by adding 45 ml (0.5 mol) methyl acrylate (Matheson) to a solution of 0.11 mol $NaOCH_3$ in 300 ml methanol and refluxing for 24 h. Yield 32 g (54%); b.p. 149—152°C. NMR ($CDCl_3$) δ 3.67 (t, J = 6.4 Hz + S, 5 H); 3.29 (S, 3 H); 2.54 ppm (t, J = 6.4 Hz, 2 H). 2-Bromoethyl methyl ether was prepared from ethylene glycol monomethyl ether (Fisher Scientific) and PBr_3, b.p.$_{760}$ 110—111°C. 4-Bromobutyl, 5-bromopentyl, and 6-bromohexyl methyl ethers were prepared by treatment of 1 equiv. of the appropriate dibromide with 1 equiv. of $NaOCH_3$, followed by fractional distillation of the products. $Br(CH_2)_4OCH_3$: b.p.$_{15}$ 60—62°C; $Br(CH_2)_5OCH_3$: b.p.$_{760}$ 183—187°C; $Br(CH_2)_6OCH_3$: b.p.$_{19}$ 97—98°C. Ethyl-2-d_3 bromide, the deuterium content of which was $\geqslant$98.5% was described previously [31]. n-Decyl-2-d_2 bromide was prepared according to LaPerriere et al. [32], starting with 20 g (0.13 mol) decanal (Aldrich) and 100 g D_2O. Yield 15.8 g (0.072 mol); b.p.$_1$ 58—62°C. ^2H NMR analysis showed the product to be 90% deuteriated at the 2-position. 3-Bromopropyl-3-d_2 methyl ether was obtained from the reduction of 3.0 g (0.025 mol) methyl 3-methoxypropionate with 1.0 g (0.024 mol) $LiAlD_4$ (Bio Rad 99% D). Yield 1.82 g (0.020 mol); b.p.$_3$ 48—52°C. The alcohol was treated with 0.022 mol NaH and 3.81 g (0.02 mol) *p*-toluenesulfonyl chloride, and the isolated tosylate added to 5 g (0.05 mol) NaBr in DMF to afford 2.78 g (0.018 mol) 3-bromopropyl-3-d_2 methyl ether; b.p.$_{760}$ 131—132°C. 3-Bromopropyl-2-d_2 methyl ether was prepared from 5.9 g (0.05 mol)

methyl 3-methoxypropionate and 10 ml CH_3OD, in which 0.1 g Na was dissolved. The mixture was allowed to sit for 6 h [33]. After 3 exchanges, the ester was isolated (4.5 g), reduced with 1.5 g (0.04 mol) $LiAlH_4$ (Alfa), and converted to the bromide, as described above. Yield 4.37 g (0.028 mol); b.p.$_{760}$ 131—132°C. ^2H NMR analysis showed the product to be 85% D at the 2-position. 3-Bromopropyl-1-d_2 methyl ether was obtained from 4.0 g (0.024 mol) methyl 3-bromopropionate and a mixture of 1.0 g (0.024 mol) $LiAlD_4$ and 3.17 g (0.024 mol) fresh anhydrous $AlCl_3$ (Fisher Scientific), as described by Nystrom [34]. The alcohol (2.89 g; b.p.$_3$ 47—53°C) was converted to the ether with NaH and dimethyl sulfate. Yield 2.73 g (0.018 mol); b.p.$_{760}$ 130—132°C. Allyl-1-d_2 methyl ether was synthesized by the procedure of Bartlett and Tate [35] with 15 g (0.084 mol) anthracene (Eastman) and 23.5 ml (0.26 mol) methyl acrylate (Matheson) in 250 ml nitrobenzene to afford 14 g (0.053 mol) methyl 9,10-ethanoanthracene-11-carboxylate, m.p. 115—117°C. The ester (9.29 g, 0.035 mol) was reduced with 1.00 g (0.024 mol) $LiAlD_4$ (99% from Merck Sharp, and Dome) in THF to 8.2 g (0.034 mol) 9,10-ethanoanthracene-11-methanol-13-d_2 melting at 107—110°C. Treatment of the alcohol (8.2 g, 0.034 mol) with NaH (0.04 mol) and 3.3 ml (0.036 mol) dimethyl sulfate in THF gave 8.0 g (0.031 mol) 9,10-ethanoanthracene-11-methyl-13-d_2 methyl ether (m.p. 81—82°C) which was cracked at 340—360°C to yield the allyl-1-d_2 methyl ether. Yield 1.93 g (0.026 mol); b.p.$_{760}$ 42—43°C.

$Fe(DBM)_3$ was synthesized earlier [9] from $FeCl_3 \cdot 6\ H_2O$ (Mallinckrodt) and dibenzoylmethane (Aldrich). $FeCl_3 \cdot THF$ was prepared from 15 g (0.09 mol) anhydrous $FeCl_3$ (Fisher Scientific) and 100 ml anhydrous THF [36]. Yield 14.9 g (0.064 mol).

Iron-catalyzed reduction of 3-bromopropyl methyl ether. Standard procedure

A hypodermic syringe was initially rinsed with 1 ml n-BuMgBr and 9.0×10^{-4} mol of the solution was forced into it under argon pressure. This solution was added to the reaction flask and diluted to 5 ml. Ethane (3.0 ml) was added as an internal standard and the flask equilibrated at 0°C. The evolved butane was measured by gas chromatography using a 15′ × 1/8″ 20% dibutyltetrachlorophthalate (DBTCP) column. Upon the addition of the deep red solution of $Fe(DBM)_3$ (4×10^{-6} mol in 100 μl THF), it first turned green then deep blue [9,22]. 3-Bromopropyl methyl ether (4×10^{-4} mol) was added, and the blue solution immediately turned yellow. Additional 100 μl aliquots of $Fe(DBM)_3$ solution were added at 5 min intervals until the solution remained green (total of 8—10 aliquots or $\sim 4 \times 10^{-5}$ mol). Analysis of the gaseous products on the DBTCP column indicated the presence of $<0.02 \times 10^{-4}$ mol (0.5%) propane or cyclopropane; 2.90×10^{-4} mol (73%) propylene; 4.50×10^{-4} mol (113%) butane; 0.26×10^{-4} mol (7%) 1-butene; 3.01×10^{-4} mol (75%) *trans*-2-butene and 0.92×10^{-4} mol (23%) *cis*-2-butene. Analysis of the liquid phase using a 25′ × 1/8″ 15% FFAP column afforded: 0.85×10^{-4} mol (21%) methyl propyl ether, 0.05×10^{-4} mol (1%) heptyl methyl ether and 0.05×10^{-4} mol (2%) 1,6-dimethoxyhexane.

Iron-catalyzed decomposition of 3-methoxypropylmagnesium bromide

The Grignard reagent (4.0×10^{-4} mol) in THF was diluted at 5 ml, 3.0 ml

ethane added and the flask equilibrated at 0°C. $Fe(DBM)_3$ (4×10^{-4} mol in 100 μl THF) was injected at 5 min intervals until the solution turned red. GC analysis indicated the presence of 2.84×10^{-4} mol (71%) propylene but less than 0.02×10^{-4} mol (0.5%) propane and cyclopropane. The liquid phase contained 1.46×10^{-4} mol methyl propyl ether (of which 0.50×10^{-4} mol was present from the Grignard) and 0.27×10^{-4} mol (13%) 1,5-hexadiene. The hexadiene was absent if 5×10^{-4} mol n-BuMgBr was initially added.

Iron-catalyzed reduction of allyl methyl ether with n-BuMgBr

The reduction was carried out as described for 3-bromopropyl methyl ether. It produced $<0.02 \times 10^{-4}$ mol (0.5%) propane and cyclopropane; 2.50×10^{-4} mol (63%) propylene; 1.44×10^{-4} mol (36%) butane; 2.71×10^{-4} mol (68%) 1-butene; 0.36×10^{-4} mol (9%) *trans*-2-butene and 0.14×10^{-4} mol (4%) *cis*-2-butene. Analysis of the liquid phase yielded $<0.05 \times 10^{-4}$ mol (1%) methyl propyl ether; 0.32×10^{-4} mol (8%) heptene and 0.35×10^{-4} mol (18%) 1,5-hexadiene. A reaction run to only 10% conversion and quenched with CO_2, followed by methylation (see below) showed no ($<0.05 \times 10^{-4}$ mol, 1%) methyl-4-methoxybutyrate.

Iron-catalyzed reductions of 1,3-dibromopropane, 3-chloro-1-bromopropane, and 3-bromopropyl phenyl ether with n-BuMgBr

These reactions were carried out with 9.0×10^{-4} mol n-BuMgBr and 4.0×10^{-4} mol substrate in 10 ml THF at either room temperature or in an ice bath. The reductions were complete after the addition of 2—3% ($0.8—1.2 \times 10^{-5}$ mol) $Fe(DBM)_3$. 1,3-Dibromopropane with $Fe(DBM)_3$ at 22°C gave 0.50×10^{-4} mol (13%) propane; 0.28×10^{-4} mol (7%) propylene; 3.09×10^{-4} mol (78%) cyclopropane; 4.10×10^{-4} mol (103%) butane; 3.44×10^{-4} mol (86%) 1-butene; 0.26×10^{-4} mol (7%) *trans*-2-butene and 0.12×10^{-4} mol (3%) *cis*-2-butene. Less than 0.05×10^{-4} mol (1%) n-PrBr was found upon GC analysis of the liquid phase (15′ × 1/8″ 20% DEGS). Reduction of 3-chloro-1-bromopropane by $Fe(DBM)_3$ with n-BuMgBr at 23°C gave 0.07×10^{-4} mol (2%) propane; 0.24×10^{-4} mol (6%) propylene; 2.54×10^{-4} mol (59%) cyclopropane; 4.20×10^{-4} mol (105%) butane; 3.39×10^{-4} mol (85%) 1-butene; 0.35×10^{-4} mol (9%) *trans*-2-butene and 0.15×10^{-4} mol (4%) *cis*-2-butene. Propyl chloride, 0.94×10^{-4} mol (22%), was present in the liquid phase. Reduction of 3-bromopropyl phenyl ether at 23°C gave 0.03×10^{-4} mol (1%) propane; 0.82×10^{-4} mol (19%) propylene; 0.36×10^{-4} (9%) cyclopropane; 3.86×10^{-4} mol (97%) butane; 3.23×10^{-4} mol (81%) 1-butene; 0.31×10^{-4} mol (8%) *trans*-2-butene and 0.17×10^{-4} mol (4%) *cis*-2-butene. 2.36×10^{-4} mol (56%) phenyl propyl ether was detected upon the analysis of the liquid.

Stoichiometry of the reduction of $FeCl_3 \cdot THF$ with n-BuMgBr

n-BuMgBr ($4.0—12.0 \times 10^{-4}$ mol) was added to a series of flasks with sufficient anhydrous THF to bring the volume to 9.5 ml. Isobutane (2.0 ml) was added, the flasks equilibrated at 0°C for for 30 min, and analyzed for butane on the DBTCP column. A solution of $FeCl_3$ (0.5 ml containing 2.0×10^{-4} mol) in THF was added, the reactions stirred for 30 min, and reanalyzed for butane and butene. From 12×10^{-4} mol n-BuMgBr, there was found 2.19×10^{-4} mol

butane, 3.56×10^{-4} mol 1-butene, 0.52×10^{-4} mol *trans*-2-butene and 0.12×10^{-4} mol *cis*-2-butene. After acidification with 50 μl acetic acid, octane was analyzed on the DEGS column. The yield after subtraction of the octane present in the Grignard reagent was 0.44×10^{-4} mol.

Cleavage of hydridoiron species

$FeCl_3 \cdot THF$ (2.0×10^{-4} mol) was reduced with 10.0×10^{-4} mol n-decyl-2-d_2 magnesium bromide in 10 ml THF at 0°C. The solution was degassed by a freeze-pump-thaw cycle and then hydrolyzed with 0.5 ml of 10% H_2SO_4. The flask was again frozen in liquid N_2, the H_2 collected with a Töppler pump and quantitated volumetrically. Yield 2.1×10^{-4} mol. Mass spectral analysis on an Associated Electrical Industries Ltd. MS-9 spectrometer showed a 10 : 1 ratio of H_2 to HD. In a similar experiment, the cleavage with water yielded almost no H_2. However, when 10% H_2SO_4 was added, 1.8×10^{-4} mol H_2 was liberated but it contained only a trace (≤1%) HD. Reduction of a sample of $FeCl_3 \cdot THF$ with n-BuMgBr followed by cleavage with DCl/D_2O (prepared from PCl_3 and D_2O) yielded a mixture of H_2, HD, and D_2 in the ratio of 1 : 5 : 6.

Grignard exchange studies: Iron-catalyzed reduction of 3-bromopropyl methyl ether with n-BuMgBr

The Grignard reagent (9.0×10^{-4} mol) in 5 ml THF was added to a flask containing 2.5 ml ethane, and equilibrated at 0°C. $Fe(DBM)_3$ (1.2×10^{-5} mol in 300 μl THF) was added, and the butane and butene analyzed. 3-Bromopropyl methyl ether (4.0×10^{-4} mol) was added, and the mixture stirred for 30 min. Analysis: butane 2.9×10^{-4} mol, 1-butene 2.62×10^{-4} mol, *trans*-2-butene 0.15×10^{-4} mol, *cis*-2-butene 0.10×10^{-4} mol. An additional 2.5 ml ethane was added (propylene 0.69×10^{-4} mol). The flask was then flushed for 2 min with bone-dry CO_2, and stirred for 30 min under 5 psig CO_2. Analysis of the liquid phase on the FFAP column afforded: methyl propyl ether 0.92×10^{-4} mol; heptyl methyl ether 0.07×10^{-4} mol; 3-bromopropyl methyl ether 0.26×10^{-4} mol; 1,6-dimethoxyhexane 0.06×10^{-4} mol. H_2SO_4 (0.2 ml, 10%) was added, followed by sufficient diazomethane in ether to turn the mixture yellow. The procedure was repeated twice, and the methyl 4-methoxybutyrate analyzed on a FFAP column. Yield 1.71×10^{-4} mol. Exchange reaction between other Grignard reagents and organic halides were carried out in a similar manner.

Ethyl-2-d_3 magnesium bromide reduction of 3-bromopropyl methyl ether catalyzed by Fe(DBM)$_3$

Ethyl-2-d_3 magnesium bromide (9.0×10^{-4} mol) was placed in a flask with 3 ml methane. After checking for ethane and ethylene on a 4′ × 1/8″ Porapak Q column, 4×10^{-6} mol $Fe(DBM)_3$ in 100 μl THF was added followed by 46 μl (4.0×10^{-4} mol) 3-bromopropyl methyl ether. Two additional aliquots of 4×10^{-6} mol $Fe(DBM)_3$ were added and the gaseous products analyzed by GC: ethane 4.9×10^{-4} mol; ethylene 3.4×10^{-4} mol and propylene 1.5×10^{-4} mol. The flask was frozen in liquid N_2 and attached to a series of 3 U-shaped cold traps connected with vacuum stopcocks. The trap closest to the reaction flask was cooled to −78°C (dry ice/ethanol); the second to −131°C (pentane slush) and the third to −196°C (liquid N_2). The system was totally evacuated and the

liquid N_2 removed from the reaction flask. The contents were allowed to transfer under dynamic vacuum. When the flask was dry, the stopcocks were closed and the ethane, ethylene and propylene which had collected in the —196°C trap was distilled into an NMR tube containing 0.984×10^{-4} mol $CDCl_3$ and 1.89×10^{-4} mol $CHCl_3$ in 0.500 ml CCl_4. The sealed tubes were analyzed by ^1H and ^2H NMR spectroscopy (vide infra). Ethylene was shown to be d_2 both by NMR analysis: 2.4×10^{-4} mol H, 2.3×10^{-4} mol D, and by mass spectral analysis: *m/e* (%) 31 (33.9), 30 (100), 29 (74.8), 28 (76.6), 27 (63.2), 26 (28.8), 25 (7.6), 24 (6.0). Ethane was a mixture of 70% d_4/30% d_3 by NMR analysis: 2.3×10^{-4} mol H, 3.7×10^{-4} mol D, and by mass spectral analysis: *m/e* (%) 35 (0.9), 34 (21.4), 33 (22.0), 32 (24.1), 31 (98.3), 30 (100), 29 (38.9), 28 (34.4), 27.(21.8); d_4 ethane: 35 (0.6), 34 (27.9), 33 (13.2), 32 (20.5), 31 (100), 30 (66.3), 29 (27.3), 28 (27.7), 27 (17.2); d_3 ethane: 34 (0.7), 33 (23.1), 32 (11.9), 31 (21.2), 30 (100), 29 (31.6), 28 (23.7), 27 (18.0). The propylene yield was calculated to be 1.4×10^{-4} mol (35%) by NMR analysis compared to 1.5×10^{-4} mol (38%) by gas chromatographic analysis. ^2H NMR analysis showed 8% propylene-1-*d*, 1% propylene-2-*d*, and 2% propylene-3-*d*. The deuterium and proton chemical shifts for ethane, ethylene, and propylene are almost the same. Chemical shifts measured relative to $CHCl_3$ ($CDCl_3$) at δ 7.25 ppm, are reported for both proton (deuterium) as: ethane 0.83 (0.86), ethylene 5.34 (5.40), propylene 5.8 (5.8), 4.9 (5.0), 1.70 ppm (1.73).

The fraction in the —131°C trap which consisted of about 0.5 ml THF enriched in methyl propyl ether was transfered to a second NMR tube and sealed with a serum cap. $CDCl_3$ (8 μl, 0.01136 g) was weighed in, and the ^2H NMR spectrum showed 0.28×10^{-4} mol deuterium to be present at the 3-position of the methyl propyl ether. GC analysis of the sample (15′ × 1/8″ 20% DEGS column) indicated 0.38×10^{-4} mol methyl propyl ether or 73% methyl propyl-3-d_1 ether. Chemical shifts were shifted in THF as shown by the calibration of $CHCl_3$ against TMS in THF: δ 7.67 versus δ 7.25 ppm in $CDCl_3$. Methyl propyl-3-d_1 ether was observed at δ 0.74 ppm relative to $CDCl_3$ δ 7.67 ppm.

The THF in the —78°C trap was pumped out and 100 μl acetic acid in 1 ml THF was added. The methyl propyl ether was transfered to a NMR tube and sufficient THF added to bring its volume to 0.5 ml. The DMR spectrum showed 0.07×10^{-4} mol deuterium at the 3-position of methyl propyl ether, representing a 5% yield of methyl propyl-3-d_1 ether.

Deuterium magnetic resonance (DMR) spectra were obtained on a Varian HR 220 spectrometer in the pulsed fast-Fourier transform mode. Chemical shifts were established relative to internal $CDCl_3$ (δ 7.25 ppm in CCl_4; δ 7.67 ppm in THF). A 400 Hz window was used at a radio frequency of 33.771 MHz to give a 11.8 ppm window. The four-pole Butterworth filter was set at 500 Hz and the rf power at 20 dB. A 17 μs pulse width (~25°) and a 2.71 s pulse interval was used to avoid saturation of the samples. Spectra were integrated with a planimeter and the mols D at each position was determined by comparison to the peak area of the $CDCl_3$ calibrant.

Proton magnetic resonance (PMR) spectra of the gaseous samples were obtained on the Varian HR 220 spectrometer operating in the continuous wave mode. Chemical shifts were established relative to internal $CHCl_3$ (δ 7.25

ppm in CCl_4). A 2500 Hz sweep width was used, and a sweep time of 500 s with integration performed with a sweep time of 100 s. The rf power was set at 18 dB to avoid signal saturation. Deuterium distribution calculated from the PMR spectra agreed to within 10% that determined directly from the DMR spectra. This procedure assumes that there is no fractionation of labeled compounds, either during the separations or by their differential solubility in CCl_4.

Ethyl-2-d_3 magnesium bromide reduction of allyl methyl ether catalyzed by Fe(DBM)$_3$

This reaction was set up as described above for 3-bromopropyl methyl ether. Using 38 μl (4.0×10^{-4} mol) allyl methyl ether, the analysis of the products by GC showed 3.5×10^{-4} mol ethylene, 1.2×10^{-4} mol ethane, and 2.5×10^{-4} mol propylene. NMR analysis indicated the ethylene to be d_2 and the ethane to be a 65/35 mixture of d_4/d_3. The propylene consisted of 82% 3-*d*, 14% 1-*d*, and 4% 2-*d*.

Decomposition of 3-methoxypropyl-2-d_2 magnesium bromide catalyzed by Fe(DBM)$_3$ with and without added allyl methyl ether

3-Bromopropyl-2-d_2 methyl ether (85% *d*) was converted to the Grignard reagent with ultrapure magnesium in anhydrous THF. The solution (~0.08 *M*) was titrated as described above, and 4.0×10^{-4} mol was transfered to a reaction flask and diluted to 9 ml. Fe(DBM)$_3$ (4.0×10^{-5} mol in 1.0 ml THF) was added in 100 μl portions over 30 min, and the propylene collected, as described above. NMR analysis showed 1.8×10^{-4} mol (45%) propylene with 0.08 *d* on C(1), 0.84 *d* on C(2) and 0.66 *d* on C(3). This analysis corresponds to a mixture of 79% propylene-2,3-d_2 and 10% propylene-1,2-d_2 assuming that deuterium at either terminal carbon is associated with a deuterium at C(2). Quantitative analysis of the material in the —131°C trap showed 0.05×10^{-4} mol allyl-2-d_1 methyl ether (δ 5.71 ppm in THF). GC analysis on the 15′ × 1/8″ 20% DEGS column gave 0.09×10^{-4} mol allyl methyl ether. The two analyses are equivalent to within experimental error. Addition of allyl methyl ether resulted in a decrease in the deuterium content of the propylene. For example, with 20.0×10^{-4} mol of added allyl methyl ether, 0.53×10^{-4} mol propylene was found by NMR analysis showing C(1) with <0.02 deuterium, C(2) with 0.04 *d*, and C(3) with 0.53 *d*. This analysis corresponds to the deuterated propylene containing 8% 2,3-d_2 and 92% 3-d_1. DMR analysis of the —131°C fraction showed 0.47×10^{-4} mol of allyl-2-d_1 methyl ether. GC analysis set the total recovery of allyl methyl ether as 7.9×10^{-4} mol or 40%. Normalizing the allyl methyl ether yield affords 1.2×10^{-4} mol (30%) of allyl-2-d_1 methyl ether.

Reduction of allyl-1-d_2 methyl ether by n-decylmagnesium bromide catalyzed by Fe(DBM)$_3$ in THF

The reduction of 4.0×10^{-4} mol allyl-1-d_2 methyl ether by 9.0×10^{-4} mol n-decylmagnesium bromide was carried out in 5 ml THF at 25°C. Fe(DBM)$_3$ (4.0×10^{-5} mol) in an addition tube was added incrementally over 5 min, and the propylene collected. DMR and PMR analysis showed the presence of 1.2×10^{-4} mol propylene. The deuterium on C(1) and C(3) was equally distributed

(52% propylene-1-d_2 and 48% 3-d_2). Approximately 2 mol % deuterium was scrambled into C(2).

Reduction of 3-bromopropyl-3-d_2 methyl ether and 3-bromopropyl-1-d_2 methyl ether by n-decylmagnesium bromide catalyzed by Fe(DBM)$_3$

The reactions were carried out by the procedure used for allyl-1-d_2 methyl ether. Small amounts (0—3%) of deuterium were found scrambled into C(2) of propylene. However, the byproduct methyl propyl ether was unrearranged as shown by the DMR analysis of the products from 3-bromopropyl-3-d_2 methyl ether (δ 0.74 ppm) and from 3-bromopropyl-1-d_2 methyl ether (δ 3.24 ppm) in THF.

Solvent effects on the reduction of deuterium-labeled 3-bromopropyl methyl ethers and allyl methyl ether

n-Decylmagnesium bromide (9.0×10^{-4} mol) in THF was added to the flask, and the THF removed in vacuo. After filling the flask with argon, 5 ml of anhydrous solvent was added and the mixture stirred at 25°C to dissolve the Grignard reagent. A white solid (probably magnesium bromide) remained. A small portion (~10%) of the Fe(DBM)$_3$ (4×10^{-5} mol total) was added from the addition tube, and the substrate (4.0×10^{-4} mol) added. The remainder of the catalyst was added over 5 min, and the propylene collected and analyzed by DMR and PMR spectroscopy. Although Fe(DBM)$_3$ was not soluble in hexane, a faint blue color was discernible.

Acknowledgments

We thank P.O. Nubel for performing some of the Grignard exchange studies, W. Lau for the GC-MS analysis of ethane and ethylene and L. Phillips for the mass spectra of dihydrogen. We also gratefully acknowledge generous gifts of magnesium from the Dow Chemical Co. and tetrahydrofuran from the E.I. DuPont de Nemours and Co. Professor R. Bau kindly provided us with a preprint of ref. 24.

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