ELIMINATION AND CATALYTIC DECOMPOSITION OF DIALKYLMANGANESE SPECIES

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SUMMARY

Alkylmanganese species are generated *in situ* by metathesis of Grignard reagents with manganous chloride in THF. The stoichiometry and the rate of decomposition of a variety of dialkylmanganese species are examined. The decomposition is shown to proceed principally by α,β-elimination of an hydrido–manganese species. The alkene is hydrogenated in a subsequent step to alkane by an active catalyst derived from the decomposition of the hydrido–manganese. The decomposition is catalyzed in a remarkable way by reduced Fe, Co, Ni, Ag and Pd. Alkylmanganeses also reacts readily with alkyl halide to form alkane and alkene by two competing heterolytic and homolytic processes.

INTRODUCTION

Alkylmanganese compounds coordinated with carbon monoxide and other π-bonding ligands are well-known and their chemistry has been studied extensively[1]. On the other hand, simple dialkylmanganese complexes which contain no π-bonding ligands are virtually unknown due to their thermal lability. Dimethylmanganese and methylmanganese chloride represent the only alkyl derivatives which have been characterized[2]. The "ate" complexes of the type $(CH_3)_3MnLi$ and several analogous have also been prepared by metathesis of alkyllithium and manganous iodide[2]. These anionic manganese complexes are substantially more stable than their neutral analogues and have been employed in cross-coupling reactions with alkyl halides[3].

Labile alkylmanganese species are of especial interest as intermediates in organic reactions catalyzed by manganese complexes. In particular, the reaction between Grignard reagents and alkyl halides is catalyzed by manganous salts[4]. Other transition metal halides, especially those of iron, cobalt and nickel, are also effective catalysts in the Kharasch reaction, but the extreme instability of the organometallic intermediates precludes their study. Alkylmanganese species represent a convenient compromise as models and were chosen for the study of the modes of decomposition of organometals of this type*.

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* Ref. 5 and also manuscript to be published; we wish to thank Dr. Zeiss for a copy of the manuscript prior to publication.

RESULTS AND DISCUSSION

*Alkylmanganese species from Grignard reagents and manganous chloride*

One mole of methylmagnesium bromide reacted with one mole of manganous chloride at 25° in tetrahydrofuran (THF) to produce a white precipitate. Analysis of the solid, after washing with diethyl ether and vacuum drying, indicated the presence of methyl, manganese(II) and magnesium in a 1/1/1 molar ratio. When an additional mole of methylmagnesium bromide was added, the solid redissolved to produce a clear

$$CH_3MgBr + MnCl_2 \rightarrow CH_3MnCl + MgBrCl \qquad (1)^*$$
$$CH_3MnCl + CH_3MgBr \rightarrow (CH_3)_2Mn + MgBrCl \qquad (2)$$

pale yellow solution of dimethylmanganese. Excess Grignard reagent (three-fold) had no perceptible effect, and there was no evidence for the formation of the "ate" complex $(CH_3)_3MnMgCl$ under these conditions. We infer from these and other observations (*vide infra*) that dimethylmanganese was the primary species formed when two or more equivalents of Grignard reagent were mixed with manganous chloride in THF solution. Dimethylmanganese has been isolated[2], but the higher homologues, especially those containing β-hydrogens, are much more labile (Table 1). Therefore we did not attempt isolation; rather dialkylmanganese species** were prepared by metathesis, usually with excess Grignard reagent, and their decomposition studied *in situ*.

Decomposition of alkylmanganese species: Stoichiometry

Alkyl groups of low molecular weight were chosen for study to enable direct observation of the gaseous products as they were formed without recourse to prior hydrolysis. Analysis was facilitated by gas chromatography using the internal standard method. When a solution of ethylmagnesium bromide (6.5 mmoles) was added to a suspension of 1.1 mmoles of anhydrous manganous chloride in THF at 25° a pale yellow solution resulted immediately. After a short induction period, ethane, ethylene,

$$2 C_2H_5MgBr + MnCl_2 \rightarrow 2 [C_2H_6, C_2H_4] + Mn + 2 MgBrCl \qquad (3)^{***}$$
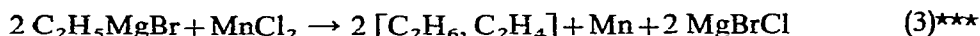
but no butane evolved from solution. Similar results were obtained with n-butyl, isopropyl and t-butyl Grignard reagents, but the methyl, neopentyl and benzyl analogues showed appreciably greater stability (Table 1). In every case the stoichiometric relationship among alkane (RH), alkene [R(-H)] and Mn^{II} charged could be expressed within 10% by a value of $Q(R)$ given in eqn. (4).

$$Q(R) = \frac{RH + R(-H)}{Mn^{II}} = 2.0 \qquad (4)$$

In the presence of styrene, the yield of alkane decreased but it was compensated by an increase in alkene yield so that $Q(R)$ remained equal to two. Significant amounts of ethylbenzene were found after hydrolysis.

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* Coordination around the metal is not included unless necessary for discussion.
** Hereafter referred to as alkylmanganese.
*** Equation not balanced.

TABLE 1

THE REACTION OF GRIGNARD REAGENTS WITH MANGANOUS CHLORIDE[a]

Run	RMgBr		Additive		Temp. (°C)	Period (min)	Products (mmole)		
	R	(mmole)	Compd.[b]	(mmole)			R(−H)	RH	EtPh[c]
1	Et[d]	6.48			25	60	0.76	1.41	
2	Et[e]	6.48	S	26.1	25	60	1.29	1.17	0.30
3	n-Pr	5.68			25	330	0.82	0.99	
4	n-Pr	5.68	S	26.1	25	330	1.66	0.31	0.88
5	n-Bu	5.00			25	420	1.09	0.93	
6	n-Bu	5.00	S	26.1	25	300	1.59	0.43	0.85
7	i-Pr[d]	5.52			2	120	1.31	0.92	
8	i-Pr	5.52	S	26.1	2	170	0.61	0.54[g]	0.03
9	i-Pr	5.52			25	60	1.24	0.77	
10	i-Pr	5.52	P	3.8	25	60	1.29	0.68	
11	i-Pr	5.52	S	26.1	25	60	1.14	0.86	0.17
12	t-Bu	3.60			2	240	1.57	0.45	
13	t-Bu	3.60			25	90	1.59	0.58	
14	t-Bu	3.60	P	3.8	25	210	1.53	0.63	
15	t-Bu	3.60	S	26.1	25	6000	0.20	0.23	− [f]
16	Me	5.70			25	7100		0.39[g]	
17	Me	5.70	S	26.1	55	360		2.01	0.02
18	Neopentyl	4.50			25	5000		< 0.1[g]	
19	PhCH$_2$	3.20			60	1440		< 0.1[g]	

[a] In 21 ml THF with 1.0 mmole MnCl$_2$. The yield of dimer R–R was negligibly small in all runs. [b] Additive, S = styrene, P = triphenylphosphine. [c] Determined after hydrolysis. [d] 1.1 mmole MnCl$_2$. [e] 1.2 mmole MnCl$_2$. [f] Styrene polymerized. [g] Partial decomposition.

The hydrogenation of the alkene occurred concomitantly with the decomposition of the alkylmanganese species. Thus, the decomposition of n-propylmanganese in the presence of added ethylene produced propylene together with ethane (Table 2). The yield of propane dropped but $Q(Pr)$ remained equal to two, independently of added alkene.

$$CH_3CH_2CH_2MgBr + CH_2{=}CH_2 \xrightarrow{\text{Mn}^{II}} CH_3CH{=}CH_2 + CH_3CH_3 + MgBr_2$$
$$(5)\text{*}$$
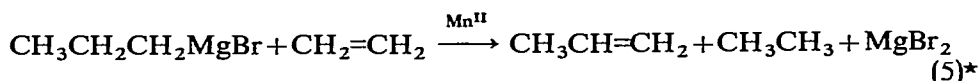
It is clear from these experiments that the decomposition of the alkylmanganese species occurred prior to and was independent of the subsequent hydrogenation of the alkene. Furthermore, since $Q(Pr)=2$ the material balance of hydrogen in the reaction is given simply by the difference in the yield between alkane and alkene. No doubt the extra hydrogen indicated by the last column of Table 2 was derived from dehydrogenation of the THF solvent (vide infra). The hydrogenation of alkene during decomposition of alkylmanganese was also promoted by molecular hydrogen.

Rates of decomposition of alkylmanganese

The decomposition of alkylmanganese can also be clearly delineated from the

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* Equation not balanced.

TABLE 2

DECOMPOSITION OF ALKYLMANGANESE IN THE PRESENCE OF ALKENE AND HYDROGEN[a]

Run	R_2Mn	Alkene R'(−H)	H_2 (mmole)	Period (min)	Products (mmole)			$D(H)$[g] (meq)
					R(−H)	RH	R'H[f]	
20	n-Pr	C_2H_4		40	2.10	0.15	1.29	0.63
21	n-Pr	C_2H_4	1.0	40	1.80	0.25	1.92	
22	n-Pr[b,c]	C_2H_4		60	1.79	0.34	1.13	0.81
23	i-Pr	C_2H_4		25	1.74	0.50	1.00	0.76
24	i-Pr	C_2H_4	1.0	25	1.68	0.50	1.67	
25	i-Pr[b,d]	C_2H_4		150	1.46	0.85	0.49	0.37
26	t-Bu	C_2H_4		240	1.36	0.66	0.86	1.02
27	t-Bu[b,e]	C_2H_4		60	1.48	0.57	0.77	0.63
28	Et	C_3H_6		60	0.75	1.26	0.06	0.39
29	Et	C_3H_6	2.0	60	0.00	2.40	0.60	
30	Et	$i-C_4H_8$	2.0	60	0.00	2.30	0.07	

[a] In 21 ml THF containing 1.1–1.2 mmole $MnCl_2$, 3.0 mmole RMgBr and 2.0 mmole alkene and H_2 at 25°. [b] Olefin added after decomposition commenced. [c] 35 min. [d] 20 min. [e] 40 min. [f] No. R'H formed after hydrolysis. [g] Hydrogen deficit = 2 R'H − [R(−H) − RH].

hydrogenation of alkene by following the rates of formation of alkene and alkane. The decomposition of n-propylmanganese illustrated in Fig. 1 shows that the yield of propylene went through a maximum after being formed initially and was then hydrogenated subsequently. The value of $Q(Pr)$ remained equal to 2 throughout. The high yield of propylene (>90%) could be preserved by adding styrene (1.2 M) prior to decomposition of the n-propylmanganese. Under these conditions styrene was preferentially hydrogenated to ethylbenzene (0.87 mole per mole Mn^{II}) and only small amounts of propane were formed. The decomposition of n-butylmanganese followed a similar pattern.

The hydrogenation of alkene occurring simultaneously with the decomposition of n-propylmanganese was also followed directly by the addition of ethylene. The rate of ethane formation was only slightly less than the rate of decomposition of n-propylmanganese as measured by the liberation of propylene shown in Fig. 2. The yield of ethane obtained in this manner (1.29 mmoles) was not appreciably higher than that obtained (1.13 mmoles) when ethylene was added 35 min later at a point corresponding to 75% decomposition. Hydrogenation of alkene, therefore, did not occur simultaneously with decomposition of the alkylmanganese, but was due to some (transient) species formed in the decomposition.

The decomposition of isopropylmanganese (Fig. 3) occurred more rapidly than n-propylmanganese. The yield of propylene did not go through a maximum nor was the yield as high in the presence of added ethylene (Table 2, run 23) or styrene (Fig. 3) as it was during the decomposition of n-propylmanganese. Furthermore, the yields of ethane or ethylbenzene (0.16 mole/mole Mn^{II}), under the latter conditions were also diminished relative to those obtained during decomposition of n-propylmanganese. Even more striking is the rapid fall-off in the activity of the species responsible for hydrogenation (compare runs 25 and 23).

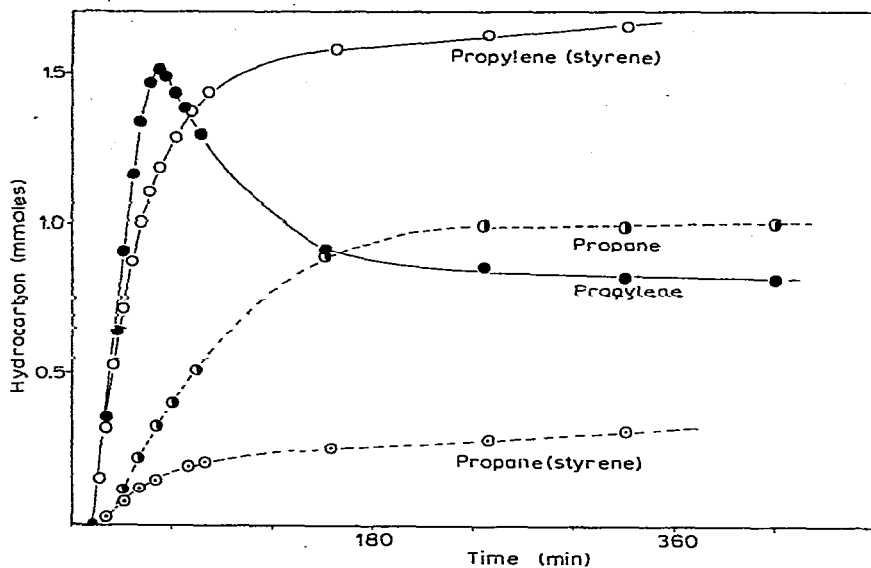The decomposition of ethylmanganese is illustrated in Fig. 4. Despite the

Fig. 1. The decomposition of di-n-propylmanganese in THF at 25° (0.048 M MnCl$_2$, 0.27 M n-PrMgBr), ◑propane, ●propylene. The effect of 1.24 M styrene, ⊙ propane, ○ propylene. Ethylbenzene (0.87 mmole) found after hydrolysis.
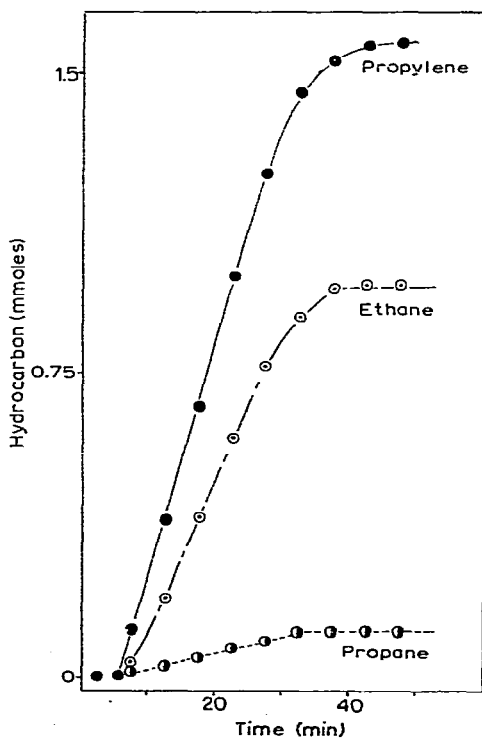

Fig. 2. The decomposition of di-n-propylmanganese in the presence of 0.1 M (2.0 mmoles) ethylene (0.052 M MnCl$_2$, 0.14 M n-PrMgBr) in THF at 25°, ● propylene, ⊙ ethane, ◉ propane.
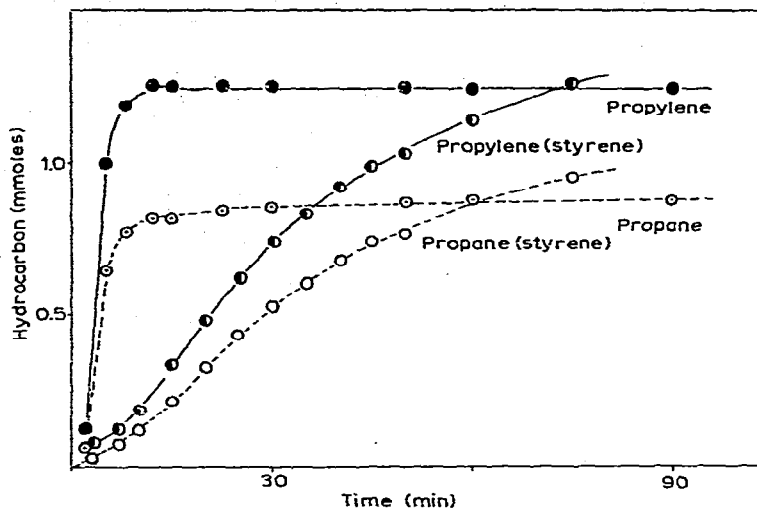
Fig. 3. The decomposition of diisopropylmanganese in THF at 25° (0.048 M MnCl$_2$, 0.26 M i-PrMgBr) ⊙ propane, ● propylene. The effect of 1.24 M styrene, ○ propane, ◑ propylene. Ethylbenzene (0.16 mmole) found.
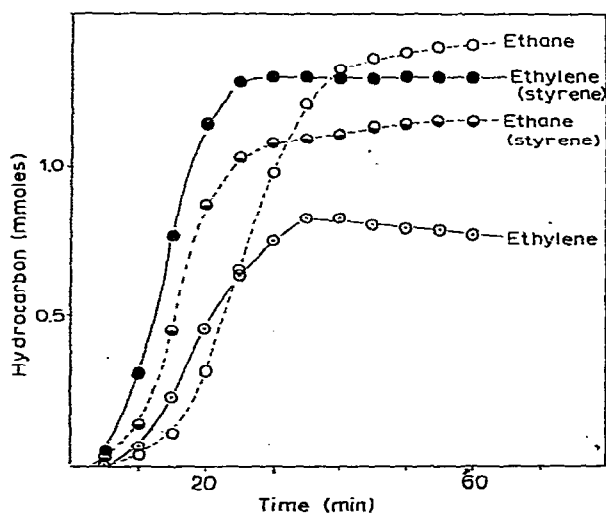

⌐Fig. 4. The decomposition of diethylmanganese in THF at 25° (0.048 M MnCl$_2$, 0.26 M EtMgBr) ○ ethane, ⊙ ethylene. The effect of 1.24 M styrene ◒ ethane, ● ethylene. Ethylbenzene (0.30 mmole) formed.

apparent difference, these results are analogous to those presented for n-propyl-manganese in Fig. 1, if one considers that ethylene is more readily hydrogenated than propylene (*vide infra*). Thus, the yield of ethylene did not build up as high as that of propylene and more ethane was produced than propane, even in the presence of styrene.

Except for a slight decrease in the induction period the rate of decomposition

of ethylmanganese prepared from 0.1 M ethylmagnesium bromide and 0.05 M manganous chloride was not affected by a four-fold excess of Grignard reagent. However, the ethylmanganese chloride formed by mixing equimolar amounts of these reactants showed an apparent rate which was three times slower than that of diethyl-manganese. These observations suggest strongly that the "ate" complex $[Et_3Mn]$-MgBr was not an important species in the presence of excess Grignard reagent. On the other hand, analogous "ate" complexes, $[Et_3Mn]Li$, are readily prepared from ethyllithium and do show enhanced stability relative to diethylmanganese[2a]. The latter prepared from ethyllithium behaved in the same manner as that derived from ethylmagnesium bromide in diethyl ether as well as in THF solution. In the presence of a four-fold excess of ethyllithium, the rate of decomposition of diethylmanganese was reduced by a factor greater than 10 due to "ate" formation. The rate of decomposition of diethylmanganese was also approximately 6 times faster in diethyl ether than in THF.
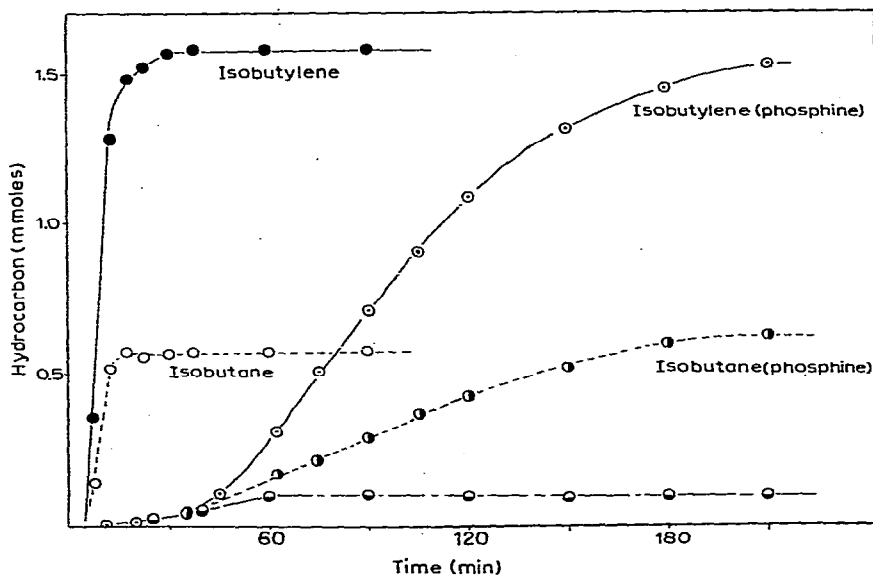

Fig. 5. The decomposition of di-tert-butylmanganese in THF at 25° (0.048 M MnCl$_2$, 0.17 M t-BuMgBr), O isobutane, ● isobutylene. The effect of 0.18 M triphenylphosphine, ◑ isobutane, ⊙ isobutylene and 1.24 M styrene, ◒ isobutane, isobutylene.
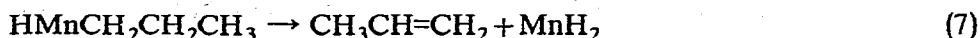
Mechanism of decomposition of alkylmanganese species

We attribute the predominant formation of alkene in the early part of the decomposition of alkylmanganese to an α,β-elimination leading to a hydridoman-

$$(CH_3CH_2CH_2)_2Mn \rightarrow CH_3CH=CH_2 + HMnCH_2CH_2CH_3 \qquad (6)$$
$$(I)$$
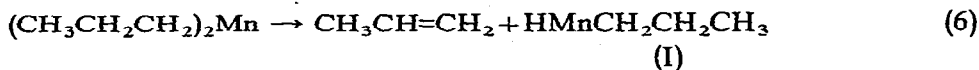
ganese species (I). Such an elimination is also consistent with the lability of isopropyl- and t-butylmanganese species (Table 1) and the much greater stability of the methyl,

neopentyl and benzyl analogues, having no β-hydrogens. The hydrido–manganese species (I) are metastable and apparently decompose via a sequence such as:

$$HMnCH_2CH_2CH_3 \rightarrow CH_3CH=CH_2 + MnH_2 \qquad (7)$$

$$MnH_2 \rightarrow Mn^0 + H_2 \qquad (8)$$

or:
$$2\ HMnCH_2CH_2CH_3 \rightarrow H_2 + 2\ MnCH_2CH_2CH_3\ \text{etc.} \qquad (9)$$

The formation of molecular hydrogen and hydrido–metal species (I) as intermediates formed during the decomposition of n-propylmanganese could be demonstrated. Thus, direct analysis of the reaction mixture at 40 min (*cf*. Fig. 1) indicated the formation of 1.37 mmoles propylene, 0.31 mmole propane and 0.33 mmole H_2. Quenching the reaction with D_2O at this point produced an additional 0.10 mmole HD. The same reaction in the presence of 1.2 *M* styrene after 80 min produced 1.52 mmoles propylene, 0.22 mmole propane and 0.05 mmole H_2. After quenching, an additional 0.77 mmole of ethylbenzene and 0.04 mmole HD were

$$H\ MnCH_2CH_2CH_3 + 2\ D_2O \rightarrow HD + CH_3CH_2CH_2D + Mn(OD)_2 \qquad (10)$$
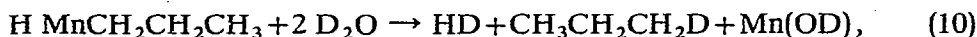
analyzed. Less H_2 and HD were detected during decomposition of isopropylmanganese. Thus after 10 min (*cf*. Fig. 3) 1.22 mmoles propylene, 0.81 mmole propane, and only 0.04 mmole of H_2 and 0.05 mmole of HD were found.

The formation of propane in the initial stage of the decomposition indicates that the hydride mechanism [eqn. (6)] may not be the only path by which decomposition of n-propylmanganese took place. Even in the presence of the readily hydrogenated styrene, propane was formed, albeit in reduced amounts. For the series of alkylmanganese species, the importance of alkane formed in the first phase of decomposition increased progressively as the alkyl group was varied from n-propyl < ethyl < tert-butyl < isopropyl (compare Figs. 1, 3–5). This sequence is reversed from the rates of subsequent hydrogenation which decreased in the manner: ethylene > propylene > isobutylene in the ratio 60/8/1. The relative amounts of alkene and alkane also remained more or less constant in this region. The decreased importance of the hydride path [eqn. (6)] for the higher homologues was also indicated by the lower yields of H_2 and HD found at intermediate stages of decomposition for these compounds.

It is conceivable that alkane arose in the initial stages of decomposition via the hydrido-manganese species (I) [eqn. (11)]. Similar processes have been proposed

$$R-Mn-R + HMnR \rightarrow RH + 2(RMn)\ \text{etc.} \qquad (11)$$
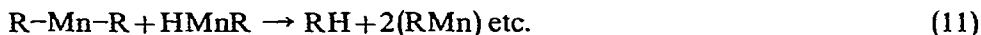
for the disproportionation of alkylcopper compounds[6]. However, such a mechanism does not readily allow for the higher yields of propane in the first phase of decomposition of isopropylmanganese compared to n-propylmanganese. We suggest that direct *intra*molecular or *inter*molecular disproportionation of alkyl groups represents the competing path for decomposition, *e.g.*:

$$(R,R)Mn \rightarrow RH + R(-H) + Mn^0 \qquad (12)^\star$$

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* The formulation (R,R)Mn indicates that two alkyl-manganese linkages may be uni- or bi-molecularly involved.

Similar mechanisms have been invoked for the decomposition of alkylcopper species[7]. The relative importance of hydride elimination [eqn. (6)] compared to direct disproportionation [eqn. (12)] in the decomposition of alkylmanganese may be related to the availability of β-hydrogens, the steric bulk of the alkyl groups as well as the concentration and the extent to which alkylmanganese species are aggregated in solution.

The decomposition of mixed alkylmanganese was examined by adding a Grignard reagent R'MgX to an alkylmanganese species R_2Mn. As shown in Table 3,
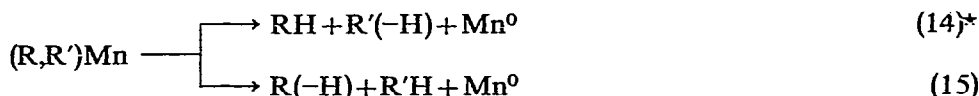
TABLE 3

REACTION OF ALKYLMANGANESE AND GRIGNARD REAGENT[a]

R_2Mn	R'MgBr	Period (min)	Products[b] (mmole)				$\Sigma R'$
			R(−H)	RH	R'(−H)	R'H	ΣR
Et	n-Pr	150	0.15	0.30	0.14	0.02	0.36
n-Pr	Et	150	0.12	0.02	0.15	0.28	3.07
Et	i-Pr	150	0.15	0.36	0.15	0.09	0.47
i-Pr	Et	30	0.28	0.18	0.38	0.67	2.28
Et	t-Bu	60[c]	0.25	0.60	0.39	0.12	0.60
t-Bu	Et	30	0.13	0.03	0.34	0.40	4.62

[a] R_2Mn prepared from 1.0 mmole $MnCl_2$ and 4.8 mmoles RMgBr at 2° and mixed with R'MgBr (4.8 mmoles) in 21 ml THF at 2°. The yield of dimers R−R was small in all runs. [b] Analyzed after partial decomposition indicated by period. [c] Reaction at 25°.

the reverse combination, RMgX and R'_2Mn, gave equivalent results indicating that rapid exchange of the alkyl groups between manganese and magnesium occurred prior to decomposition of the mixed alkylmanganese species. The decomposition was carried out at 2° and only to partial completion in order to minimize further

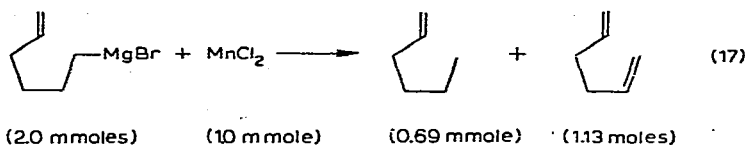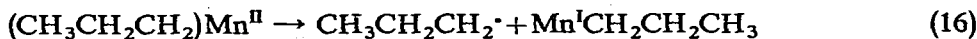$$RMnR + R'MgX \rightleftharpoons RMnR' + RMgX \qquad (13)$$

hydrogenation of the alkenes. Under these conditions the combined yield of alkanes approximately equaled that of alkenes, and a hydrogen deficit was not serious. If it is assumed that only disproportionation occurred in the initial stage of decomposition, four routes are possible: two involving self-disproportionation [(R,R)Mn or (R',R')Mn] and two involving cross-disproportionation. The latter is given by:

$$(R,R')Mn \quad \overbrace{}^{\longrightarrow RH + R'(−H) + Mn^0 \qquad (14)^*}_{\longrightarrow R(−H) + R'H + Mn^0 \qquad (15)}$$

The *difference* between the yields of RH and R(−H) [or alternatively R'(−H) and R'H] is a direct measure of the extent to which reaction (14) predominated over (15)[7]. The results presented in Table 3 show the consistency of the data and indicate that the cross-disproportionation between R=ethyl and R'=n-propyl, isopropyl or tert-butyl always favored RH (ethane) in preference to R'H (propane or isobutane).

* The formulation (R,R)Mn indicates that two alkyl–manganese linkages may be uni- or bi-molecularly involved.

Otherwise there was little quantitative differentiation among n-propyl, isopropyl or tert-butyl groups.

$$(CH_3CH_2CH_2)Mn^{II} \rightarrow CH_3CH_2CH_2 \cdot + Mn^{I}CH_2CH_2CH_3 \tag{16}$$

$$\qquad (17)$$

(2.0 mmoles)   (1.0 mmole)   (0.69 mmole)   (1.13 moles)

There is no evidence that alkylmanganese species decomposed by homolysis of the alkyl–manganese bond under these conditions. Thus 5-hexenylmanganese at 25° and 65° produced no methylcyclopentane*. The latter should have resulted from the ready cyclization of the 5-hexenyl radical[8]. The absence of homolytic decomposition is also consistent with the much greater stability of alkylmanganese species containing methyl, neopentyl and benzyl groups which have no β-hydrogens (Table 1 and Fig. 6).
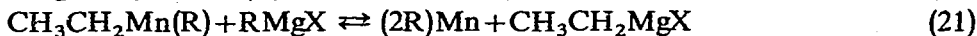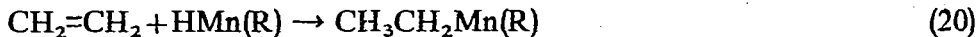

$$\qquad (18)$$
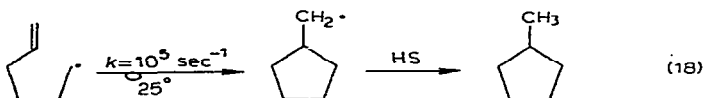
Hydrogenation of alkenes during decomposition of alkylmanganese

The quenching experiments with D_2O [eqn. (10)] indicate that hydrido–manganese species (I) can be intermediates in the decomposition of alkylmanganese. The amounts present, however, cannot account directly for the extent of hydrogenation observed. The hydrogenation of ethylene added after commencement of decomposition of n-propylmanganese must be attributed to H_2. We associate the manganese species responsible for this catalysis as those probably present in eqn. (7), (8) or (9). The
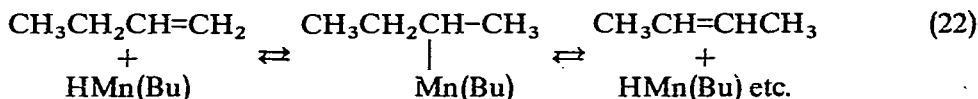

$$\qquad (19)$$
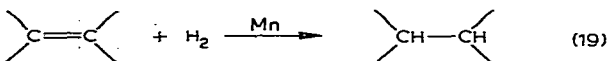
active life of the catalyst generated from the decomposition of n-propylmanganese was longer than that derived from isopropylmanganese (compare Table 2, runs 22 and 25). Differences in the rates of aggregation of the active (and possibly monomeric) manganese species prior to precipitation can account for slower rate of hydrogenation and is supported on the macroscopic scale by the finer sizes of particles obtained from isopropylmanganese.

Hydrido–manganese species (I), moreover, apparently do not participate directly in the hydrogenation of alkene. For example, if an addition such as (20) were involved, it would have been followed by rapid exchange with Grignard reagent

$$CH_2{=}CH_2 + HMn(R) \rightarrow CH_3CH_2Mn(R) \tag{20}$$

$$CH_3CH_2Mn(R) + RMgX \rightleftharpoons (2R)Mn + CH_3CH_2MgX \tag{21}$$

* A small amount of methylenecyclopentane (0.16 mmole), however was found.

[compare eqns. (21) and (13)]. However, the results in Table 2 show that *no* additional ethane was formed on subsequent hydrolysis of the reaction mixture. Furthermore, such hydrido–metal additions are usually reversible and contribute to the isomerization of alkenes[9]. We observed no isomerization of 1-butene from the decomposition of n-butylmanganes.

$$CH_3CH_2CH=CH_2 \qquad CH_3CH_2CH-CH_3 \qquad CH_3CH=CHCH_3 \qquad (22)$$
$$+ \qquad \rightleftarrows \qquad | \qquad \rightleftarrows \qquad +$$
$$HMn(Bu) \qquad\qquad Mn(Bu) \qquad HMn(Bu) \text{ etc.}$$

The decomposition of alkylmanganese cannot be adequately explained by eqns. (6)–(9), (12) and (19), since these reactions alone do not account for all the hydrogen required for hydrogenation (*cf.* Table 2). For example, after the decomposition of n-propylmanganese in the presence of ethylene, the material balance should have been:

$$C_3H_6-C_3H_8 = \tfrac{1}{2}C_2H_6$$
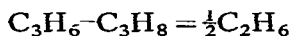
if hydrogen was not derived from any source other than the n-propyl moiety. The actual result was:

$$2 \, C_2H_6-(C_3H_6-C_3H_8) = 0.63 \text{ eq. hydrogen}$$
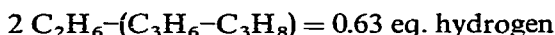
Therefore, the extra 0.63 eq. of hydrogen was derived from the solvent. An active form of manganese, possibly related to the species [eqn. (19)] involved in the hydrogenation of alkene, may participate in the dehydrogenation of THF, *e.g.*:

$$+ \text{ Mn } \rightleftarrows \qquad + \text{ MnH}_2 \text{ etc.} \qquad (23)$$
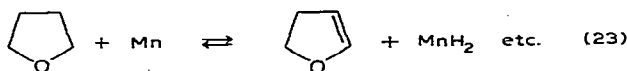
Catalyzed decomposition of alkylmanganese

The rates of decomposition of various alkylmanganese compounds are shown in Fig. 6, which indicates that the decomposition was accelerated, once started. This autocatalytic behavior could also be induced by small amounts of a variety of soluble metals (Table 4). The pronounced effect exerted by palladium and iron at $2°$ on the decomposition of n-propylmanganese is illustrated in Fig. 7. Cobalt, nickel and silver complexes showed similar catalytic activity. The relative amounts of propane and propylene formed in the presence of these metals varied in the same way as that described earlier (*e.g.*, Fig. 1), despite the greater than 50-fold spread in rates of decomposition. The value of $Q(Pr)$ remained equal to 2 throughout the series. Moreover, these catalysts were also remarkably effective in the decomposition of methylmanganese which has no β-hydrogens. Methane was still the predominant product (>90 mole %) and ethane was formed in less than 10% yield.

The behavior shown by these reduced metals in catalyzing the decomposition of alkylmanganese species is similar to that shown earlier for alkylcopper(I). The effect is difficult to explain fully at this juncture, but the fact that (*a*) the ratio of propylene to propane formed during the catalytic decomposition of n-propylmanganese is independent of the transition metal as well as its concentration, despite a marked acceleration of rate and (*b*) the catalytic decomposition of methylmanganese which has no available β-hydrogens occurs smoothly, suggest that these catalysts do not act
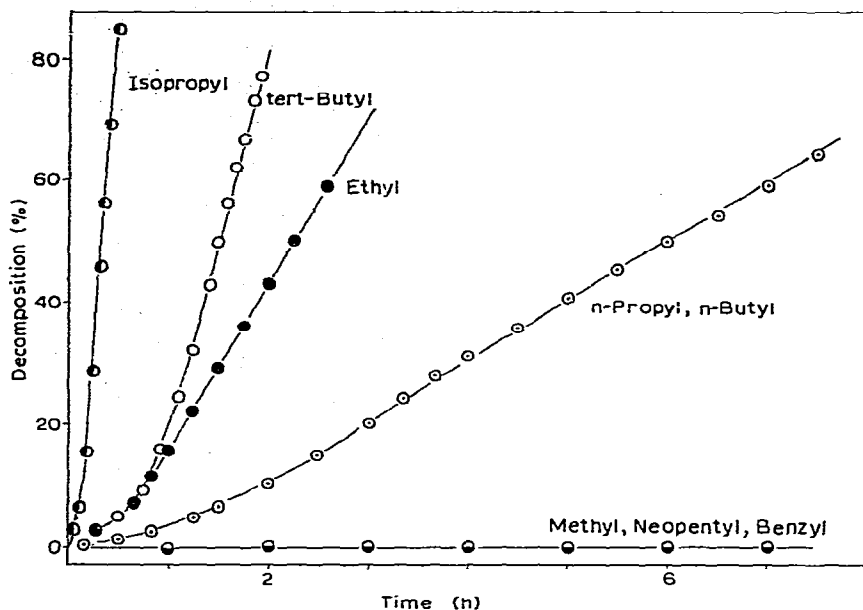
Fig. 6. Comparative rates of decomposition of dialkylmanganese in THF at $2°$ (0.048 M MnCl$_2$, 0.27 M Grignard reagent): ◑ isopropyl, ○ tert-butyl, ●ethyl, ⊙ n-propyl, n-butyl, ⊖ methyl, neopentyl, benzyl.

TABLE 4

CATALYZED DECOMPOSITION OF ALKYLMANGANESE[a]

RMgBr		Catalyst[c]		Temp.	$t^{\frac{1}{2}}$ (min)[d]	R(−H)[e]
R	(mmole)	Metal	(mole/1)	(°C)		RH
n-Pr	5.7			2.0	∼ 400	2.8
n-Pr	5.7[b]	Pd	4.4×10^{-4}	2.0	∼ 30	2.7
n-Pr	5.7[b]	Fe	1.2×10^{-4}	2.0	< 5	2.1
n-Pr	5.7[b]	Co	1.2×10^{-4}	2.0	∼ 5	2.1
n-Pr	5.7[b]	Ni	1.2×10^{-4}	2.0	∼ 10	2.1
n-Pr	3.8[b]	Ag	9.5×10^{-3}	2.0	∼ 35	3.2
Me	4.9			25	> 1.5×10^{4}	f
Me	4.9	Fe	1.2×10^{-4}	25	∼ 35	f
Me	4.9	Ni	1.2×10^{-4}	25	∼ 40	f

[a] In 21 ml THF containing 1.0 mmole MnCl$_2$. [b] 2.0 mmoles MnCl$_2$. [c] Catalyst prepared from supernatant solution after reaction of 1.0 mmole PdCl$_2$, FeCl$_3$, CoBr$_2$, NiCl$_2$ or AgNO$_3$ with 6.5 mmoles EtMgBr in 20 ml THF at 2°. Concentration determined by analysis of soluble metal. [d] Time required for half-reaction (apparent). [e] Propylene/propane at 50% decomposition. [f] The major product was CH$_4$ (>90%) the remainder (< 10%) was ethane in all runs.

directly by abstraction of hydrogen from the alkylmanganese species. One possibility is the activation of the alkylmanganese species by complex formation with the catalyst (including the change in the degree of association of alkylmanganese in solution) to form a more active mono or binuclear species. The latter are similar to the complexes formed between Grignard reagents and reduced cobalt species[10]. Mechanisms
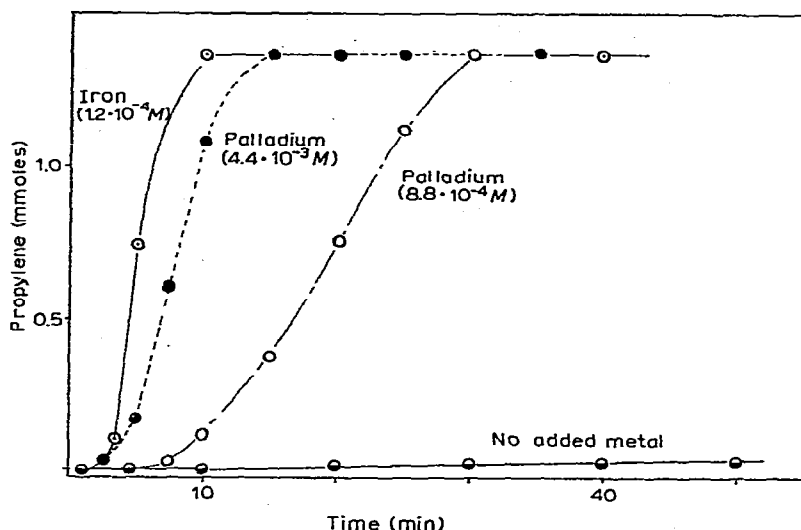
Fig. 7. Metal-catalyzed decomposition of di-n-propylmanganese in THF at 2° (0.048 M MnCl$_2$, 0.27 M n-PrMgBr) ⊙ 1.2×10^{-4} M iron, ● 4.4×10^{-3} M palladium, ○ 8.8×10^{-4} M palladium, ◒ no added metal.

involving hydrogen transfers to and from reduced metal species should also be considered.

The reaction of alkylmanganese with alkyl halide

Ethylmanganese reacted with ethyl bromide slowly at 25° to afford equimolar amounts of ethane and ethylene (Table 5). The reaction was unaffected by 0.4 M

$$(Et)_2Mn + 2\ EtBr \rightarrow 2\ C_2H_6 + 2\ C_2H_4 + MnBr_2 \tag{24}$$
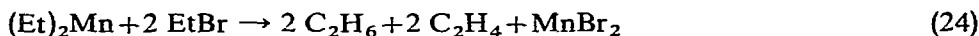
styrene and no ethylbenzene was found. The absence of butane under these conditions contrasts with the cross-coupling reaction recently reported for the "ate" complex[3].

$$R_3MnLi + R'X \rightarrow R-R' + R_2Mn + LiX \tag{25}$$
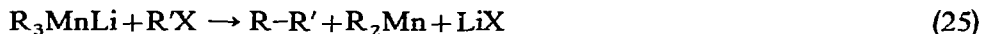
The reaction between ethylmanganese and n-propyl bromide generated ethane, ethylene, propane and propylene. However, significant amounts of ethyl bromide and additional propane (as a result of alkyl exhange) were found upon hydrolysis of the reaction mixture before completion. Ethyl exchange was progressively

$$R_2Mn + R'Br \rightleftharpoons RMnR' + RBr \tag{26}$$

less important with isopropyl and tert-butyl bromides. A mechanism involving alkyl radicals in the exchange process is unlikely in view of its insensitivity to the styrene scavenger.

The disproportionation between ethylmagnesium bromide and alkyl (R) bromides such as n-propyl, isopropyl or tert-butyl bromide does not appear to proceed via a single process. Thus, the relative amounts of products derived from the ethyl group relative to the alkyl group [ΣEt/ΣR in Table 5] varied with R and were

TABLE 5

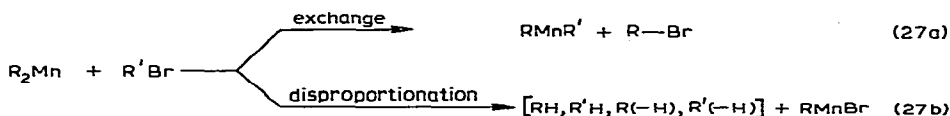REACTION OF ETHYLMANGANESE WITH ALKYL BROMIDES IN THE PRESENCE OF STYRENE[a]

EtMgBr (mmole)	RBr	Styrene (mmole)	Period (min)	Products (mmoles)				After hydrolysis (mmoles)[b]			ΣR[c]	ΣR(-H)+C₂H₄[d]
				C₂H₄	C₂H₆	R(-H)	RH	RH	EtBr	EtPh	ΣEt	ΣRH+C₂H₆
3.0	EtBr		1440	2.98	3.00							1.0
3.0	EtBr	8.3	1440	2.90	3.02					0.00		1.0
3.2	n-PrBr[e]		60	1.58	0.76	0.24	0.16	0.60	0.10		0.17	2.0
3.2	n-PrBr[e]	8.3	45	1.43	0.87	0.35	0.21	0.54	0.11	0.00	0.24	1.6
3.2	i-PrBr[e]		30	0.40	0.65	0.58	0.22	0.14	Trace		0.76	1.1
3.2	i-PrBr[e]	8.3	30	0.63	0.84	0.73	0.29	0.16	Trace	0.02	0.70	1.2
3.2	t-BuBr[e]		10	0.29	1.97	2.47	0.25	0.07	0.02		1.20	1.2
3.2	t-BuBr[e]	8.3	10	0.81	1.12	0.41	0.00	0.02	0.02	0.29	0.21	1.1

[a] In 21 ml THF with 2.0 mmoles MnCl₂ and 5.9 mmoles RBr at 25°. The reaction of MnCl₂ and EtMgBr carried out for 15 min at 2° prior to addition of RBr. [b] Analysis after hydrolysis. [c] ΣR/ΣEt = ratio of all products derived from R and Et. [d] Total alkene to alkane ratio. [e] Reaction incomplete within period indicated.
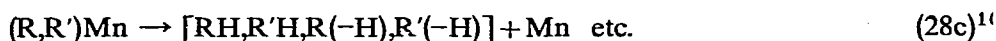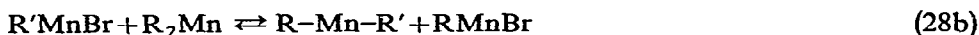
unaffected by styrene except for tert-butyl bromide. Ethylbenzene was not a significant product from reactions carried out with n-propyl or isopropyl bromide, but was formed during reaction of tert-butyl bromide.

These observations are consistent with at least two principal processes (27) and (28) proceeding simultaneously. Thus, alkyl exchange and disproportionation could result from the direct reaction between alkylmanganese and alkyl halide [eqns. (27a) and (27b)] and would be unaffected by styrene. Primary alkyl halides are

$$\text{R}_2\text{Mn} + \text{R}'\text{Br} \begin{cases} \xrightarrow{\text{exchange}} \text{RMnR}' + \text{R—Br} & (27a) \\ \xrightarrow{\text{disproportionation}} [\text{RH, R'H, R(—H), R'(—H)}] + \text{RMnBr} & (27b) \end{cases}$$

the most reactive, in analogy with a comparable reaction between alkyl halides and alkylcopper studied earlier[7].

The competing process involves a rate-determining oxidative addition [eqn. (28a)] of the alkyl halide to the active manganese species formed in the decomposition of alkylmanganese. The presence of active manganese also accounts for the hydro-

$$\text{Mn} + \text{R}'\text{Br} \rightarrow \text{R}'\text{MnBr} \tag{28a}$$

$$\text{R}'\text{MnBr} + \text{R}_2\text{Mn} \rightleftarrows \text{R—Mn—R}' + \text{RMnBr} \tag{28b}$$

$$(\text{R,R}')\text{Mn} \rightarrow [\text{RH, R'H, R(—H), R'(—H)}] + \text{Mn} \quad \text{etc.} \tag{28c}[11]$$

genation of styrene. tert-Butyl bromide is more reactive than n-propyl bromide in oxidative addition involving Mn (in analogy with other reduced metals, Ag, Cu and Fe)[7]. The decrease in products derived from the tert-butyl moiety in the presence of styrene (Table 5) is also consistent with the formation of tert-butyl radicals generated in oxidative addition[11].

EXPERIMENTAL

Materials

Diethylmagnesium was prepared by precipitation of magnesium halide from the Grignard reagent with dioxane followed by replacement of ether with THF. All other Grignard reagents were prepared at 5–25° in THF with a one and a half-fold excess of triply sublimed magnesium (Found: Ag, < 0.001; Co, < 0.005; Cr, < 0.005; Cu, < 0.001; Fe, < 0.0003; Mn, < 0.001; Mo, < 0.005; Ni, < 0.0005; Pb, < 0.003; Pd, < 0.001; Rh, < 0.005; Ti, < 0.005%.) and the solutions were colorless after filtration. The concentration of the Grignard reagent was determined both by acid titration and quantitative gas chromatographic analysis of the hydrocarbon released after hydrolysis. Tetrahydrofuran was obtained in small sealed containers from E. I. DuPont Co. and purified further by refluxing over lithium aluminum hydride for 2 days, fractionating under nitrogen and storing under helium. Diethyl ether was purified similarly. Styrene and all organic halides were commercial samples purified by distillation before use. Commercial anhydrous manganese chloride was dried *in vacuo* at 130° for 50 h. Anhydrous nickel chloride was prepared from the reaction of

its hexahydrate and thionyl chloride. Anhydrous palladium chloride, ferric chloride, cobalt bromide, lithium chloride, lithium nitrate and silver nitrate, nitrogen dioxide, ethyllithium (benzene solution, purchased from Lithium Corporation of America, Inc.) triphenylphosphine were all commercial grade and were used without further purification.

Analysis. Organic products were analyzed by gas chromatography using the internal standard method after careful calibration under reaction conditions. The low molecular hydrocarbons were analyzed directly by extracting a small sample of the gas from the reaction vessel. Internal standards were added prior to reaction in most cases.

Reactions

Reactions carried out under typical conditions are given below.

Reaction of manganous chloride and ethylmagnesium bromide in the presence of styrene. In a 250 ml round bottom flask equipped with a magnetic stirrer bar and a serum cap, 0.14 g (1.1 mmoles) of anhydrous manganous chloride was added under nitrogen. After the flask was sealed, the atmosphere was replaced with helium. To this flask, 14 ml of THF and 3.0 ml of styrene were introduced with hypodermic syringes, followed by 25 ml of methane (internal standard) after cooling in a dry-ice acetone bath. The flask was transferred to a constant temperature bath (25°), and 4.0 ml of a solution of ethylmagnesium bromide (6.5 mmoles) was added with agitation. A clear pale yellow solution resulted after a few minutes. The small sample of the gas phase was removed with a hypodermic syringe at 5 min intervals and analyzed by gas chromatography. After reaction was complete a black metallic precipitate of manganese was observed. After 60 min, 1.0 ml of dilute aqueous sulfuric acid and 0.50 ml of a THF solution toluene marker (1.0 *M*, 0.50 mmole) was added to the reaction mixture. The yield of ethylbenzene (0.30 mmole) was determined by gas chromatography.

Reaction of manganous chloride and lithium chloride with ethylmagnesium bromide. To the suspension of manganous chloride (1.0 mmole) in THF (17.75 ml) 2.0 ml of a solution of lithium chloride in THF (0.50 *M*, 1.0 mmole) was added. The mixture was agitated at room temperature for 60 min. Manganous chloride dissolved gradually and finally an almost colorless and clear solution was obtained (no absorption was observed between 350–700 nm). After the addition of 25 ml of methane, the flask was immersed in an ice-water bath (2.0°), and 1.25 ml of a THF solution of ethylmagnesium bromide (2.0 mmoles) was added with stirring. The color of the solution immediately changed to pale yellow. The rates of formations of ethylene and ethane were determined by gas chromatography. No ethyl chloride was detected, and the yield of butane was small.

Catalyzed decomposition of n-propylmanganese. To a suspension of manganous chloride (1.0 mmole) in THF (16 ml) 25 ml of isobutane (internal standard) and 4.0 ml of a THF solution of n-propylmagnesium bromide (5.67 mmoles) was added at 2.0°. After several minutes the reaction mixture was transformed to a pale yellow solution and 15 min later a solution of reduced palladium (1.0 ml, 1.85×10^{-2} mmoles) prepared separately (see below) was added to the n-propylmanganese solution at 2.0°. Propylene was evolved rapidly after a short (5 min) induction period. The rates of formation of propane and propylene were measured periodically. The solution of

the palladium catalyst was prepared as follows: To a suspension of palladous chloride (1.0 mmole) in 16 ml of THF, 4.0 ml of a solution of ethylmagnesium bromide (6.5 mmoles) was added at 2.0° with agitation. The reaction was completed within 10 min when no additional ethylene and ethane were generated. A brown solution together with a black precipitate (Pd) were formed. An aliquot of this supernatant solution was used as a catalyst for the decomposition of n-propylmanganese. The concentration of palladium in this solution was determined by the dimethylglyoxime method after filtration under nitrogen and oxidation with nitric acid. Reduced iron, cobalt and nickel complexes were also prepared in the same manner. The concentrations of these reduced metal complexes were determined: nickel (dimethylglyoxime), cobalt (pyridine thiocyanate), iron (potassium permanganate). The silver complex was prepared by the reaction of silver nitrate with diethylmagnesium and the concentration of silver was determined by titration with thiocyanate after oxidation with nitric acid.

Reaction of ethylmanganese and n-propyl bromide. To the suspension of manganous chloride (2.0 mmoles) in THF (19 ml) 25 ml of methane, 25 ml of isobutane and 1.85 ml of a solution of ethylmagnesium bromide (3.0 mmoles) was added at 2.0° in the usual manner. After 15 min, 0.54 ml (5.9 mmoles) of n-propyl bromide was added to the pale yellow suspension at 25°. There was no apparent change in color of the solution. Analysis of the gas after 60 min showed the presence of 1.58 mmoles of ethylene, 0.76 mmole of ethane, 0.24 mmole of propylene and 0.16 mmole of propane. After gas analysis, 1.0 ml of dilute sulfuric acid was added to the reaction mixture (hydrolysis), reanalysis indicated that 0.60 mmole of additional propane and 0.69 mmole of additional ethane were formed on hydrolysis. The yield of ethyl bromide was 0.10 mmole.

The reaction between methylmanganese (prepared from 1.0 mmole manganous chloride and 3.0 mmoles methylmagnesium bromide) and 1-bromopropene (13 mmoles 70% *cis* and 30% *trans*-isomers) was negligible after 5 h at 25°. After 40 h at 40°, 2-butene (67% *cis* and 33% *trans*) was obtained in 60% yield together with 40% methane. A similar reaction with ethylmagnesium bromide at 2° produced 45% each of ethane and ethylene but little (10%) 2-pentene in 1 h.

Reaction of ethylmanganese and n-propylmagnesium bromide. To the suspension of manganous chloride (1.0 mmole) in THF (15 ml), 25 ml of methane, 25 ml of isobutane and 3.0 ml of ethylmagnesium bromide (4.8 mmoles) solution were added at 2.0°. After 30 min, 3.0 ml of a solution of n-propylmagnesium bromide (4.8 mmoles) was added to the clear solution. The color of the solution did not change on addition of n-propylmagnesium bromide. The yields of gaseous products were determined by gas chromatography (Table 5).

Oxidation of alkylmanganese with oxygen, nitrogen dioxide and nitrate. The decomposition of methylmanganese proceeded to only 20% at 25° after 135 h, but in the presence of molecular oxygen the color of the solution changed immediately from pale yellow to red-brown and ethane evolved almost quantitatively (Table 6). The autoxidation of n-propylmanganese, on the other hand, produced propane, propylene, but little hexane. n-Propyl alcohol was also produced in low yields compared to that obtained from the autoxidation of n-propylmagnesium bromide under the same conditions[12]. Interestingly, the ratio of propylene to propane was 1.0 and remained invariant with the amount of oxygen added. The inefficient oxidative

dimerization of the n-propyl moiety during autoxidation of n-propylmanganese contrasts with the behavior of n-propylcopper under similar conditions[7].

Nitrogen dioxide and lithium nitrate were also capable of rapidly oxidizing alkylmanganese species (Table 6). The value of Q(Et) for lithium nitrate was high

TABLE 6

OXIDATION OF ALKYLMANGANESE WITH OXYGEN, NITROGEN DIOXIDE OR NITRATE[a]

RMgBr		Oxidant		Temp. (°C)	Period (min)	Products (mmole)				RH[c] (mmole)
R	(mmole)	Oxid.	(mmole)			R–H	RH	R–R	ROH[b]	
Me	5.7			25	8100		0.39	0.02		
Me	5.7	O₂	1.00	25	60		0.04	1.03	n.d.	1.36
n-Pr	5.0			2.0	780	1.05	0.60	0.00		
n-Pr	5.0	O₂	1.00	2.0	180	0.89	0.86	0.16	n.d.	1.32
n-Pr	2.0	O₂	1.00	2.0	60	0.48	0.55	0.14	0.68	0.00
n-Pr	2.0	O₂	0.60	2.0	60	9.53	0.54	0.09	0.52	0.20
n-Pr	2.0	O₂	0.20	2.0	60	0.29	0.27	0.03	0.14	1.24
n-Pr[d]	2.4	O₂	1.00	2.0	60	0.00	0.00	0.00	2.00	0.30
Me	1.9			25	7200		0.34	0.04		
Me	1.9	NO₂	1.0	25	1		0.35	0.20		
Me	5.7	NO₂	2.0	25	60		0.79	0.63		
Et	8.8			30	60	0.62	1.58	0.00		
Et	18.0	LiNO₃	0.95	30	360	2.63	4.28	0.04		

[a] In 21 ml THF with 1.0 mmole MnCl₂. Reaction of Grignard reagent with MnCl₂ carried out for 15 min prior to addition of oxidant. [b] Analysis after hydrolysis. [c] Additional alkane formed after hydrolysis. [d] In the absence of MnCl₂.

(7.0) indicating substantial recycling of the manganese species through several oxidation states similar to that observed earlier for silver[7]. In both cases the mixtures after reaction contained excess Grignard reagent and were homogeneous brown solutions in which the manganese species are as yet unidentified.

Oxidation of n-propylmanganese with molecular oxygen. To the suspension of manganous chloride (1.0 mmole) in THF (19.6 mmoles) 25 ml of isobutane and 1.4 ml of n-propylmagnesium bromide (2.0 mmoles) solution were added at 2.0°. After 15 min 25 ml of oxygen was added to the pale yellow solution. The color of the reaction mixture immediately turned to reddish brown and propylene and propane were evolved. The reaction was complete in 10 min (Table 6). More than 90% of oxygen was consumed in the reaction. After 60 min of agitation at 2.0°, 1.0 ml of dilute sulfuric acid was added to the reaction mixture (hydrolysis, and n-hexane and n-propyl alcohol were analyzed. Additional propane was not detected on hydrolysis. The oxidations of methylmanganese with oxygen and nitrogen dioxide and the oxidation of ethylmanganese with lithium nitrate in the presence of excess ethylmagnesium bromide were carried out in the same manner (Table 6).

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