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ALKYL-TRANSITION METAL COMPOUNDS
VI.* FRAGMENTATION AND ISOMERIZATION STUDIES

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SUMMARY

The final products from the interaction of stoichiometric ratios of n- and sec-alkylmagnesium halides with some first row transition metal salts (VCl_3, $CrCl_2$, $FeCl_3$, $CoCl_2$, $NiBr_2$ and $CrCl_3(THF)_3$) in tetrahydrofuran have now been shown to consist of unequal quantities of alkane and alkenes ($70/30 \pm 8$), some dimer and a metal based hydrogen transfer catalyst.

INTRODUCTION

The interaction of alkylmagnesium halides with first row transition metal complexes has been extensively investigated within recent years. From the results it is evident that, in the presence of certain ligands (*e.g.* CO, CN, pyridine, 2,2′-bipyridine, triaryl- and trialkyl-phosphines etc.) this reaction** can, in some instances, lead to stable, isolable σ-bonded alkyl-transition metal complexes[2-6].

On the other hand the interaction of alkylmagnesium halides with simple transition metal halides, in diethyl ether or tetrahydrofuran solutions, has only been investigated sporadically over the past hundred years. The overall results implied that there are differences in the reactions of methylmagnesium halides and other alkylmagnesium halides with first row transition metal halides. The former, and methyllithium, react with certain halides to give moderately stable σ-bonded methylmetal compounds [*e.g.* eqn. (1)[2,10], $n=1$ to 4; eqn. (2)[11-13], $n=1$ or 3; eqn. (3)[14,15], $n=1$ and 2].

$$n\,CH_3MgX + TiCl_4 \xrightarrow{Et_2O} (CH_3)_nTiCl_{4-n} \tag{1}$$

$$n\,CH_3MgCl + CrCl_3(THF)_3 \xrightarrow{THF} (CH_3)_nCrCl_{3-n}(THF)_x \tag{2}$$

$$n\,CH_3Li + MnCl_2 \xrightarrow{Et_2O} (CH_3)_nMnCl_{2-n} \tag{3}$$

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* For part V see ref. 1.

** σ-Bonded alkyl-transition metal complexes can also be prepared by a variety of other routes [*e.g.* the interaction of other alkylating agents (Et_2AlOEt) and metal acetylacetonates in the presence of 2,2′-bipyridine[7,8]; the two step oxidative reaction between chromous complexes and alkyl halides[9], etc.].

With higher alkylmagnesium halides it was generally accepted[16–21] that the initial reaction gave the unstable alkyltransition metal compound and this subsequently underwent homolytic (free-radical) fragmentation. On the basis of the relative amounts of alkane, alkene and dimeric hydrocarbon formed, the alkyl-transition metal compounds were divided into four classes[19–21] : eqn. (4) (Ti); eqn. (5) (Mn, Cr^{III}, Fe^{II}); eqn. (6) (Cu^{I}); eqn. (7) (V^{III}) (R_{+H}, R_{-H} and RR signify alkane, alkene and dimer respectively, and M, the metal).

$$R_nM \rightarrow [n\,R\cdot + M] \xrightarrow{\text{Solvent}} n\,R_{+H} + M^0\ (+\text{traces of}\ R_{-H}) \tag{4}$$

$$2\,R_nM \rightarrow [2n\,R\cdot + M] \xrightarrow{\text{Dispropn.}} n\,R_{+H} + n\,R_{-H} + M^0 \tag{5}$$

$$2\,R_nM \rightarrow [2n\,R\cdot + M] \xrightarrow{\text{Coupling}} n\,RR + M^0 \tag{6}$$

$$2\,R_nM \rightarrow [2n\,R\cdot + M] \longrightarrow \tfrac{1}{2}xn\,RR + \tfrac{1}{2}yn\,R_{+H} + \tfrac{1}{2}yn\,R_{-H} + M^0 \tag{7}$$

The "instability" of simple solvated alkyl-transition metal compounds was interpreted[20–22] in terms of homolytic (radical) fragmentation leading to alkane, alkene, dimeric hydrocarbon plus "colloidal" or "active" metal. No reference was ever made to the formation of metal hydrides, reported much earlier as a product from diethylzinc and ferrous chloride[23], or to the formation of isomeric alkenes.

It is only recently that studies with the alkyl-chromium[24] and related alkylcobalt[25] and -nickel[26] compounds have proved that in these systems, as in the "ethyl-iron system"[23] one of the fragmentation products was, in fact, the metal hydride. Subsequent investigations revealed that both the n- and sec-alkylchromium systems underwent fragmentation to give, consistently, unequal quantities of alkane and alkene (approximately 70/30), traces of dimer plus a chromium based isomerization and hydrogenation catalyst[27].

It was further possible to prove, using specifically deuterated alkylchromium systems, that the fragmentation involved at least four fundamental processes[27–29] *viz*:

(1). β-metal hydride elimination;

(2). α-metal hydride elimination;

(3). hydrogen transfer from solvent to one of the alkyl groups bonded to chromium;

(4). hydrogen transfer between the β-position of one alkyl group originally bonded to chromium to the α-position of another.

In the light of these observations it seemed pertinent to reinvestigate the fragmentation of other first row alkyltransition metal systems. The present paper describes preliminary results in this field.

RESULTS AND DISCUSSION

Fragmentation of alkyltransition metal systems

The interaction of stoichiometric ratios of (4-phenylbutyl)- and (3-phenyl-1-methylpropyl)magnesium bromides with VCl_3, $CrCl_2$, $MnCl_2$, $FeCl_3$, $CoCl_2$ and

$NiBr_2$ in tetrahydrofuran in the temperature range −70° to +20° has been studied. In the present work no attempt was made to prove unequivocally the formation of the solvated σ-bonded organometallic species, eqn. (8). Instead, emphasis was placed on identifying and evaluating the overall fragmentation products eqn. (9), and on

$$n\,\mathrm{RMgX}+\mathrm{MCl}_n \xrightarrow{\mathrm{THF}} \mathrm{R}_n\mathrm{M(THF)}_x \qquad (8)$$

screening these alkylmetal systems for catalytic activity in hydrogen transfer reactions.

$$n\,\mathrm{RMgX}+\mathrm{MCl}_n \xrightarrow[(2)\ \mathrm{H_2O}]{(1)-70^\circ\ \mathrm{to}\ +20^\circ/\mathrm{THF}} \text{products} \qquad (9)$$

In order to avoid possible side effects all the reactions were carried out in the *absence* of internal standards. In these experiments it was therefore not possible to check the overall material balance by direct gas chromatographic analysis (GLC). It was however possible to determine directly, by GLC, the identity and relative percentages of alkanes and alkenes present in the reaction mixture. Wherever possible the amount of dimeric material was estimated (GLC) separately. Control experiments with the alkylchromium(III) systems[27] in the presence of internal standards gave the same relative proportions of alkane, total alkenes and dimer. With the alkyliron(III) systems however substantial differences were found for the experiments in the presence of internal standards (see Experimental). In both the n- and sec-alkyliron systems appreciable quantities of dimer were formed, and although the relative percentage of alkane to total other monomeric products remained the same, the isomer distribution amongst the alkenes was different.

The results for the experiments, carried out in the absence of internal standards are given in Table 1. These show that, with the exception of the n-alkylmanganese system (expt. 7), in all the systems studied the overall products consist of some dimer and unequal quantities of alkane and alkene (approximately 70% alkane to 30% total alkene, ±8%). Dimer formation is at a maximum with the alkyliron systems.

One striking feature of the present results is the variation in the relative amounts of the isomeric alkenes produced by the different systems. Thus the sec-alkylmanganese system (ratio 2/1) produces considerable quantities of 1-alkene. This indicates that the organomanganese system is probably a poor isomerization catalyst (see later) and that the fragmentation is homolytic [(eqn.) 10][27].

$$\mathrm{(PhCH_2CH_2CHCH_3)_2Mn} \rightarrow \mathrm{PhCH_2CH_2CH_2CH_3}+\mathrm{PhCH_2CH_2CH{=}CH_2}+ \\ +\text{2-alkene and dimer (?)} \qquad (10)$$

The chromium(III) and chromium(II) systems are unique in forming preponderately the 2-alkenes and 3-alkenes respectively. The other metal systems form differing proportions of both 2- and 3-alkenes (and dimer).

The simplest explanation for the foregoing is that there are either differences in the respective fragmentation processes (*i.e.* homolysis, as against metal hydride elimination), or differences in the catalytic species produced by the various systems (*i.e.* different isomerization mechanisms).

Isomerization by alkyl-transition metal systems

In order to decide which of the observed products actually arise from the

TABLE 1

INTERACTION OF n- AND sec-ALKYLMAGNESIUM HALIDES WITH 1ST ROW TRANSITION METAL HALIDES; FINAL HYDROLYSIS PRODUCTS

Expt. no.[a]	Metal halide	Products					
		Alkane[b]	1-Alkene[b]	*trans*-2-Alkene[b]	*cis*-2-Alkene[b]	3-Alkene[b]	Dimer[c]
0 n[d]	None	99.2	0.4[g]				0.6
0 sec[d]	None	91.0	5.0	3.1	0.9	0.0	1.8
1 n	VCl_3	77.4	0.8	8.2	2.1	11.5	[e]
2 sec	VCl_3	77.8	1.6	11.9	4.2	4.4	[e]
3 n	$CrCl_3$	69.1	1.6	23.1	4.3	1.9	1.4
4 sec	$CrCl_3$	61.3	1.5	23.2	6.2	7.8	2.0
5 n	$CrCl_2$	74.0	0.8	0.8	0.5	24.1	1.8
6 sec	$CrCl_2$	75.7	0.8	3.9	1.1	18.2	2.3
7 n	$MnCl_2$	96.0	3.7	0.1	0.04	0.1	1.6
8 sec	$MnCl_2$	69.8	17.1	8.8	3.6	0.6	[e]
9 n	$FeCl_3$	69.8	0.8	11.2	3.0	14.2	4.3
10 sec	$FeCl_3$	69.6	0.5	4.7	1.0	24.1	5.0
11 n	$CoCl_2$	64.9	0.5	20.0	6.5	8.1	1.7
12 sec	$CoCl_2$	61.5	0.2	18.8	4.8	14.6	[e]
13 n	$NiBr_2$	74.6	0.2	12.4	3.4	9.3	1.8
14 sec	$NiBr_2$	69.1	0.2	16.3	4.6	9.8	[e]
15 n[f]	$FeCl_3$	62.5	0.8	30.9	5.0	0.8	10.8
16 sec[f]	$FeCl_3$	56.0	3.6	11.4	2.4	25.9	6.4

[a] n and sec represent the (4-phenylbutyl)- and (3-phenyl-1-methylpropyl)-magnesium bromides respectively. [b] Relative percentages of hydrocarbons present as measured by GLC. [c] Expressed in mmoles per 100 mmoles alkyl-Grignard used. [d] Analysis of alkyl-Grignard used. [e] Not measured. [f] In the presence of internal standards. [g] Tetralin 0.4%.

fragmentation of an alkylmetal system, it is first necessary to establish whether or not the system in question effects the isomerization of terminal olefins. The following isomerization studies were therefore carried out under the conditions used in the fragmentation work. In order to simplify the GLC analysis, pure 1-decene and 1-dodecene were used as terminal olefin, this, despite the disadvantage that GLC analysis although permitting identification of the *cis*- and *trans*-2-alkenes does not permit distinction between the 1- and 3-alkenes.

The results, summarized in Table 2 show that with the exception of both n- and sec-alkylmanganese systems (Expts. 24, 25 and 31), all the alkyl-transition metal systems studied interact with terminal olefins to give *hydrogenation* and *isomerization* products.

The possibility that the poor activity of the alkylmanganese systems in the isomerization of terminal olefins was due to the fact that they isomerized internal olefins to terminal ones, was excluded by testing their activity with mixed dodecenes (Table 2, Expt. 31). In this experiment the recovered dodecene mixture had nearly the same composition as that used at the start. These results, together with those from the fragmentation studies indicate that the n- and sec-alkylmanganese systems are poor olefin isomerization catalysts.

With the other alkyl-transition metal systems, the major products are the *trans*- and *cis*-2-alkenes, and from the relative percentages of these it would appear

TABLE 2

ISOMERIZATION OF OLEFINS BY ALKYL-TRANSITION METAL SYSTEMS; ANALYSIS OF PRODUCTS

Expt. no.	System[a]	Olefin	Metal halide	Isomerization products[b]			
				Alkane	1- and 3-Alkene[c]	*trans*-2-Alkene	*cis*-2-Alkene
17	$PhBu_n$	1-Decene	VCl_3	10.5	12.0	49.5	28.2
18[d]	Bu_s	1-Decene	VCl_3	11.3	17.1	55.0[d]	16.5
19	$PhBu_n$	1-Decene	VCl_3	21.8	32.0	29.7	16.7
20[d]	$PhBu_n$	1-Dodecene	$CrCl_3(THF)_3$	12.3	8.5	61.3[d]	17.9
21[d]	$PhBu_s$	1-Decene	$CrCl_3(THF)_3$	6.7	5.7	67.2[d]	20.3
22	Bu_n	1-Decene	$CrCl_2$	14.9	23.8	48.8	12.6
23[d]	Bu_s	1-Decene	$CrCl_2$	17.0	41.4	33.8[d]	7.8
24[e]	$PhBu_n$	1-Dodecene	$MnCl_2$	0.0	96.7[e]	3.3	0.0
25[e]	$PhBu_s$	1-Decene	$MnCl_2$	1.6	91.2[e]	3.8	3.4
26[d]	Bu_s	1-Decene	$FeCl_3$	17.0	27.8	44.5[d]	10.7
27	$PhBu_n$	1-Dodecene	$CoCl_2$	3.8	57.0	22.0	17.3
28	$PhBu_s$	1-Decene	$CoCl_2$	8.5	18.0	56.4	17.1
29	$PhBu_n$	1-Dodecene	$NiBr_2$	2.5	33.4	52.0	12.0
30	$PhBu_s$	1-Decene	$NiBr_2$	4.1	32.9	50.2	12.6
31	$PhBu_s$	Dodecenes	$MnCl_2$	7.0 (7.0)[f]	19.7 (19.4)[f]	52.7 (54.7)[f]	20.5 (18.8)[f]

[a] Bu_n, $PhBu_n$ and Bu_s, $PhBu_s$ represent respectively n-butyl-, n-4-phenylbutyl-, sec-butyl- and (3-phenyl-1-methylpropyl)magnesium bromides. [b] Relative percentages of C_{10} or C_{12} hydrocarbons established by GLC. [c] 1- and 3-alkenes not separated on column used. [d] Major olefin component isolated and identified by IR and NMR spectroscopies as *trans*-2-alkene. [e] Major olefin component isolated and identified by IR and NMR spectroscopies as terminal olefin, 1-alkene. [f] Figures in brackets indicate the composition of the dodecene mixture used.

that the alkylchromium(III) systems are the more selective in 1-alkene → 2-alkene isomerization. The present data however, does not indicate how much 3-alkene is formed and how much 1-alkene is unchanged. A subsidiary set of experiments with 1-phenyl-2-butene (only slowly isomerized by the alkyl–chromium system) was therefore carried out (Table 3).

The results indicate that with the three n- and sec-alkyl systems studied, a considerable proportion of 3-alkene is formed. This, together with the fragmentation

TABLE 3

ISOMERIZATION OF 4-PHENYL-2-BUTENE BY ALKYL-TRANSITION METAL SYSTEMS; ANALYSIS OF PRODUCTS

Expt. no.	System[a]	Metal halide	Isomerization products[b]				
			Alkane	1-Alkene	*trans*-2-Alkene	*cis*-2-Alkene	3-Alkene
32	Bu_n	VCl_3	10.8	0.5	58.2	9.4	21.1
33	Bu_s	VCl_3	7.7	0.7	59.0	11.9	20.6
34	Bu_n	$CrCl_2$	5.6	0.3	38.2	7.6	48.3
35	Bu_s	$CrCl_2$	7.4	0.6	54.4	9.5	27.8
36	Bu_n	$FeCl_3$	29.4	0.1	3.0	0.5	67.1
37	Bu_s	$FeCl_3$	29.2	0.3	40.5	7.4	22.6

[a] Bu_n and Bu_s refer respectively to n- and sec-butylmagnesium bromide. [b] Relative percentages of 4-phenylbutane, 4-phenyl-1-butene, *trans*- and *cis*-4-phenyl-2-butene and 4-phenyl-3-butenes as established by gas chromatographic analysis.

results (Table 1) would indicate that the alkylchromium(III) systems are somewhat unique in isomerizing 1-alkenes to 2-alkenes.

The data from the isomerization of 4-phenyl-2-butene (Table 3) again indicate that alkyl-vanadium, -chromium(II) and -iron(III) systems interact with olefins to give appreciable quantities of hydrogenation products.

It has been reported that the presence of added olefin or diene alters the alkane to alkene ratio found in the fragmentation of the alkyl–chromium system from 70/30 to 60/40, or even lower[1]. A similar effect has been noticed in the present isomerization studies with the n- and sec-alkyl-chromium, -cobalt and -nickel systems.

Both of the foregoing results are compatible with the fragmentation processes already established for alkylchromium compounds. Thus fragmentation of the σ-bonded alkylmetal compound can give rise to the metal hydride, which can react with the added terminal olefin or diene to give new mixed alkyl–metal species, eqn. (11). These can subsequently undergo fragmentation either by metal hydride elimination, or by internal β-hydrogen transfer.

$$\begin{array}{l}(RCH_2CH_2)_nM \rightarrow MH(CH_2CH_2R)_{n-1} + RCH{=}CH_2 \\ \qquad\qquad\qquad \xrightarrow{R'CH=CH_2} R'CH_2CH_2M(CH_2CH_2R)_{n-1} \\ \qquad\qquad\qquad\qquad\qquad\qquad \text{or} \\ \qquad\qquad\qquad\qquad R'CH(CH_3)M(CH_2CH_2R)_{n-1}\end{array} \qquad (11)$$

$$\left.\begin{array}{l}R'CH_2CH_2M(CH_2CH_2R)_{n-1} \\ R'CH(CH_3)M(CH_2CH_2R)_{n-1}\end{array}\right] \rightarrow R'CH_2CH_3 + RCH{=}CH_2 \qquad (12)$$

In the latter case the products can be alkane, derived from added olefin, and alkene, derived from the alkyl group originally bonded to the metal eqn. (12). Such a scheme would account for both the formation of larger proportions of alkene, and hydrogenation products derived from added alkene.

This demonstrates the probability that other first row alkyl-transition metal systems, like the alkylchromium ones, can undergo fragmentation either homolytically or by metal hydride elimination.

EXPERIMENTAL (with Miss U. FEISST and Mrs. A. BRINK)

The techniques employed for the preparation and handling of the air and moisture sensitive organometallic compounds have already been described[24].

Product identification

The alkanes and alkenes were analyzed by gas chromatography on an F and M, 5750 equipped with a 12 ft, 1/4" 20% Carbowax 20M column. The relative retention times, (column temperature 150°, He flow rate, 60 ml per min), for the anticipated products are: (I) 4-phenylbutane (10 min), (II) 4-phenyl-1-butene (15 min); (III) *trans*-4-phenyl-2-butene (18 min); (IV)–(VI) *cis*-4-phenyl-2-butene, 1-methylindane and 2-methyl-3-phenyl-2-propene (22 min); (VII) 4-phenyl-3-butene (32 min); (VIII) tetralin (45 min); (IX) α-methylindene (56 min). It is evident that the "fourth peak" could represent either *cis*-4-phenyl-2-butene, 1-methylindane, or 2-methyl-

3-phenyl-2-propene. Thus GLC analysis is sufficient for the anticipated fragmentation products from the 1-(4-phenylbutyl) systems [*i.e.* compounds (I)–(IV), (VII) and perhaps (VIII)]. With the 2-(4-phenylbutyl) systems however, four of the anticipated products [*i.e.* compounds (I)–(III) and (VII)] are readily identified by GLC; the other, *cis*-4-phenyl-2-butene could be confused with potential cyclization or rearrangement products [*i.e.* (V) and (VI)]. It was therefore necessary. (Table 1, expts. 2, 4, 8, 12 and 14) to isolate, wherever feasible, the individual hydrocarbons and identify these by NMR spectroscopy[24].

In the isomerization experiments, with 1-decene, 1-dodecene and 4-phenyl-2-butene, the compounds quoted in Tables 2 and 3 were identified by their GLC retention times, though in some instances Table 2, expts. 18, 20, 21 and 23 to 26, the major olefin was isolated and identified by NMR and IR spectroscopies.

Fragmentation of alkyl-transition metal systems

(*a*). *In the absence of internal standards.* Expts. 1 to 14 were carried out without the addition of internal standards to the alkyl-Grignard used. In every case the appropriate quantity of alkylmagnesium halide, in tetrahydrofuran (Table 1a) was added to a briskly stirred suspension of the metal halide (Table 1a) in tetrahydrofuran at −70°. The reaction mixture was allowed to warm slowly (6 h) to 20°. In most cases the initial reaction mixture was a brightly coloured solution or suspension, at −30 to −20° the Gilman test No. 1 was negative. On warming, the solutions darkened

TABLE 1a

STOICHIOMETRY OF REACTION OF n- AND sec-ALKYLMAGNESIUM HALIDES WITH 1ST ROW TRANSITION METAL SALTS

Expt. no.[a]	Grignard				Metal halide			Color	Hydrolysis
	n-		sec-		MX_n	(g)	(mmole)		
	(ml)	(mmole)	(ml)	(mmole)					
1	56.5	38.7			VCl_3	2.04	12.9	Brown	Gas
			132	42.3	VCl_3	2.23	14.1	Brown	Gas
3	25	9.7			$CrCl_3(THF)_3$	1.21	3.23	Black	Gas
4			50	16.0	$CrCl_3(THF)_3$	1.98	5.3	Blue	Gas
5	53	37.2			$CrCl_2$	2.28	18.6	Brown	Gas
6			37.5	12.6	$CrCl_2$	0.74	6.03	Brown	Gas
7	25	9.7			$MnCl_2$	0.61	4.85	Yellow solid and liquid	No Gas
8			25	10	$MnCl_2$	0.63	5.0	Brown	Slight gas
9	42	30			$FeCl_3$	1.58	9.75	Intense yellow changing to brown	Slight gas
10			144	46.2	$FeCl_3$	2.505	15.4	As above	Slight gas
11	25	9.7			$CoCl_2$	0.63	4.85	Black-brown	Gas
12			25	10	$CoCl_2$	0.65	5.0	Black-brown	Gas
13	25	9.7			$NiBr_2$	1.05	4.85	Black-brown	Gas
14			25	10	$NiBr_2$	1.09	5.0	Black-brown	Gas
15	104	47.7			$FeCl_3$	2.59	15.97	Intense yellow changing to brown	Slight gas
16			62	23.5	$FeCl_3$	1.27	7.8	As above	Slight gas

[a] Numbers correspond to those in Table 1.

(except alkylmanganese) becoming black at 0 to 20°. The final solutions or suspensions were hydrolyzed after 24 h at 20°, gas evolution (except alkylmanganese), and the organic material isolated with the aid of ether. Any coloured ether extract was filtered through a short plug of alumina, to ensure complete removal of metal ions, and the resulting colourless eluate analyzed for alkane and alkene content by GLC.

The ether extracts were concentrated and treated with a known volume of a standard solution of eicosane in benzene. Subsequent gas chromatographic analysis on a Silicone Gum Rubber column (200°), gave the absolute concentration of dimeric material present (Table 1).

(*b*). *In the presence of internal standards.* In expts. 15 and 16 the n- and sec-alkyl-Grignards used contained dodecane (112 and 135 mmoles to 196 and 260 mmoles RMgX, respectively) and eicosane (both 7.1 mmoles) as internal GLC standards for the monomeric and dimeric hydrocarbons. Gas chromatographic analysis of the hydrolysate of the n-alkyl-Grignard indicated a total of 193 mmoles available alkyl, 3.3 mmoles alkenes and tetralin and 7.3 mmoles dimer; for the sec-alkyl-Grignard 215 mmoles available alkyl, 42.7 mmoles alkenes and α-methylindane, and 8.9 mmoles dimer.

The appropriate quantities of alkylmagnesium halide and $FeCl_3$ (Table 1a, expts. 15 and 16) were allowed to interact as described under (*a*) above. The relative percentages of the monomeric products isolated after hydrolysis are given in Table 1 (expts. 15 and 16). The overall material balances for the n-alkyl system and sec-alkyl system are, respectively, alkane (47.0, 49.4%), 1-alkene (0.5, 3.2%), *trans*-2-alkene (23.2, 10.0%), *cis*-2-alkene (4.3, 2.0%), 3-alkenes (0.5, 23.2%), tetralin (traces, 0), dimeric hydrocarbon (24.1, 11.9%).

TABLE 2a

ISOMERIZATION OF OLEFINS BY ALKYL-TRANSITION METAL SYSTEMS; STOICHIOMETRY OR REACTANTS

Expt. no.[a]	Alkyl-Grignard				Metal halide		
	n-		sec-		MX_n	(g)	(mmole)
	(ml)	(mmole)	(ml)	(mmole)			
17	35	23.3			VCl_3	1.22	7.75
18			41	19	VCl_3	1.0	6.3
19	67.5	37.8			VCl_3	1.98	12.6
20	20	12.4			$CrCl_3(THF)_3$	1.55	4.13
21			25	10	$CrCl_3(THF)_3$	1.24	3.3
22	53	33			$CrCl_2$	2.07	16.8
23			28	12.6	$CrCl_2$	0.78	6.3
24	20	12.4			$MnCl_2$	0.78	6.2
25			25	10	$MnCl_2$	0.63	5.0
26			58	25.8	$FeCl_3$	1.4	8.6
27	20	12.4			$CoCl_2$	0.8	6.2
28			25	10	$CoCl_2$	0.65	5.0
29	20	12.4			$NiBr_2$	1.35	6.2
30			25	10	$NiBr_2$	1.09	5.0
31			50	12	$MnCl_2$	0.75	6.0

[a] Numbers correspond to those on Table 2.

Isomerization of olefins by alkyl-transition metal systems

In the following experiments, the appropriate stoichiometric ratios of alkylmagnesium halide and transition metal halide (Table 2a) were mixed in tetrahydrofuran at −70°. Dry oxygen-free olefin (5 ml), previously filtered through alumina, was added and the whole allowed to warm to 20° (6 h). After 24 h at 20° the total reaction mixture was hydrolyzed and the organic material isolated with the aid of ether. The relative percentages of hydrocarbons present were determined by GLC (Table 2). No check was made for dimer formation.

Isomerization of 4-phenyl-2-butene by alkyl-transition metal systems

In a similar set of expts. (Table 3a) the olefin used was 4-phenyl-2-butene (5 ml). After 24 h at 20° the total reaction mixture was hydrolyzed and the relevant hydrocarbons isolated with the aid of ether are listed in Table 3. No check was made for dimer formation.

TABLE 2b

FRAGMENTATION OF (4-PHENYLBUTYL)- AND (3-PHENYL-1-METHYLPROPYL)-TRANSITION METAL SYSTEMS IN PRESENCE OF ADDED OLEFIN

Expt. no.[a]	System	Metal halide	Fragmentation products[b]				
			Alkane	1-Alkene	*trans*-2-Alkene	*cis*-2-Alkene	3-Alkene
17	n	VCl_3	63.0	1.3	18.6	5.0	12.2
20	n	$CrCl_3(THF)_3$	50.8	1.7	29.8	5.1	12.3
21	sec	$CrCl_3(THF)_3$	47.2	3.1	33.3	9.0	7.4
27	n	$CoCl_2$	61.3	7.2	19.4	8.7	3.3
28	sec	$CoCl_2$	49.3	0.0	22.8	6.9	21.0
29	n	$NiBr_2$	71.2	0.0	8.9	2.0	17.8
30	sec	$NiBr_2$	56.6	0.0	16.0	6.0	21.3

[a] Numbers correspond to those in Tables 2 and 2a. [b] Relative percentages of hydrocarbons present, as measured by GLC.

TABLE 3a

ISOMERIZATION OF 4-PHENYL-2-BUTENE BY ALKYL-TRANSITION METAL SYSTEMS; STOICHIOMETRY

Expt. no.[a]	Alkyl-Grignard				Metal halide		
	n-		sec-		MCl_n	(g)	(mmole)
	(ml)	(mmole)	(ml)	(mmole)			
32	52	32.1			VCl_3	1.69	10.7
33			65	30.2	VCl_3	1.58	10.0
34	42	26.2			$CrCl_2$	1.61	13.1
35			22	10.1	$CrCl_2$	0.62	5.04
36	46.5	28.9			$FeCl_3$	1.57	9.6
37			65	29.6	$FeCl_3$	1.6	9.87

[a] Numbers correspond to those on Table 3.

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