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ALKYLTRANSITION METAL COMPOUNDS
VII*. FRAGMENTATION OF THE tert-ALKYLCHROMIUM SYSTEM

R. P. A. SNEEDEN AND H. H. ZEISS
Monsanto Research S.A., Eggbühlstrasse 36, CH-8050 Zürich (Switzerland)

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SUMMARY

The tri-tert-alkylchromium system [from $PhCH_2CH_2C(CH_3)_2MgCl$ and $CrCl_3(THF)_3$] undergoes stepwise fragmentation on warming. At low temperatures a homolytic process leads to the exclusive formation of alkane and 1-alkene. At higher temperatures the products consist of alkane, 1- and 2-alkene and a chromium based olefin isomerization catalyst.

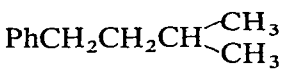
INTRODUCTION

The tert-alkyl derivatives of the Groups I and II metals are relatively stable compounds, whilst those of some Group III metals (Al and B) are thermally unstable[2,3]. Thus tri-tert-butylaluminum etherate isomerizes to the tri-isobutyl compound [eqn. (1)[2]]. Similarly, attempts to prepare the tert-butylboron compound resulted in the isolation of di-isobutyl-tert-butylboron, which in turn isomerizes thermally to tri-isobutylboron, eqn. (2)[3].

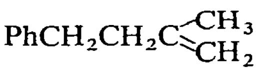
$$3\ \text{t-BuMgCl} + AlCl_3 \xrightarrow{Et_2O} \text{t-Bu}_3AlOEt_2 \xrightarrow{\Delta} \text{i-Bu}_3AlOEt_2 \qquad (1)$$

$$3\ \text{t-BuMgCl} + BF_3 \rightarrow \text{i-Bu}_2\text{B-t-Bu} \xrightarrow{\Delta} \text{i-Bu}_3B \qquad (2)$$

Nothing, however, is known concerning the stability and reactions of tert-alkyltransition metal systems. We therefore extended our present studies of alkylchromium compounds[1,4] to the tert-alkylchromium system, derived from $PhCH_2CH_2C(CH_3)_2MgCl$ and $CrCl_3(THF)_3$. Tris(3-phenyl-1,1-dimethylpropyl)chromium was chosen since the derived alkane (I), alkenes [(II) and (III)] and dimer (IV) are readily separated, analyzed and identified by gas chromatographic and ^{1}H-NMR spectroscopic analysis.


$PhCH_2CH_2CH{<}^{CH_3}_{CH_3}$

(I)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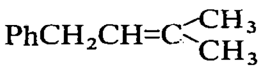
(II)


$PhCH_2CH{=}C{<}^{CH_3}_{CH_3}$

(III)

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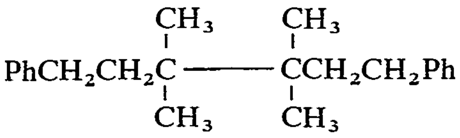
* For Part VI see ref. 1.



$$\mathrm{PhCH_2CH_2}\overset{\mathrm{CH_3}}{\underset{\mathrm{CH_3}}{\mathrm{C}}}\text{——}\overset{\mathrm{CH_3}}{\underset{\mathrm{CH_3}}{\mathrm{C}}}\mathrm{CH_2CH_2Ph}$$

(IV)

RESULTS AND DISCUSSION

tert-Alkylmagnesium halides

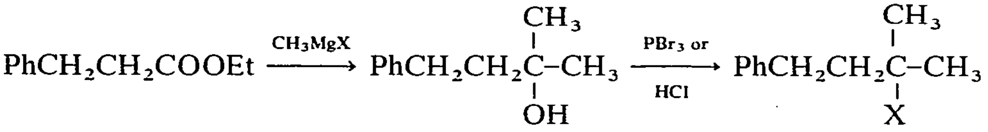
The interaction of an alkyl halide with magnesium, in tetrahydrofuran, can lead to the formation of either the organomagnesium halide [eqn. (3)] or to the formation of the magnesium halide and equal quantities of alkane and alkene together with some dimer [eqn. (4)][5].

$$\mathrm{RCH_2CH_2X+Mg \rightarrow RCH_2CH_2MgX} \tag{3}$$

$$\mathrm{4\,RCH_2CH_2X+2\,Mg \rightarrow RCH_2CH_3+RCH{=}CH_2+(RCH_2CH_2)_2+2\,MgX_2} \tag{4}$$

With n- and sec-alkyl bromides and chlorides the usual product of reaction with magnesium is the corresponding alkyl-Grignard[5,6]. With the tert-alkyl halides, however, the reaction with magnesium is known to give erratic results[5,6].

In the present work it was found that the tert-alkyl bromide [(V), X = Br], prepared according to eqn. (5), reacted with magnesium as outlined in eqn. (4). No



$$\mathrm{PhCH_2CH_2COOEt} \xrightarrow{\mathrm{CH_3MgX}} \mathrm{PhCH_2CH_2}\overset{\mathrm{CH_3}}{\underset{\mathrm{OH}}{\mathrm{C}}}\mathrm{-CH_3} \xrightarrow[\mathrm{HCl}]{\mathrm{PBr_3\ or}} \mathrm{PhCH_2CH_2}\overset{\mathrm{CH_3}}{\underset{\mathrm{X}}{\mathrm{C}}}\mathrm{-CH_3} \tag{5}$$

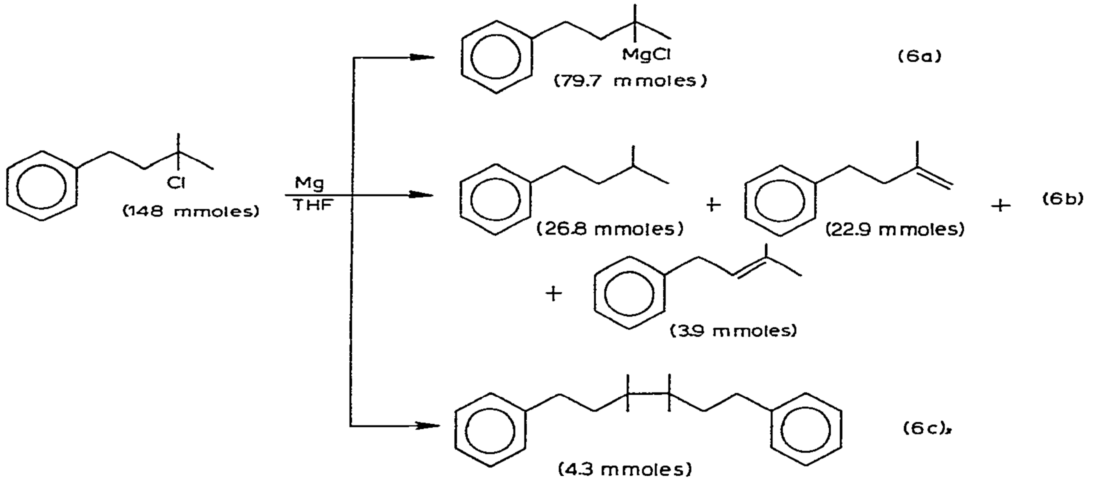
(V)

alkyl-Grignard was formed and the final products, after hydrolysis, contained no unreacted halide. The hydrocarbon consisted of alkane (I), alkenes [(II) and (III)] and dimer (IV) (see Experimental).

In a representative experiment (see Experimental) it was shown that the tert-alkyl chloride on the other hand reacts with magnesium, in tetrahydrofuran, to give the tert-alkyl-Grignard [eqn. (6a)], equal quantities of alkane and alkenes [eqn. (6b)] and dimer [eqn. (6c)].

tert-Alkylmagnesium chloride and $CrCl_3(THF)_3$, ratio 3/1

The interaction of the tert-alkyl-Grignard and $\mathrm{CrCl_3(THF)_3}$ ratio 3/1 in tetrahydrofuran at −70° in the presence of internal standards led to a red-brown heterogeneous reaction mixture. On warming to +20°, the color gradually darkened but the reaction mixture never really became homogeneous. Analysis of the final hydrolysis products, from samples withdrawn at different temperatures (see Experimental) indicates that between −70° and −15°C the major olefin present was the 1-alkene, eqn. (7) ($\mathrm{R = PhCH_2}$).



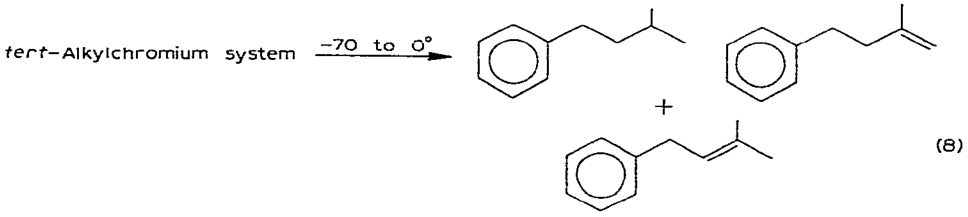
$$\begin{array}{c}3\,\mathrm{RCH_2C(CH_3)_2MgCl}\\+\\\mathrm{CrCl_3(THF)_3}\end{array}\xrightarrow[(2)\ \mathrm{H_2O}]{(1)\ -70\ \mathrm{to}\ -15^{\circ}}\mathrm{RCH_2CH(CH_3)_2+RCH_2C(CH_3){=}CH_2}\qquad(7)$$

At higher temperatures the final deuterolysis products (20°) consist of undeuterated alkane, 1-alkene, 2-alkene together with some dimer.

tert-Alkylmagnesium chloride and $CrCl_3(THF)_3$, ratio 3/1, deuterolysis

In an analogous experiment the alkyl-Grignard and $CrCl_3(THF)_3$ were allowed to interact in a more dilute solution. After 12 h at −70° a clear red solution was obtained, which was allowed to warm to +20°.

The nature and isotopic composition of the hydrocarbons present after the deuterolysis of samples withdrawn at −40, 0, 20 (0 h) 20° (20 h) (see Experimental) indicates that at low temperatures a tert-alkylchromium compound is formed and this undergoes rather rapid fragmentation to alkane and 1- and 2-alkene [eqn. (8)]. After a few hours at room temperature fragmentation is complete and there are no alkyl groups left bonded to chromium.



Fragmentation of the tert-alkylchromium system

A solution of the organochromium compound, in tetrahydrofuran, was allowed to warm from −70 to +20°. Aliquots were withdrawn periodically, hydrolyzed and the products analyzed (GLC). The results are summarized graphically in Fig. 1. The upper curves represent the relative percentages of the various hydrocarbons

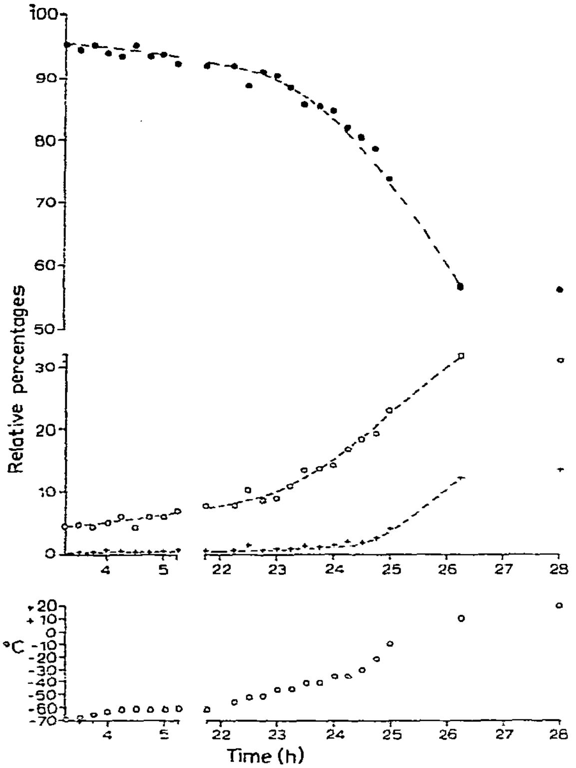


Fig. 1. Fragmentation of tert-alkylchromium system with dodecane as internal standard. ●, 4-phenyl-2-methylbutane; ○, 4-phenyl-2-methyl-1-butene; +, 4-phenyl-2-methyl-2-butene.

present in the total hydrolysis mixture at a given time, the lower one, the temperature profile. The results show that:

(1). The overall fragmentation products consist of 1- and 2-alkenes and alkane; no 3-alkene is formed.

(2). There is little, or no, isomerization of the terminal 1-alkene to the 2-alkene. Control experiments (see Experimental) proved that the present tert-alkylchromium system will however isomerize an unbranched terminal olefin.

(3). Two fundamental processes are involved in the fragmentation of the tert-alkylchromium system. The first, low temperature, process (−70 to −50°) has a low activation energy and leads to the 1-alkene. The second, with a higher activation energy, leads to the 2- and 1-alkenes.

In discussing the thermal stabilities of carbon–metal bonds, and the thermal decomposition of σ-bonded organometallic compounds, it is therefore necessary to define first the precise fragmentation process(es) involved, (*e.g.* homolysis, metal-hydride elimination or heterolysis) and subsequently the factors affecting these reactions. The accumulated results from the alkylchromium system[1,4] show that:

(1). The stability sequence is n >sec >tert (from the temperatures at which fragmentation occurs).

(2). Free radical[7] and anionic processes[8,9] are probably not involved in the fragmentation of alkylchromium compounds (formation of only small amounts of cyclization and coupling products).

(3). The fragmentation does involve homolytic and hydrogen transfer processes (*e.g.* metal hydride elimination) and takes place within a monomeric or dimeric σ-bonded organochromium species.

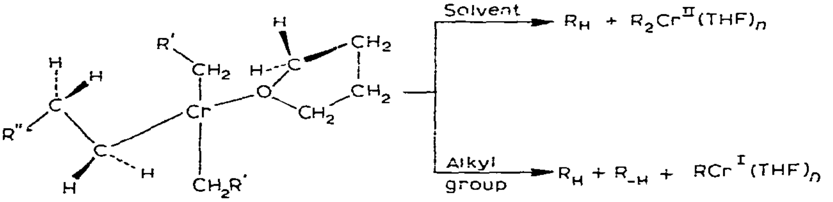
(4). The fragmentation processes are influenced by the electron density of the metal center.

(5). The organic products formed in the initial fragmentation are controlled by steric factors and not by differences in the relative bond strengths (or polarities) in the CH_2 and CH_3 groups flanking the metal center (the initial product is always 1-alkene and the second product is mainly the *trans*-2-alkene).

In tetrahydrofuran solution the monoalkyldichlorochromium compounds are considerably more stable (high inductive effect of Cl) than the analogous trialkylchromium species. Studies with a mono-(2,2-dideuterioalkyl)chromium dihalide proved that, in these species the fragmentation is entirely homolytic [formation of $Cr^{II}]^+$, eqn. (9). The trideuterioalkane is formed by deuterium abstraction from the β-position of an alkyl group bonded to chromium. No hydrido(deuterio)chromium species is formed.

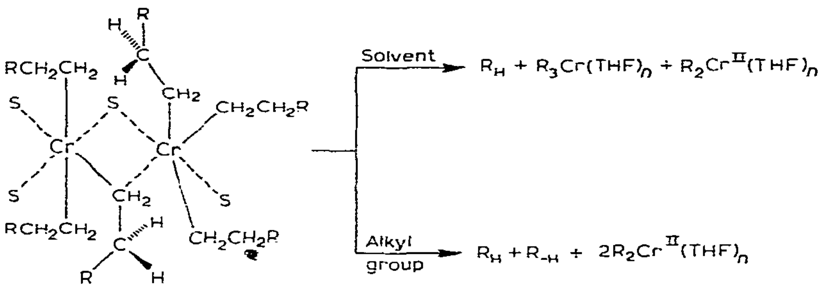
$$RCD_2CH_2CrCl_2(THF)_n \xrightarrow{\Delta} RCD_2CH_3 + CrCl_2(THF)_n + \\ + RCD_2CH_2D + RCD{=}CH_2 \quad (9)$$

With the trialkylchromium systems the present results together with those of experiments with specifically deuterated alkyl groups[10] indicate that the initial fragmentation at low temperatures is homolytic. The hydrogen required for the alkane formation originated either in the coordinated solvent or in the β-position of one of the alkyl groups bonded to chromium. Thus in a monomeric species attack on solvent would give the alkane and a Cr^{II} species whereas β-hydrogen abstraction from a second alkyl group bonded to the metal would give equal quantities of alkane and 1-alkene and a chromium(I) species, eqn. (10). Similar processes in a dimeric species would lead to alkane and an alkyl-$Cr^{III}Cr^{II}$ species, whereas attack on a second alkyl group would give alkane, alkene and an alkylchromium(II) species, eqn. (11).



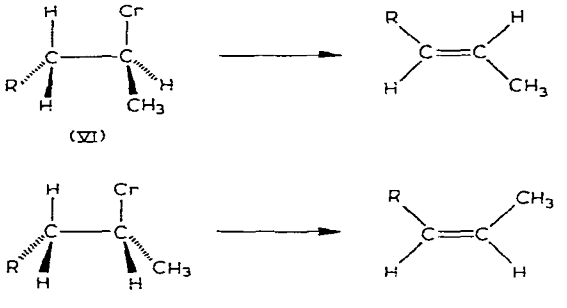
(10)

Both α- and β-metal hydride elimination occur at higher temperatures, and require a free coordination site at the chromium center and a change in the conformation of the organometallic species. The α-elimination could proceed via carbenoid formation, and β-elimination via a 4-center transition state. In both cases the overall products are the hydridochromium species and the 1- and/or 2-alkene. In the β-metal hydride elimination there is an additional steric restraint; thus the transition state can have either one of two conformations [(VI) and (VII), eqn. (12)], of which (VI)



(11)

is the more stable. The overall elimination would therefore be expected to give, and indeed does give, more *trans*-2-alkene than *cis*-2-alkene.



(VI) (12)

(VII)

The new hydridochromium species generated in the elimination process may either undergo intramolecular hydrogen transfer leading to alkane and a reduced chromium species, eqn. (13), or interact with olefin substrate to give a new (mixed) alkyl chromium species [eqn. (14)].

$$HCrR_{n-1}(THF)_x \rightarrow R_H + R_{n-2}Cr(THF)_x \quad (13)$$

$$HCrR_{n-1}(THF)_x \xrightarrow{R'CH=CH_2} R'CH_2CH_2CrR_{n-1}(THF)_x + (R'CHCH_2)CrR_{n-1}(THF)_x \quad (14)$$

It is now evident that the initial step in the thermal decomposition of alkylchromium(III) compounds [and probably other σ-bonded organochromium(III) compounds[11]] involves the homolysis of the carbon–chromium bond with the formation of a chromium(II) or -(I) species. The latter then undergo subsequent metal hydride elimination (with no change in valency) to give alkene and hydridochromium species. The catalytic activity of organochromium systems is therefore not associated with the chromium(III) state but rather with the chromium(II) or some lower valent chromium species.

EXPERIMENTAL (with Miss U. FEISST)

Experiments with organometallic compounds were carried out, under argon, in flame dried equipment. The diethyl ether and tetrahydrofuran used were freshly distilled, under argon, first from sodium wire then from $LiAlH_4$.

The gas chromatographic analyses were carried out on a F and M model 5750 equipped with a 20% carbowax 20M column (for alkanes and alkenes) and a Silicone Gum Rubber column (for dimer and eicosane). The procedure adopted for the GLC analysis of the hydrocarbon mixtures, with dodecane and eicosane as standards, has already been described[4]. In the deuterolytic studies the isotope compositions* quoted are for hydrocarbons isolated by preparative scale GLC.

The micro-analyses are by Mr. W. Manser, Eidg. Technische Hochschule, Zürich, Switzerland.

Starting materials

(1). *2-Hydroxy-2-methyl-4-phenylbutane*[12,13]. 2-Hydroxy-2-methyl-4-phenylbutane was prepared by the interaction of ethyl hydrocinnamate (80 g, 440 mmoles) and methylmagnesium bromide (1000 mmoles) in tetrahydrofuran. It was obtained as a colorless oil b.p. 63–65°/0.1 mm; m.p. 26–27°; n_D^{20} 1.5091. (Found: C, 80.3; H, 9.85. $C_{11}H_{16}H_{16}O$ calcd.: C, 80.4; H, 9.8%.) δ_{TMS} 7.09 (singlet, 5 protons, C_6H_5), 2.6 (multiplet, 3.01 protons, $ArCH_2$ and OH), 1.7 (multiplet, 1.99 protons, CH_2), 1.22 ppm [singlet, 5.98 protons, $C(CH_3)_2$], (lit.[13] m.p. 24–25°).

(2). *2-Bromo-2-methyl-4-phenylbutane.* The carbinol prepared above (62 g, 378 mmoles) was treated with phosphorus tribromide (7.5 ml, 126 mmoles) as described previously[14]. In this way 2-bromo-2-methyl-4-phenylbutane (60 g) b.p. 64–68°/0.1 mm; n_D^{20} 1.5293; δ_{TMS} 7.12 (singlet 5.00 protons. C_6H_5), 2.80 (multiplet, 2.02 protons $ArCH_2$), 2.0 (multiplet, 2.02 protons, CH_2), 1.76 ppm [singlet, 5.94 protons, $BrC(CH_3)_2$] was obtained.

(3). *2-Chloro-2-methyl-4-phenylbutane.* The tertiary carbinol, prepared above, (20 g) dissolved in hexane (30 ml) and cooled to 0° was subjected to a slow stream of gaseous HCl, at 0°. When the solution was saturated with HCl, the whole was allowed to warm to room temperature and subsequently heated under reflux (1 h). The cooled reaction mixture was poured onto ice and the hexane washed thoroughly with NaOH (10%).

Fractional distillation of the dried ($MgSO_4$) extract gave 2-chloro-2-methyl-4-phenylbutane (19.94 g) b.p. 50–52°/0.05 mm, n_D^{20} 1.5078; m.p. 27–28°. (Found: C, 72.4; H, 8.2; Cl, 19.2. $C_{11}H_{15}Cl$ calcd.: C, 72.3; H, 8.3; Cl, 19.4%.) δ_{TMS} 7.12 (5.00 protons, C_6H_5), 2.75 (multiplet, 2.02 protons $ArCH_2$), 1.95 (multiplet, 2.04 protons, CH_2CCl), 1.57 [singlet, 5.98 protons $C(CH_3)_2$].

Authentic specimens

Specimens of 2-methyl-4-phenylbutane, 2-methyl-4-phenyl-1-butene, 2-methyl-4-phenyl-2-butene and 3,3,4,4-tetramethyl-1,6-diphenylhexane were obtained by the interaction of magnesium with 2-bromo-2-methyl-4-phenylbutane (see Experimental). The individual hydrocarbons, isolated by distillation and preparative scale gas chromatography had the following characteristics:

(1). *2-Methyl-4-phenylbutane.* Colorless liquid, δ_{TMS} 7.08 (singlet, 5.00 protons,

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* All the mass-spectroscopic data, corrected for natural isotopic abundances were kindly determined by Dr. W. E. Koerner and his associates of Monsanto Company, Research Center, St. Louis, U.S.A.

C_6H_5), 2.57 (multiplet, 1.98 protons, $ArCH_2$), 1.50 (multiplet, 2.93 protons CH_2CH), 0.92 ppm [doublet, *J* 6 Hz, 6.04 protons, $CH(CH_3)_2$].

(2). *2-Methyl-4-phenyl-1-butene*. Colorless liquid, δ_{TMS} 7.10 (singlet, 5.06 protons, C_6H_5), 4.66 (multiplet, 1.97 protons $CH_2{=}C$), 2.70 (multiplet, 2.03 protons $ArCH_2$) 2.25 (multiplet, 1.94 protons, $CH_2C{=}$), 1.74 ppm (triplet?, 2.98 protons $={CCH_3}$). Decouple δ 4.66 ppm ($CH{=}C$), CH_3 at 1.70 ppm becomes a singlet; ν_{max} 885 cm^{-1}.

(3). *2-Methyl-4-phenyl-2-butene*. Colorless liquid, δ_{TMS} 7.07 (singlet, 5.00 protons, C_6H_5), 5.27 (multiplet, 0.97 protons, $CH{=}$), 3.27 (multiplet, 1.94 protons, $ArCH_2$), 1.72 ppm [triplet?, 6.01 protons $(CH_3)_2$]. Decouple δ 1.72 ppm [$(CH_3)_2$], CH_2 at 3.27 ppm gives doublet (*J* 7 Hz) [$ArCH_2CH{=}C$] and $CH{=}$ at 5.27 ppm gives triplet (*J* 7 Hz); ν_{max} 850 cm^{-1}.

(4). *3,3,4,4-Tetramethyl-1,6-diphenylhexane*. Colorless solid, m.p. 107–108°. (Found: C, 89.4; H, 10.5. $C_{22}H_{30}$ calcd.: C, 89.7; H, 10.3%.) δ_{TMS} 7.08 (singlet, 10 protons, C_6H_5), 2.5 (multiplet, 4 protons $ArCH_2$), 1.55 (multiplet, 4 protons, CH_2), 0.92 ppm (singlet 11.9 protons, CH_3).

(5). *2-Methyl-4-phenyl-3-butene*. This substance was prepared by the dehydration[15] ($KHSO_4$) of 2-methyl-4-phenyl-4-butanol. When purified by preparative scale gas chromatography it was obtained as a colorless oil. δ_{TMS} 7.15 (multiplet, 5 protons, C_6H_5), 6.15 (multiplet 2.09 protons, $CH{=}CH$); 2.40 (multiplet, 0.97 protons, CH); 1.06 ppm [doublet, 6.09 protons $(CH_3)_2$]; ν_{max} 912 cm^{-1} (*trans* $CH{=}CH$).

The alkane and isomeric alkenes were readily separated by GLC; their relative retention times on a Carbowax column, 150°, helium flow rate 60 ml/min, were: 2-methyl-4-phenylbutane (18.0 min); 2-methyl-4-phenyl-1-butene (26.25 min); 2-methyl-4-phenyl-2-butene (31.50 min); 2-methyl-4-phenyl-3-butene (36.00 min).

In all the following experiments, the individual hydrocarbon products were isolated and characterized by NMR spectroscopy.

Interaction of 2-bromo-2-methyl-4-phenylbutane with magnesium

In a series of experiments the tert-alkyl bromide, prepared above, (20 g, 88.5 mmoles) was allowed to react with various qualities of magnesium in either tetrahydrofuran or diethyl ether. When the reaction was complete most of the magnesium had disappeared, titration of an aliquot of the solution did not indicate the presence of any alkylmagnesium halide (Gilman test No. I, negative). The total reaction mixtures were hydrolyzed and the organic material, isolated with the aid of ether, was separated by distillation into volatile products (b.p. 32–40°/0.05 mm, 10.8 g and solid residue m.p. 107–108°, 1.8 g). The volatile materials were analyzed by gas chromatographic analysis. The overall products formed are listed in Table 1. In experiments 2, 3 and 4 the NMR spectra of the total distilled hydrolysates were taken, and the absence of any signal at δ_{TMS} 1.76 ppm [$CBr(CH_3)_2$] confirmed that all the halide had reacted.

Interaction of 2-chloro-2-methyl-4-phenylbutane with magnesium

The crystalline tert-alkyl chloride (27 g, 148.3 mmoles) (in tetrahydrofuran 50 ml) was added dropwise to magnesium (3.55 g 148.3 mmoles) in tetrahydrofuran (20 ml). The reaction mixture was warmed in order to initiate the reaction and the whole kept warm during the addition of the alkyl halide. When the addition was complete the reaction mixture was diluted with tetrahydrofuran and warmed to 50° (2 h),

TABLE 1

INTERACTION OF 2-BROMO-2-METHYL-4-PHENYLBUTANE AND MAGNESIUM, FINAL HYDROLYSIS PRODUCTS

Exper. No.	Solvent	Products[a]			
		Alkane	1-Alkene	2-Alkene	Dimer
1[b]	THF	37.4	31.2	31.4	+
2[b]	THF	35.3	31.5	33.2	+
3[c]	Ether	39.4	32.8	27.8	+
4[d]	Ether	42.9	32.9	24.2	+

[a] Alkane and alkenes expressed in relative percentages; presence of dimer established by GLC analysis. [b] Merck magnesium. [c] Fluka magnesium. [d] Dow triply distilled magnesium.

cooled and filtered under argon. Dry oxygen-free dodecane (7 ml) and eicosane (2.00 g) were added to the clear dark filtrate (for subsequent use as internal standards in GLC analysis). Acid–base titration of an aliquot (5 ml) indicated a total concentration of 83.0 mmoles alkyl-Grignard (56%) yield. A second aliquot (10 ml) was deuterolyzed and the hydrocarbon mixture isolated with the aid of ether, consisted of: "2-methyl-4-phenylbutane" (79.8%); "2-methyl-4-phenyl-1-butene" (17.1%); "2-methyl-4-phenyl-2-butene" (3.1%) and dimer. Quantitative evaluation gave for the total alkyl-Grignard alkane (106.5 mmoles), 1-alkene (22.9 mmoles), 2-alkene (3.9 mmoles), dimer (4.3 mmoles), (total alkyl groups 142 mmoles). The alkane, isolated by preparative scale GLC [δ_{TMS} 7.07 (5 protons), 2.55 (multiplet, 2 protons), 1.47 (multiplet 2.30 protons), 0.92 and 0.90* ppm (doublet J 6 Hz and three lines J 1 Hz); decoupling with CH_2 at 1.4 ppm gave singlet at δ 2.55 ppm; decoupling with CH at δ 1.55 ppm gave singlet at δ 0.90 ppm; ν_{max} 2140 [2100 (sh)] cm^{-1}, alkyl C–D; isotopic composition D_0 28.8%, D_1 71.2%, D_2 0.0%**] was a mixture of 2-methyl-4-phenylbutane and 2-deuterio-2-methyl-4-phenylbutane (95% isotopic purity). The 1-alkene, ν_{max} 985 cm^{-1} (=CH_2), no C–D absorption, consisted of non deuterated 2-methyl-4-phenyl-1-butene. In

TABLE 2

tert-ALKYLMAGNESIUM CHLORIDE WITH $CrCl_3(THF)_3$. FINAL HYDROLYSIS (DEUTEROLYSIS) PRODUCTS

Sample	Temp. (°C)	Products			
		Alkane[a]	1-Alkene[a]	2-Alkene[a]	Dimer[b]
1	−70	88.1	10.9	1.0	0.0
2	−30	86.3	11.7	1.9	0.4
3	−15	81.3	16.0	2.6	0.9
4	0	59.6	28.9	11.5	1.00
5	20	58.6	29.9	11.4	2.00

[a] Corrected for alkyl-Grignard content and expressed in relative percentages. [b] Corrected for alkyl-Grignard content and expressed in mmoles per 100 mmoles titratable alkyl-Grignard.

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* The presence of the $CD(CH_3)_2$ grouping is confirmed by the new three line signal at δ 0.90 ppm.

** See footnote p. 107.

TABLE 3

DEUTEROLYSIS OF tert-ALKYLCHROMIUM SYSTEM

Sample	Temp. (°C)	Compound (%)[a,b]	Isotopic composition[c]			IR absorption, ν_{max} (cm^{-1})	NMR average proton count					
			D_0	D_1	D_2		Ar	C_5	C_4	C_3	C_2	C_1
1	−40°[e]	Alkane (79.9)	38.2	61.8	0.0	2139 [(sh) 2083]	5.00	1.97	2.20		5.92[d]	
		1-Alkene (17.3)				No C–D, 885	5.00	1.98	1.98	0	1.90	2.93
		2-Alkene (2.7)										
2	0°	Alkane (57.5)	83.2	15.7	1.1	2139 [(sh) 2094]	5.00		2.85		6.02[d]	
		1-Alkene (34.1)				No C–D, 885	5.00	2.00	2.00	0	2.05	2.95
		2-Alkene (8.4)				No C–D, 850	5.00	1.98	0.93	0	6.02	
3	20°[e]	Alkane (55.3)	96.0	4.0	0.0	2139	5.00	1.78	2.89		5.85	
		1-Alkene (35.4)				No C–D, 885	5.00	2.06	2.06	0	1.96	2.98
		2-Alkene (9.3)										
4	20°[f]	Alkane (54.8)	100.0	0.0	0.0	No C–D	5.00	1.98	3.05		5.85	
		1-Alkene (34.8)				No C–D, 885	5.00	2.00	1.97	0	1.91	2.96
		2-Alkene (10.3)				No C–D, 850	5.00	1.98	0.99	0	5.86	
5	20°[g]	Alkane (80.7)					5.00	2.01	3.01		5.90	
		1-Alkene (15.3)					5.00	1.91	2.01	0	1.91	2.95
		2-Alkene (4.0)										

[a] Expressed in relative percentages, uncorrected for alkyl-Grignard content. [b] In every case small quantities of dimer were formed. [c] Expressed in relative percentages. [d] The presence of the $CD(CH_3)_2$ grouping is confirmed by the new three line signal at δ 0.90 ppm. [e] 0 h. [f] 20 h. [g] Grignard.

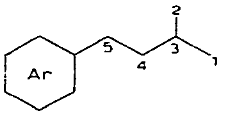
subsequent experiments with the tert-alkyl-Grignard containing internal standards, the peak areas (GLC) of the alkanes and alkenes were calculated with respect to dodecane $\equiv 1000$, and of the dimer with eicosane $\equiv 1000$. This gave the overall material balance and permitted the appropriate corrections to be made for the alkane, alkenes, and dimer present in the original alkyl-Grignard. In the experiments in the absence of internal standards, the relative percentages as determined by GLC are given.

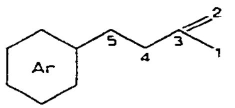
tert-Alkylmagnesium chloride with $CrCl_3(THF)_3$ ratio 3/1

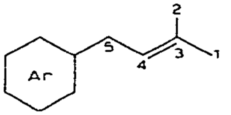
A solution of the tert-alkyl-Grignard (40 ml, 26 mmoles) (with internal standards) was added dropwise to a briskly stirred suspension of $CrCl_3(THF)_3$ (3.24 g, 8.7 mmoles) in tetrahydrofuran (50 ml) at −70°. The resulting red heterogeneous reaction mixture was allowed to warm to +20°; aliquots were withdrawn at −70 (after 1.5 h), −30, −15 and 0° and hydrolyzed. The final black heterogeneous reaction mixture was allowed to stand at +20° (19 h) then deuterolyzed. The hydrocarbons, isolated with the aid of ether, and estimated by GLC, are given in Table 2. The individual hydrocarbons from the deuterolysis were identified as 2-methyl-4-phenylbutane (D_0 100%; D_1 0.0%)*, 2-methyl-4-phenyl-1-butene and 2-methyl-4-phenyl-2-butene respectively by IR and NMR spectroscopies.

tert-Alkylmagnesium chloride and $CrCl_3(THF)_3$, ratio 3/1, deuterolysis

In an analogous experiment the tert-alkyl-Grignard (30 ml, 31.8 mmoles) without internal standards was added dropwise to a briskly stirred suspension of $CrCl_3(THF)_3$ (3.96 g, 10.6 mmoles) in tetrahydrofuran (100 ml) at −70°. After 12 h at −70° a clear red solution was obtained which was allowed to warm to +20°. Aliquots were withdrawn at −40, 0, 20 (0 h) and 20° (20 h) and added to deuterium oxide. The individual hydrocarbons isolated with the aid of ether, together with their relevant analytical data are given in Table 3. The numbering for the NMR data is:







The products from the different reactions are thus:

(1). At −40° the total alkane is a mixture of non- and monodeuteroalkane, correction of the non-deuterated alkane present in the alkyl-Grignard gives the major component (ca. 83%) as 2-deuterio-2-methyl-4-phenylbutane.

(2). At 0 and 20° (0 h) the alkane is again a mixture of alkane and 2-deuterio-2-methyl-4-phenylbutane.

(3). At 20° (20 h) the alkane is undeuterated 2-methyl-4-phenylbutane.

(4). In all experiments the alkenes consist of undeuterated 2-methyl-4-phenyl-1-butene and -2-butene respectively.

(5). In *no case* was there any evidence for the formation of the isomeric 2-methyl-4-phenyl-3-butene.

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* See footnote p. 107.

Fragmentation of the "tert-(2-methyl-4-phenylbutyl)chromium system", −70 to +20° with dodecane as internal standard

A solution of the tert-alkylchromium system [from the prolonged (16 h) interaction of the tert-alkyl-Grignard (40 ml 29.6 mmoles), containing dodecane, and $CrCl_3(THF)_3$ (3.69 g, 9.86 mmoles) in tetrahydrofuran (100 ml) at −70°] was allowed to warm slowly to +20°. Throughout this period aliquots (2 ml) were withdrawn, hydrolyzed and the hydrocarbons isolated with the aid of ether. The estimation of the hydrocarbons present was effected by GLC analysis. The relative peak areas were calculated with respect to dodecane ≡1000 thereby giving the overall material balance. The resulting areas were corrected for alkane and alkenes present in the tert-alkyl-Grignard used and the true relative percentages of the respective fragmentation and hydrolysis products calculated from these data. The results are summarized in Fig. 1. A control analysis on a silicone column indicated that only small amounts of dimer were formed during the fragmentation.

The total reaction mixture was hydrolyzed after it had stood at 20° (19 h). The individual hydrocarbons, isolated by preparative scale GLC consisted of 2-methyl-4-phenylbutane, 2-methyl-4-phenyl-1-butene, 2-methyl-4-phenyl-2-butene, identified by IR and NMR spectroscopies.

tert-Alkylchromium system with 1-decene

A suspension of the tert-alkylchromium system containing internal standards [from tert-alkyl-Grignard (20 ml, 13 mmoles) and $CrCl_3(THF)_3$ (1.6 g, 4.3 mmoles)] in tetrahydrofuran (50 ml) at −70° was treated at −70° with dry, oxygen and peroxide free 1-decene (10 ml). The whole was allowed to warm to +20°, and after 16 h the total reaction mixture was hydrolyzed. The hydrocarbons, isolated with the aid of ether, consisted of: C_{10} compounds, decane (6.5%), 1- and/or 3-decene (9.6%), *trans*-2-decene (59.8%), *cis*-2-decene (24.1%): C_{11} compounds 2-methyl-4-phenylbutane (40.4%), 2-methyl-4-phenyl-1-butene (45.7%), 2-methyl-4-phenyl-2-butene (13.9%)*. The *trans*-2-decene was isolated by preparative scale GLC and identified by IR spectroscopy. (ν_{max} 960 cm^{-1}). All the C_{11} compounds were isolated by preparative scale GLC and identified by NMR spectroscopy.

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* These figures represent relative percentages corrected for the alkane and alkene content of the original alkyl-Grignard.

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