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ALKYL-TRANSITION METAL COMPOUNDS IV*. FRAGMENTATION OF n- AND sec-ALKYLCHROMIUM COMPOUNDS

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SUMMARY

The tris(4-phenyl-n-butyl)- and tris(4-phenyl-sec-butyl)chromium systems undergo stepwise fragmentation on warming. At low temperatures the products, in both cases, are the alkane and terminal olefin. At higher temperatures they are alkane, 1- and 2-alkene, respectively, and a chromium based isomerization catalyst. Both (4-phenyl-n-butyl)- and (4-phenyl-sec-butyl)chromium dichlorides undergo fragmentation to alkane and terminal olefin. We conclude that the two fundamental processes of homolysis and β-metal hydride elimination are involved in the fragmentation of alkylchromium compounds.

INTRODUCTION

Sigma-bonded n-, sec- and tert-alkyl-transition metal compounds are key intermediates in many catalytic processes. It is customary in discussing the mechanisms of these processes not only to assume the stability sequence n- > sec- > tert- for the alkylmetal compound, but also to hypothesize that sec-alkylmetal compounds undergo metal hydride elimination to give internal olefins[2-7].

Thus in the metal hydride catalyzed isomerization of terminal olefins (and related reactions), the two initial steps are, the reversible formation of the n-alkylmetal compound [eqn. (1)], and the formation of the sec-alkylmetal compound [eqn. (2A)].

$$RCH_2CH{=}CH_2 + HM \rightleftharpoons RCH_2CH_2CH_2M \qquad (1)$$

$$RCH_2CH{=}CH_2 + HM \overset{A}{\rightleftharpoons} RCH_2CHMCH_3 \overset{B}{\rightleftharpoons} RCH{=}CHCH_3 + HM \qquad (2)$$

It is presumed[2-7], that though the latter process is reversible[8], the preferred fragmentation of sec-alkylmetal compounds is via metal hydride elimination to give the *internal olefin* [eqn. (2B)]. There is however very little chemical evidence concerning the actual products of fragmentation of σ-bonded alkylmetal compounds. Recent studies with specifically deuterated compounds[1] indicated that the fragmentation of

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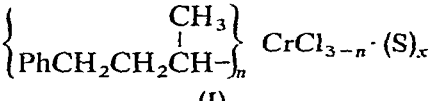
* For Part III see ref. 1.

tri-n-alkylchromium compounds involved the three fundamental processes of homolysis, β- and α-metal hydride elimination. It is therefore more realistic to consider the "stabilities" of alkylmetal compounds in terms of the factors influencing these processes. These fragmentation studies[1] also indicated that there was scrambling of deuterium over C_3, C_2 and C_1 in a 1,1-dideuterio-1-alkene, this, without double bond migration. Such an observation is not novel[9], but it does imply that sec-alkylmetal (chromium) compounds do undergo fragmentation to 1-alkene.

In order, therefore, to obtain definitive information concerning the actual products formed, the fragmentation of the (4-phenyl-sec-butyl)chromium systems [(I), $n=3$ and 1] were studied in detail. The corresponding (4-phenyl-n-butyl)chromium systems (II) and (III) were used as comparison standards*.



$$\left\{\mathrm{PhCH_2CH_2}\overset{\overset{\displaystyle \mathrm{CH_3}}{|}}{\mathrm{C}}\mathrm{H}-\right\}_n \mathrm{CrCl}_{3-n}\cdot(\mathrm{S})_x$$

(I)

$(\mathrm{PhCH_2CH_2CH_2CH_2})_3\mathrm{Cr}\cdot(\mathrm{S})_x$

(II)

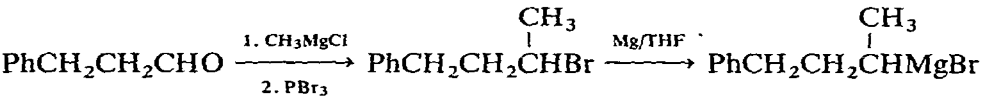
$\mathrm{PhCH_2CH_2CD_2CH_2CrCl_2}\cdot(\mathrm{S})_x$

(III)

RESULTS AND DISCUSSION

Control experiments

The purity of the starting alkylmagnesium bromides was established by hydrolyzing or deuterolyzing aliquots of the solutions used. Thus hydrolysis of the (4-phenylbutyl)- and (2,2-dideuterio-4-phenylbutyl)magnesium bromide gave respectively 4-phenylbutane (97.4%) and 2,2-dideuterio-4-phenylbutane (99.6%). Deuterolysis of the (4-phenyl-sec-butyl)magnesium bromide, prepared according eqn. (3), gave 2-deuterio-4-phenylbutane (92.0%).



$$\mathrm{PhCH_2CH_2CHO}\xrightarrow[\text{2. PBr}_3]{\text{1. CH}_3\text{MgCl}}\mathrm{PhCH_2CH_2}\overset{\overset{\displaystyle \mathrm{CH_3}}{|}}{\mathrm{C}}\mathrm{HBr}\xrightarrow{\text{Mg/THF}}\mathrm{PhCH_2CH_2}\overset{\overset{\displaystyle \mathrm{CH_3}}{|}}{\mathrm{C}}\mathrm{HMgBr}\qquad(3)$$

Deuterolysis of the derived tris(4-phenyl-n-butyl)- and tris(4-phenyl-sec-butyl)chromium systems, at zero time and after 20 h at 20° (see Experimental) confirmed that fragmentation is complete at this temperature. Whereas at zero time at +20° there are still some alkyl groups bonded to chromium, after standing at this temperature there are none (no deuteroalkane on deuterolysis).

The above experiments not only establish the purity of the starting materials but they also show that there is no H/D exchange at the hydrolysis (deuterolysis) and isolation steps.

Fragmentation of tris(4-phenyl-n-butyl)chromium system

A suspension of the triorganochromium compound, in tetrahydrofuran was allowed to warm from −40° to 19°. Aliquots were withdrawn periodically, hydrolyzed,

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* Throughout the text (S) represents tetrahydrofuran of solvation.

and the products analyzed. The results are summarized graphically in Fig. 1 (p. 457); the upper curves represent the percentages of the various hydrocarbons present in the total mixture at given time, the lower one, the temperature profile.

The steady concentrations of alkane and 1-alkene at −40° reflect the stability of the organochromium compound at this temperature.

The drop in total alkane content, paralleled by the rise in 1-alkene concentration, in the temperature range −40 to 0° proves that the fragmentation of the organochromium compound gives alkane and only 1-alkene [eqn. (4), $R = PhCH_2CH_2-$].

$$(RCH_2CH_2)_3Cr \cdot (S)_x \xrightarrow{-40 \text{ to } 0^\circ} RCH_2CH_3 + RCH{=}CH_2 \qquad (4)$$

At higher temperatures, 0° to 20°, the levelling off of the alkane concentration indicates that the fragmentation of the organochromium compound is complete [eqn. (5), $R = PhCH_2CH_2-$].

$$(RCH_2CH_2)_3Cr \cdot (S)_x \xrightarrow{0 \text{ to } 20^\circ} RCH_2CH_3 + RCH{=}CH_2 + \text{“HCr”} \qquad (5)$$

The fall in 1-alkene concentration, and rise in the concentration of the internal olefins is due to the isomerization of the former by the hydridochromium species generated [eqn. (6), $R = PhCH_2CH_2$].

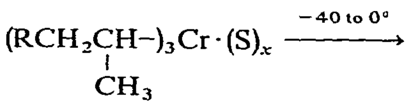
$$(RCH_2CH_2)_3Cr \cdot (S)_x \rightarrow \left\{ \begin{array}{l} RCH_2CH_3 \\ RCH{=}CH_2 \\ \text{“HCr”} \end{array} \right. \begin{array}{c} \\ \xrightarrow{\text{Isom}} \\ \\ \end{array} \begin{array}{l} RCH_2CH_3 \\ \text{Internal olefins} \\ \text{“HCr”} \end{array} \qquad (6)$$

These results are in keeping with a mechanism of fragmentation involving homolysis of a C–Cr bond and concerted metal hydride elimination. They do not indicate, however, whether the processes are concurrent or if the fragmentation is indeed stepwise.

Fragmentation of tris(4-phenyl-sec-butyl)chromium system

In an analogous experiment the fragmentation of the title compound was studied over the temperature range −40° to 20°. The results are summarized in Fig. 2 (p. 458); the upper curve represents the relative percentage of hydrocarbons, corrected for Grignard content, the lower one, the temperature profile.

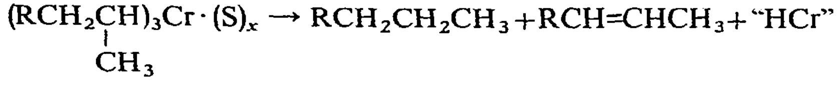
In the temperature range −40 to 0°, there is a steady build-up of 1-alkene, indicating an *initial* fragmentation to terminal olefin [eqn. (7), $R = PhCH_2-$].



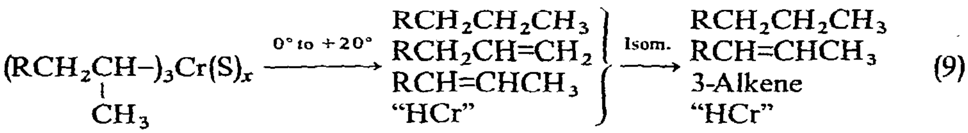
$$(RCH_2\underset{\displaystyle CH_3}{\underset{|}{C}}H-)_3Cr \cdot (S)_x \xrightarrow{-40 \text{ to } 0^\circ}$$

$$RCH_2CH{=}CH_2 + RCH_2CH_2CH_3 + \text{organochromium compound} \qquad (7)$$

From 0° to +20°, there is further fragmentation, this time to 2-alkene, [eqn. (8), $R = PhCH_2-$] and a chromium based catalyst which isomerizes the terminal and internal olefins to 3-alkenes [eqn. (9), $R = PhCH_2-$].



$$(RCH_2\underset{\displaystyle CH_3}{\underset{|}{C}}H)_3Cr \cdot (S)_x \rightarrow RCH_2CH_2CH_3 + RCH{=}CHCH_3 + \text{“HCr”} \qquad (8)$$



$$\underset{\displaystyle CH_3}{(RCH_2\overset{}{C}H\text{-})_3}Cr(S)_x \xrightarrow{0° \text{ to } +20°} \left.\begin{matrix} RCH_2CH_2CH_3 \\ RCH_2CH{=}CH_2 \\ RCH{=}CHCH_3 \\ \text{“HCr”} \end{matrix}\right\} \xrightarrow{\text{Isom.}} \begin{matrix} RCH_2CH_2CH_3 \\ RCH{=}CHCH_3 \\ \text{3-Alkene} \\ \text{“HCr”} \end{matrix} \qquad (9)$$

The presence of an isomerization catalyst in the reaction mixture makes it impossible to distinguish between fragmentation to 1-alkene and 2-alkene at temperatures above 0°. Furthermore there are certain inaccuracies inherent to sampling the reaction mixture at low temperatures. For these reasons, and because of the novelty of fragmentation of a sec-alkyl compound to a terminal olefin, more detailed deuterolytic studies were undertaken.

Deuterolysis of the tris(4-phenyl-sec-butyl)chromium system

In parallel experiments, suspensions or blue solutions of the organochromium compound were deuterolyzed, both immediately and after the system had stood for some time at −70, −40, −20, 0 and +20° respectively. The hydrocarbons formed were analyzed and the isotopic composition of the alkane determined by mass-spectrometry. The results, summarized in Table 1 indicate:

1. In the temperature range −70 to −20°, and at zero time at 0° and +20° fragmentation occurs to give alkane and 1-alkene plus some 2-alkene.
2. In the temperature rang −70 to −20°, and at zero time at 0° and +20° there are still alkyl-groups sigma-bonded to the chromium (deuteroalkane).
3. At 0° and +20°, the 1-alkene is isomerized, indicating the presence of an isomerization catalyst.
4. In the temperature range −20° to +20°, there is concomitant fragmentation to 2-alkene (and hydridochromium species).

In the absence of isolable intermediates any mechanism must remain specula-

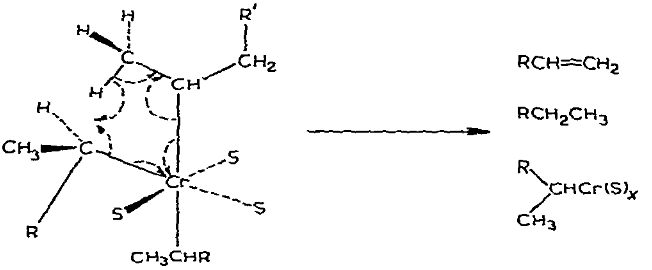
TABLE 1

HYDROLYSIS AND DEUTEROLYSIS PRODUCTS FROM SEC-ALKYL–CHROMIUM SYSTEM [(I), $n=3$]

System	Alkane				1-Alkene	2-Alkene[a]	3-Alkenes[a]
(temp/time)	Yield[b]	D_0[c]	D_1[c]	D_2[c]	yield[b]	yield[b]	yield[b]
Grignard (1)[d]	91.2	9.2	90.5	0.3	4.2	3.7	0.8
Grignard (2)[d]	92.0	11.0	89.0	0.0	4.3	3.7	0.0
Cr (−70/5 h)	89.1	22.1	77.9	0.0	7.0	3.8	0.0
Cr (−40/0 h)	90.3	[e]	[e]	[e]	6.9	2.8	0.0
Cr (−40/6 h)	86.7	24.9	75.1	0.0	7.6	5.7	0.0
Cr (−20/0 h)	87.2	[e]	[e]	[e]	6.2	6.6	0.0
Cr (−20/6 h)	87.3	29.5	70.5	0.0	5.2	7.4	0.0
Cr (0/0 h)	83.7	26.0	74.0	0.0	10.1	6.2	0.0
Cr (0/5 h)	80.3	42.1	57.9	0.0	1.8	17.6	0.0
Cr (20/0 h)[f]	84.7	59.7	40.0	0.3	9.2	5.9	0.0
Cr (20/20 h)[f]	60.8	98.8	0.6	0.6	1.5	29.4	7.8

[a] Major product was the *trans*-alkene. [b] Relative percentage in total hydrocarbon mixture. [c] Isotopic composition expressed in relative percentages, corrected for natural isotopic abundances. [d] Analysis of alkyl-Grignard, (1) at the start, (2) at the end of the series of experiments. [e] Not measured. [f] Gas evolution.

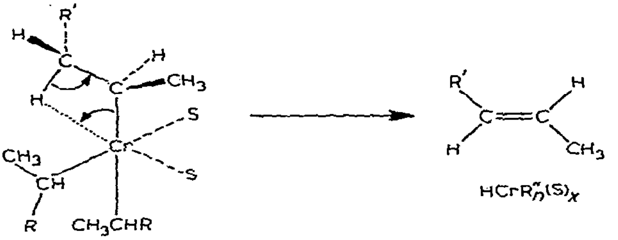
tive. The above facts, however, are in keeping with the fragmentation mechanisms, previously established for n-alkylchromium compounds[1], of homolysis and metal hydride elimination. Thus the *initial fragmentation* involves homolysis of the metal–carbon bond, and the organic radical thus produced can abstract hydrogen, from a second alkyl group, or solvent to give alkane and 1-alkene. This can take place either in monomeric species, via a five center transition state [eqn. (10), $R = PhCH_2CH_2$–],



(10)

$R = PhCH_2CH_2$—, $R' = PhCH_2$—

or in a dimeric species[1] (leading in this case to a dialkyl Cr^{II} species). It is therefore the relative ease of homolysis of a sec-C–Cr bond (as compared with an n-C–Cr one) which plays a determining role in this initial fragmentation, and not the relative C–H bond strengths (or polarity) in a $-CH_3$ and $-CH_2-$ group.



(11)

$R = PhCH_2CH_2$—, $R' = PhCH_2$—, $R'' = PhCH_2CH_2\overset{|}{C}HCH_3$, $n = 0,1$ or 2

The second (or concomitant) fragmentation involves β-metal hydride elimination via a four center transition state leading to *trans*- and *cis*-2-alkene, eqn. (11). In this instance differences in polarizability of the C–H bonds in the $-CH_2-$ and $-CH_3$ groups will play an important role in determining the products formed*.

Fragmentation of (2,2-dideuterio-4-phenyl-n-butyl)- and (4-phenyl-sec-butyl)chromium dichlorides [(III) and (I), (n = 1)]

Compelling evidence for the homolytic fragmentation of alkylchromium compounds has resulted from a study of the title systems. Thus when these compounds are warmed, in tetrahydrofuran solution to +30°, they undergo the homolytic process

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* The alternative theory that the 1-alkene is formed by β-metal hydride elimination (towards the $-CH_3$ group) is untenable, since the present results would imply that this is the preferred product of metal hydride elimination and therefore no isomerization would ever occur.

characteristic of monoorganochromium dihalides[10]. In the case of the specifically deuterated compound (III) the final hydrolysis products are given in eqn. (12), (R = $PhCH_2CH_2$–). Mass- and ^1H NMR-spectroscopies indicate that all the deuterium lost in olefin formation is found as trideuteroalkane.

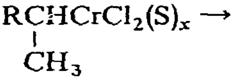
$$100\,RCD_2CH_2CrCl_2\cdot(S)_x \xrightarrow{\Delta}$$

$$50.8\,RCD_2CH_3+22.5\,RCD_2CH_2D+22.0\,RCD{=}CH_2 \qquad (12)$$

(No non-condensable gases)

This proves that in this homolytic process all of the alkene and part of the alkane are formed by the direct transfer of hydrogen.

The final hydrolysis products from the fragmentation of (4-phenyl-sec-butyl)-chromium dichloride are given in eqn. (13) (R = $PhCH_2CH_2$–).



$$R\underset{CH_3}{\underset{|}{C}}HCrCl_2(S)_x \xrightarrow{\Delta}$$

$$RCH_2CH_3(62.6\%)+RCH{=}CH_2(27.1\%)+\text{Other alkenes}\ (10.1\%) \qquad (13)$$

(No non-condensable gases)

The predominant formation of 1-alkene in this instance proves that the homolytic fragmentation of sec-alkylchromium compounds does indeed lead to terminal olefin.

All the foregoing results show that the two processes of homolysis and metal hydride elimination are intimately involved in the fragmentation both of n- and of sec-alkylchromium (and other transition metal?) compounds. Therefore the mechanisms of catalytic processes (isomerization, oligomerization etc.) involving, in particular, the sec-alkylmetal species should be reconsidered in terms of the factors influencing these two processes.

EXPERIMENTAL (with Mrs. A. Brink and Miss U. Feisst)

The general techniques used in the preparation and handling of organometallic compounds, and for product analysis have already been described[11].

1. *4-Phenyl-2-hydroxybutane; 4-phenyl-sec-butanol*

Freshly distilled dihydrocinnamaldehyde (65 ml, 0.5 mole) was added dropwise to a cooled, stirred, solution of methylmagnesium chloride [from CH_3Cl (25 ml, 0.5 mole) and magnesium (13.1 g, 0.54 mole)] in tetrahydrofuran (200 ml). When the addition was complete, the reaction mixture was allowed to warm to room temperature, poured on to ice, and acidified with ice cold HCl (10%). The organic material, isolated with the aid of ether, was thoroughly washed with Na_2CO_3 (5%), dried ($MgSO_4$) and distilled. In this way 4-phenyl-2-hydroxybutane (56.4 g), b.p. 75°/0.3 mm, n_D^{20} 1.5178 was obtained. δ_{TMS}, 7.06 (5 protons, C_6H_5–), 3.68 (sextet, $J=6$ cps, 1 proton, –CH–), 3.58 (singlet, 1 proton, –OH), 2.63 (multiplet, 2 protons, $PhCH_2$–), 1.67 (multiplet, 2.0 protons, $-CH_2-$), 1.13 (doublet, $J=6$ cps, 3 protons, $-CH_3$).

2. *4-Phenyl-2-brombutane*; *4-phenyl-sec-butylbromide*

Phosphorous tribromide (15 ml, 0.16 mole) was added dropwise to the stirred and cooled (−5°) alcohol prepared above (56.4 g). When the addition was complete the whole was allowed to warm to room temperature and the homogeneous reaction mixture warmed gently in the hot-water-bath until two separate layers were formed. The cooled mixture was poured on to ice and the organic halide isolated with aid of hexane. The hexane extract was washed thoroughly with NaOH (5%), water and dried ($MgSO_4$) and subsequently distilled. In this way 4-phenyl-2-bromobutane (71.1 g), b.p. 60–65°/0.2 mm, n_D^{20} 1.5340 was obtained. (Found: C, 56.4; H, 6.2; Br, 37.4. $C_{10}H_{13}Br$ calcd.: C, 56.4; H, 6.1; Br, 37.5%.) δ_{TMS} 7.09 (5 protons, C_6H_5–), 3.92 (sextet, $J=6$ cps, 0.9 protons, –CHBr), 2.73 (multiplet, 2.00 protons, $PhCH_2$–), 1.97 (multiplet, 1.99 protons, $-CH_2-$), 1.63 (doublet, $J=6$ cps, 2.97 protons, $-CH_3$).

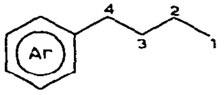
3. *Control experiments*

(*a*). *Hydrolysis of* (*4-phenyl-n-butyl*)- *and* (*2,2-dideuterio-4-phenylbutyl*)*magnesium bromides.* Aliquots (5 ml) of the solutions of the non-deuterated (A) and specifically deuterated (B) alkyl-Grignards used in the subsequent experiments were hydrolyzed at 0°. The hydrocarbons, isolated with the aid of ether, were shown by gas-chromatographic mass-* and ^1H NMR-spectroscopic analyses to consist of: (A): 4-phenylbutane (97.4%) and 4-phenyl-1-butene (2.5%); (B): 2,2-dideuterio-4-phenylbutane (99.6%); D_0 0.0, D_1 3.5, D_2 96.3, D_3 0.2%; ν_{max} 2112, 2174, 2220 cm^{-1}; δ_{TMS} 7.08 (5 protons, C_6H_5–), 2.53 (2 protons, $PhCH_2$–), 1.54 (2 protons, $-CH_2CD_2-$), 0.89 (3 protons, $-CH_3$), and a deuterio-4-phenyl-1-butene (0.38%).

(*b*). *Deuterolysis of* (*4-phenyl-sec-butyl*)*magnesium bromide.* Two aliquots of

TABLE 2

^1H NMR AND IR SPECTRA OF DEUTERIO-4-PHENYLBUTANES FROM THE $(PhCH_2CH_2\underset{CH_3}{CH})_3Cr\cdot(S)_x$ SYSTEM



System (temp/time)	Number of protons per average molecule[a] Ar				ν_{max} (2220–2140 cm^{-1})
	Ar	C_4	C_3 and C_2	C_1	
Reference	5.00	2.00	4.00	3.00	No adsorbtion
Grignard (1)	5.00	1.97	3.01	2.97	2151, 2141, 2174 (sh)
Grignard (2)	5.00	2.09	3.1	3.1	2151, 2141, 2174 (sh)
Cr (−70°/5 h)	5.00	1.98	3.21	2.95	2151, 2141, 2174 (sh)
Cr (−40°/6 h)	5.00	1.99	3.21	2.98	2150, 2140, 2172 (sh)
Cr (−20°/6 h)	5.00	1.97	3.31	3.09	2149, 2139, 2171 (sh)
Cr (0°/0 h)	5.00	1.99	3.33	2.92	2150, 2140, 2172 (sh)
Cr (0°/5 h)	5.00	2.00	3.47	2.97	2148, 2138, 2170 (sh)

[a] The relevant δ_{TMS} values for the respective protons are 7.06 (C_6H_5=Ar), 2.52 ($PhCH_2=C_4$), 1.49 [CH_2-$CH\binom{H}{D}=C_3$ and C_2], 0.89 ($CH_3=C_1$).

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* The isotopic compositions, corrected for natural isotopic abundances were determined mass-spectrometrically by Dr. W. E. Koerner and his associates, Research Center, Monsanto Company, St. Louis, U.S.A.

the alkyl-Grignard reagent used in the deuterolytic studies below, the one taken at the start of the experiments (1), the other at the end (2), were deuterolyzed. The hydrocarbons isolated with the aid of ether are listed in Table 1. The alkanes, isolated by preparative scale gas chromatography were shown, by mass-spectrometry (Table 1), ^{1}H NMR and IR spectroscopy (Table 2) to consist, in both cases, of 2-deuterio-4-phenylbutane, together with small quantities of undeuterated species.

(*c*). *Deuterolysis of tris(4-phenyl-n-butyl)chromium system at* 20° (0 *and* 20 *h*). In two parallel experiments a suspension of tris(4-phenylbutyl)chromium [from the alkyl-Grignard (30 ml, 23.4 mmoles) and $\mathrm{CrCl_3 \cdot (THF)_3}$ (2.92 g, 7.8 mmoles) in tetrahydrofuran (100 ml) at −70° to −40°] was allowed to warm from −40° to 20°. In one case the resulting dark solution was deuterolyzed after one hour at 20°, in the other after 20 h. In both cases the hydrocarbons thus formed were isolated with the aid of ether and analyzed by GLC.

Exp. 1 (1 h): alkane (69.1%), 1-alkene (1.6%), *trans*-2-alkene (23.1%), *cis*-2-alkene (4.3%), *trans*- and *cis*-3-alkene (1.9%).

Exp. 2 (20 h): alkane (66.7%), 1-alkene (0.6%), *trans*-2-alkene (14.0%), *cis*-2-alkene (3.1%), *trans*- and *cis*-3-alkene (15.6%).

The alkane from Exp. 1 had δ_{TMS} 7.08 (5 protons, $\mathrm{C_6H_5}$–), 2.53 (2.04 protons, $\mathrm{PhCH_2}$–), 1.54 (3.94 protons, $\mathrm{CH_2CH_2}$–), 0.89 (2.52 protons, $\mathrm{CH_2}\binom{\mathrm{H}}{\mathrm{D}}$); ν_{max} 2178 cm^{-1} (alkyl C–D), mass-spectrum* (D_0 65.6%, D_1 33.9, D_2 0.3, D_4 0.2%) indicating that it was a mixture of 4-phenylbutane and 1-deuterio-4-phenylbutane.

The *trans*- and *cis*-2-alkenes and *trans*-3-alkene from experiment 1 were shown, from their ^{1}H NMR and IR spectra to contain no extra deuterium.

The alkane from experiment 2 was shown from its mass-spectrum* (D_0 99.6, D_1 0.3, D_2 0.1%) and its ^{1}H NMR and IR spectra to consist entirely of 4-phenylbutane.

Similarly the ^{1}H NMR and IR spectra of the *trans*-2-alkene and *trans*- and *cis*-3-alkenes indicated that these compounds were not enriched in deuterium.

(*d*). *Deuterolysis of tris(4-phenyl-sec-butyl)chromium system at* 20° (0 *and* 20 *h*). In an analogous experiment the clear purple solution of the title compound [from alkyl-Grignard (50 ml, 16 mmole) and $\mathrm{CrCl_3 \cdot (THF)_3}$ (1.98 g, 5.3 mmole) in THF (50 ml) at −70°] was allowed to warm from −40° to +20°. In one case the resulting black solution was deuterolyzed upon reaching 20° in the other after 20 h at 20°. The hydrocarbons, isolated with the aid of ether, are listed in Table 1.

The alkane from the experiment 0 h at 20° had the isotopic composition given in Table 1 and had ν_{max} 2178 (alkyl C–D) and δ_{TMS} 7.08 (5 protons, $\mathrm{C_6H_5}$–), 2.53 (1.96 protons, $\mathrm{PhCH_2}$–), 1.54 (3.66 protons, $-\mathrm{CH_2CH}\binom{\mathrm{H}}{\mathrm{D}}-$), 0.92 (3.00 protons, $-\mathrm{CH_3}$), indicating that it was a mixture of 4-phenylbutane and 2-deuterio-4-phenylbutane.

The alkane from the experiment 20 h at 20° was shown from its mass-spectrum* (Table 1) and its IR and ^{1}H NMR spectra to consist entirely of 4-phenylbutane.

4. *Fragmentation of the tris(4-phenyl-n-butyl)chromium, −70° to +20° with dodecane as internal standard*

A solution of (4-phenylbutyl)magnesium bromide (50 ml, 35 mmoles) contain-

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* See footnote page 455.

ing dodecane was added slowly* (1 h) to a briskly stirred suspension of $CrCl_3 \cdot (THF)_3$ (4.34 g, 11.6 mmoles) in tetrahydrofuran at −70°. The rection mixture was allowed to warm to −40° (1 h) the starting point of the reaction. The reaction mixture was kept at −40° for $\frac{1}{2}$ hour, and then allowed to warm gradually (1.5 h) to 0° (ice water bath) and finally to 20° (7.75 h). Throughout this period aliquots (2 ml) were withdrawn periodically; the samples were hydrolyzed and the hydrocarbons (isolated with the aid of ether) identified and estimated by GLC**. The results obtained concerning the appearance of the respective hydrocarbons are given in Fig. 1.

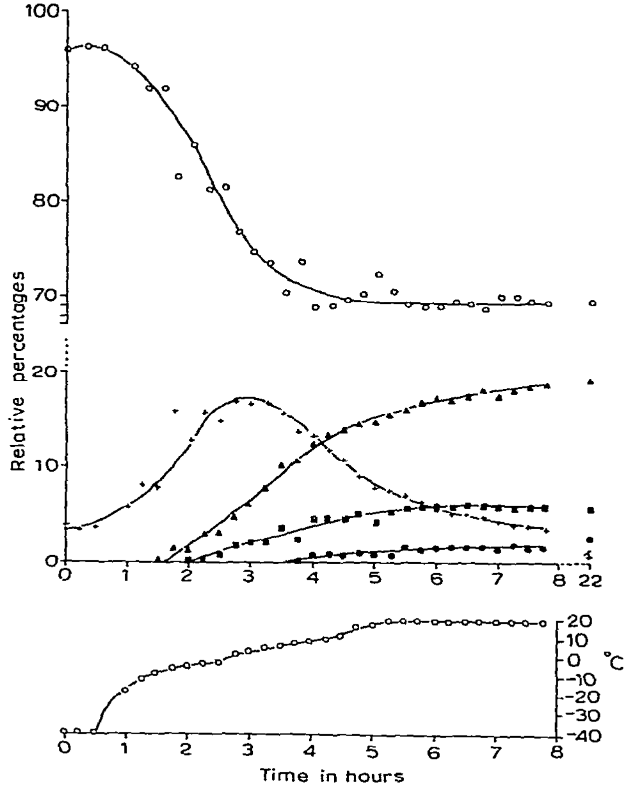

Fig. 1. Fragmentation of $(PhCH_2CH_2CH_2CH_2)_3Cr \cdot (THF)_n$ in THF. Dodecane as internal standard. ○, 4-phenylbutane; +, 4-phenyl-1-butene; ▲, *trans*-1-phenyl-2-butene; ■, *cis*-1-phenyl-2-butene; ●, *trans*-1-phenyl-1-butene ("3-alkene").

The reaction mixture was allowed to stand overnight and then hydrolyzed. The hydrocarbons thus formed (Fig. 1, 22 h) were isolated by preparative scale gas chromatography and identified as 4-phenylbutane, 4-phenyl-1-butene, *trans*- and *cis*-1-phenyl-2-butene and *trans*-1-phenyl-1-butene by ^1H NMR and IR spectroscopies.

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* It has been observed that despite intensive external cooling (CO_2/Acetone slurry) a too rapid addition of alkyl-Grignard causes a marked increase (−70° to −50°) in the temperature of the contents within the flask.

** The procedure adopted for the estimation of the hydrocarbons present was to normalize all the relevant peak areas on dodecane = 1000 in order to check the material balance. The relative percentages of phenylbutane and -butenes were subsequently calculated from these values.

5. *Fragmentation of the tris(4-phenyl-sec-butyl)chromium system*

In an analogous experiment a suspension of the title compound [from alkyl-Grignard (50 ml, 20.5 mmole containing dodecane) and CrCl$_3$·(THF)$_3$ (2.56 g, 6.83 mmole)] in tetrahydrofuran (50 ml) was allowed to warm from −70° to −40° (1 h). The resulting clear blue solution was warmed slowly (3.5 h) to +20° and kept at this temperature for (3 h). Throughout this time aliquots (2 ml) were withdrawn, hydrolyzed, and the hydrocarbons present identified and estimated by GLC*. The results obtained are given in Fig. 2.

The final black reaction mixture was allowed to stand overnight and then hydrolyzed. The hydrocarbons thus formed (Fig. 2, 22 h) were isolated by preparative scale gas chromatography and identified (by ^{1}H NMR and IR spectroscopies) as 4-phenylbutane, *trans*- and *cis*-1-phenyl-2-butenes and *trans*-1-phenyl-1-butene.

6. *Deuterolysis of tris(4-phenyl-sec-butyl)chromium system at various temperatures*

In a series of parallel experiments, suspensions and solutions of the title compound [from alkyl-Grignard (50 ml, 16 mmole) and CrCl$_3$·(THF)$_3$ (1.98 g, 5.3 mmole) in THF (50 ml) prepared at −70°] were deuterolyzed after various times at different temperatures. Thus:

After 5 h at −70°, MeOD (5 ml) was added; at zero time at −40° and after 6 h at −40°, at zero time at −20° and after 6 h at −20° MeOD (5 ml) was added in

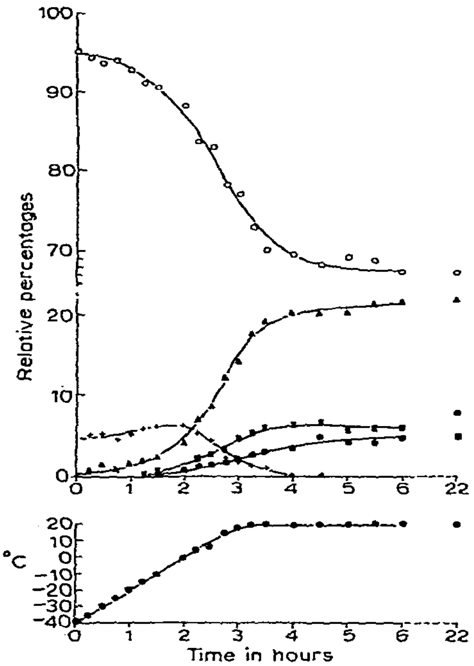

Fig. 2. Fragmentation of [PhCH$_2$CH$_2$CH(CH$_3$)]$_3$Cr·(THF)$_n$ in THF. Dodecane as internal standard. ○, 4-phenylbutane; +, 4-phenyl-1-butene; ▲, *trans*-1-phenyl-2-butene; ■, *cis*-1-phenyl-2-butene; ●, *trans*-1-phenyl-1-butene ("3-alkene").

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* See footnote page 457.

each case; at zero time at 0° and after 5 h at 0° D_2O (5 ml) was added. In each case the resulting solutions were allowed to stand overnight at the respective temperatures in order to ensure complete deuterolysis. The individual reaction mixtures were then allowed to warm to +20°, poured into water and the organic material isolated with the aid of ether. The individual hydrocarbons thus isolated together with the isotopic compositions of those alkanes isolated by preparative scale GLC, are given in Table 1. This data together with the ^1H NMR spectra and IR spectra (Table 2) indicated that the alkane in all the experiments consisted of mixtures 4-phenylbutane and 2-deuterio-4-phenylbutane. The 1-alkene and *trans*-2-alkene from the experiments at 0°, 0 h and 5 h respectively were shown by ^1H NMR and IR spectroscopies to contain no additional deuterium.

7. *Fragmentation of* (*2,2-dideuterio-4-phenylbutyl*)*chromium dichloride*

A clear green solution of the title compound [from the specifically deuterated alkyl-Grignard* (50 ml, 18 mmole) and $CrCl_3 \cdot (THF)_3$ (6.72 g, 18 mmole) in tetrahydrofuran at −70°] was allowed to warm to 20° then heated to 30°. During this time a copious off-white precipitate was formed and the colour of the solution gradually faded. The total mixture was finally hydrolyzed and the hydrocarbons isolated with the aid of ether consisted of deuterio-4-phenylbutane (75%), deuterio-4-phenyl-1-butene (22.5%), deuteriotetralin (2.3%).

The alkane: mass-spectrum** D_0 0.0, D_1 2.3, D_2 67.7, D_3 30.0; δ_{TMS} 7.08 (5 protons, C_6H_5–), 2.53 (2.01 protons, $PhCH_2$–), 1.54 (2.01 protons, $-CH_2CD_2-$) 0.89 (2.63 protons, $-CH_2(^{H}_{D})$); ν_{max} 2105, 2123 (sh), 2174, 2198 (sh) cm^{-1}, consisted of 2,2-dideuterio- and 1,2,2-trideuterio-4-phenylbutane.

The alkene: mass spectrum** D_0 1.5, D_1 98.0, D_2 0.5, D_3 0.0; δ_{TMS} 7.09 (5 protons, C_6H_5–), 4.93 (1.99 protons, $=CH_2$), 5.8 (0.0 protons, $-CD=$) 2.55 (3.96 protons, allylic and benzylic CH_2); ν_{max} 2227 cm^{-1}, consisted of 2-deuterio-4-phenyl-1-butene.

8. *Fragmentation of* (*4-phenyl-sec-butyl*)*chromium dichloride*

In an analogous experiment with the clear green solution of the title compound [from alkyl-Grignard (50 ml, 15 mmoles) and $CrCl_3 \cdot (THF)_3$ (5.62 g, 15 mmoles) in tetrahydrofuran (100 ml) at −70°] from −70 to +30°, the final hydrocarbons after hydrolysis consisted of 4-phenylbutane (62.6%), 4-phenyl-1-butene (27.1%), *trans*-1-phenyl-2-butene (6.2%), *cis*-1-phenyl-2-butene (3.5%), 1-phenyl-1-butene (0.5%). The alkane, 1-alkene and *trans*-2-alkene were isolated by preparative scale gas chromatography and identified by a direct comparison of their ^1H NMR and IR spectra with those of authentic specimens.

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* For the preparation of the specifically deuterated alkyl-Grignard see reference 12.

** See footnote page 455.

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