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ALKYLTRANSITION METAL COMPOUNDS
I*. n-ALKYLCHROMIUM SYSTEMS: DEUTEROLYSIS

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SUMMARY

Deuterolytic and hydrolytic studies with the n-decyl- and (4-phenylbutyl)-chromium systems indicate that the interaction of the appropriate stoichiometric ratios of an alkylmagnesium halide and $CrCl_3(THF)_3$ leads to the formation of monodecylchromium dihalide and solvated tri-n-alkylchromium compounds. The latter are unstable and on warming undergo fragmentation to a system which will isomerize terminal olefins. The initial fragmentation products have been shown to contain a hydridochromium species and unequal quantities of n-alkane and n-1-alkene.

INTRODUCTION

σ-Bonded alkyl derivatives of transition metal compounds have been proposed as key intermediates in many catalytic processes[1,2,3]. However, surprisingly little is known about the stabilities and reactions of simple solvated alkyl metal derivatives of the first row transition metal compounds. In the case of chromium the interaction of alkylmagnesium halides and chromium trichloride has been investigated sporadically[4,5,6] over the years. More recently it was shown that the reaction leads in fact to the formation of trialkylchromium complexes[7,8] (eqn. 1, where $R=CH_3$ and CH_2CH_3). The compounds were reported to be unstable at room temperature, and their reactions with disubstituted acetylenes[7,8] and ketones were described[9]. The present investigation is concerned with the preparation and properties of solvated σ-bonded n-decyl- and (4-phenylbutyl)chromium compounds. Deuterolytic studies of these systems were chosen not only because the expected products, n-alkanes and n-alkenes were amenable to rapid gas chromatographic analysis but also because previous work[10] had established the value of deuterolysis for distinguishing between products formed by homolytic and hydrolytic processes, *i.e.* the former are found as non-deuterated species and the latter as monodeuterated.

$$3\,RMgX + CrCl_3(THF)_3 \xrightarrow[-60^\circ]{THF} R_3Cr(THF)_n + 3\,MgXCl \qquad (1)$$

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* Part of the material in this paper was presented at the 9th International Conference on Coordination Chemistry, St. Moritz-Bad, Switzerland, September 1966. Proceedings page 172, and part at the Symposium on Allyl and Olefin Complexes of Metals, University of Sheffield, England, April 1967.

MONODECYLCHROMIUM SYSTEM

Equimolar ratios of decylmagnesium chloride and $CrCl_3(THF)_3$ interact in tetrahydrofuran between −70 and −20° to give a clear green solution (Gilman test No. I, negative) which on treatment with mercuric chloride gives decylmercuric chloride (70%). The hydrocarbons isolated after methanolysis of the green solution at −20° were decane and 1-decene (Table 1, expt. 2) and after deuterolysis at +20° were partially deuterated decane and 1-decene (Table 1, expt. 3). Solid solvated monodecylchromium dichloride gives monodeuterodecane containing some decane on deuterolysis (Table 1, expt. 4). Heating the solution of monodecylchromium dichloride under reflux gave after hydrolysis, decane, 1-decene and solvated $CrCl_2$ (Table 1, expt. 5).

TABLE 1

HYDROCARBONS FROM DECYLMAGNESIUM AND -CHROMIUM SYSTEMS AFTER HYDROLYSIS AND DEUTEROLYSIS[a]

No.	System ($R=C_{10}H_{21}$)	Final react. temp. (°C)	Hydrocarbons							
			Decane			1-Decene		*trans*-2-Decene		*cis*-2-Decene
			total[b]	D_0[c]	D_1[c]	total[b]	D_0[c]	total[b]	D_0[c]	total
1	RMgX	20	97	3	97	2	[d]	0		0
2	$RCrCl_2(THF)_n$	−20	84	[d]	[d]	15	[d]	0		0
3	$RCrCl_2(THF)_n$	20	84	64	36	15	100	0		0
4	$RCrCl_2(THF)_n$ solid	20	97	26	74	3	[d]	0		0
5	$RCrCl_2(THF)_n$	65	75	[d]	[d]	24	[d]	0		0
6	RMgX	20	98	4.7	95.3	1.0	[d]	0		0
7	$R_3Cr(THF)_n$	−40	89	24	76	9	99	0		0
8	$R_3Cr(THF)_n$[e]	20/4h	76	[d]	[d]	10	[d]	10	[d]	3
9	$R_3Cr(THF)_n$[e]	20/2½h	75.0	98.9	1.1	10.7	99	8.8	98.9	3.8
10	$R_3Cr(THF)_n$[e,f]	20/20h	70	[d]	[d]	2.3	[d]	19	[d]	6

[a] In every experiment 1–2% of eicosane, corresponding to that present in the RMgX solution was also found. [b] Expressed in relative percentages of total decane and decenes present. [c] Relative percentages, determined by mass spectrometry and corrected for natural isotopic abundances. [d] Not measured. [e] The non-condensable gases formed in these hydrolyses/deuterolyses were collected and analyzed (see *Experimental*). [f] In this experiment small quantities (2.7%) of other isomeric decenes were formed (see *Experimental*).

The above facts indicate that equimolar ratios of n-decylmagnesium chloride and $CrCl_3(THF)_3$ interact, in tetrahydrofuran, to give finally the very soluble, solvated monodecylchromium dichloride (eqn. 2). In solution the compound is

$$C_{10}H_{21}MgCl + CrCl_3(THF)_3 \xrightarrow[-70\text{ to }-10^\circ]{\text{THF}} C_{10}H_{21}CrCl_2(THF)_n + MgCl_2 \quad (2)$$

moderately stable at 0° undergoing slow homolysis at 20° and rapid homolysis at +65° (eqn. 3). The consistent formation of small quantities of 1-decene in the original

$$C_{10}H_{21}CrCl_2(THF)_n \xrightarrow{\Delta} C_{10}H_{22} + C_{10}H_{20} + CrCl_2(THF)_n \quad (3)$$

reaction can be ascribed to a competing fragmentation of the tridecylchromium compound, an intermediate in the formation of the monodecyl compound (eqns. 4, 5 and 7) (7 see later).

$$3\ C_{10}H_{21}MgCl+CrCl_3(THF)_3 \xrightarrow{\text{rapid}} (C_{10}H_{21})_3Cr(THF)_n+3\ MgCl_2+2\ CrCl_3(THF)_3 \quad (4)$$

$$(C_{10}H_{21})_3Cr(THF)_n+2\ CrCl_3(THF)_3 \rightarrow 3\ C_{10}H_{21}CrCl_2(THF)_n \quad (5)$$

TRIDECYLCHROMIUM SYSTEM

Decylmagnesium chloride and $CrCl_3(THF)_3$, ratio 3 : 1, interact in tetrahydrofuran between -70 and $-40°$ to give a red-brown solution, or suspension depending on the final concentration. The hydrocarbons isolated after deuterolysis of the solvated organochromium compound at $-40°$ consist of decane and 1-decene (Table 1, expt. 7). When the solution is allowed to warm to 20° it becomes homogeneous and black. The products isolated after deuterolysis now consist of H_2, HD, D_2, decane and isomeric decenes (Table 1, expt. 9). The percentage of monodeuterodecane present in the decanes isolated in these experiments indicate that the initial reaction led to the formation of a solvated tridecylchromium (eqn. 1, $R=C_{10}H_{21}$). This compound is moderately stable at $-40°$ but undergoes fragmentation at 20° to alkane and alkene. Few, if any, of the decyl groups originally present remain bonded to the chromium at 20°. In the deuterolysis at $-40°$, 1-decene is the only olefin present, while at 20° *trans*- and *cis*-2-decene are also present. This implies either that the isomeric olefins are formed by the fragmentation process (eqn. 6) or that the fragmentation of the tridecylchromium leads to decane, 1-decene and a catalyst system. The latter subsequently isomerizes the terminal olefin to the observed products (eqn. 7). The latter interpretation is supported by the observation that when the reaction mixture is allowed to stand for 20 h at 20°, the hydrocarbons isolated after deuterolysis contain small quantities of other isomeric decenes, probably *trans*-5-, *trans*-4- and *trans*-3-decene. The fact that 1-dodecene is isomerized to *trans*-2-dodecene (and smaller quantities of other isomeric olefins, see *Experimental*) by the tridecylchromium system proves that the original solvated tridecylchromium undergoes fragmentation, on warming, to a catalyst system capable of isomerizing added terminal olefin*.

$$(C_{10}H_{21})_3Cr(THF)_n \xrightarrow{\Delta} C_{10}H_{22}+\text{isomeric decenes} \quad (6)$$

$$(C_{10}H_{21})_3Cr(THF)_n \xrightarrow{\Delta} C_{10}H_{22}+[\text{1-decene/catalyst}] \rightarrow \text{decane}+\text{isomeric decenes} \quad (7)$$

The catalyzed (UV) and non-catalyzed fragmentation of trialkylchromium compounds has been variously described as involving the formation, via a radical process, of equal quantities of alkane and alkene and an "active chromium species" or colloidal metal respectively[4,5,6,11]. The present work with the tri-n-decyl- and

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* Control experiments with n-decylmagnesium chloride solution and the earlier experiments with the monodecylchromium system exclude the possibility that the observed isomerization is caused by the n-alkylmagnesium halide[12], magnesium halide or chromous salts.

tris(4-phenylbutyl)chromium systems (see *Experimental*) has shown that the alkane and alkene are formed not in equal amounts but in the approximate ratio of 2:1. Also the formation of hydrogen deuteride, in the deuterolysis of the decylchromium system is evidence for the presence of a hydridochromium species among the fragmentation products.

The evidence now points to a fragmentation of the tridecylchromium system to decane, a hydridochromium species and probably only 1-decene. On warming the latter is isomerized and the hydridochromium species either undergoes decomposition or is consumed in the reaction. The deuterolytic studies further reveal that the decane is formed by a homolytic or hydrogen transfer process.

In order to discuss the origins of the alkene it is first necessary to know whether or not the terminal olefin is the only olefin formed on fragmentation of the trialkylchromium compound. Since gas chromatographic analysis with Carbowax 20 M columns does not separate quantitatively the simple n-1-alkenes from the *trans*-3-alkenes (this applies also to the heptenes, octenes and decenes) similar experiments with the (4-phenylbutyl)chromium system were carried out*. These indicated that after two hours at 20° the olefins present consisted mainly of 4-phenyl-1-butene together with traces of the isomeric olefins. After four hours at 20° the majority of the terminal olefin was converted to *trans*- and *cis*-1-phenyl-2-butene (see *Experimental*).

It seems probable therefore that the initial fragmentation of the trialkylchromium compound does indeed give the terminal olefin. This can arise either by a radical abstraction process (eqn. 8) or by an α- or β-elimination of metal hydride (eqns. 9 and 10). Further experiments are in hand to clarify this point and to determine the origins of the hydrogen required for the formation of the hydridochromium species.

$$2\,RCH_2CH_2^{\cdot} \rightarrow RCH_2CH_3 + RCH{=}CH_2 \tag{8}$$

$$\text{“}RCH_2CH_2Cr\text{”} \rightarrow RCH{=}CH_2 + \text{“}HCr\text{”} \tag{9}$$

$$\text{“}RCH_2CH_2Cr\text{”} \rightarrow (RCH_2CH{:}\!\rightarrow RCH{=}CH_2) + \text{“}HCr\text{”} \tag{10}$$

EXPERIMENTAL
(with Miss U. FEISST)

For general techniques involving the handling of organometallic compounds see earlier papers[13,14]. Gas chromatographic analyses were carried out on F & M Model 5750 using the columns: Carbowax 20 M, 20%, Bis(methoxyethyl) adipate 20% and Silicone rubber. Preparative scale gas chromatography was carried out on Carbowax 20 M, 20% or Tricresyl phosphate 20% columns. The n-decyl chloride was redistilled and showed only one peak on gas chromatographic analysis on Silicone rubber, Carbowax 20 M and Tricresyl phosphate columns. The n-1-dodecene was redistilled from sodium under argon, and was shown to be pure both by infra-red and gas chromatographic analysis. Infrared spectra were obtained using a Grubb–Parsons "Spectromaster", the frequencies used to characterize the olefins were $-CH{=}CH_2$, 1818, 1644, 992 and 909 cm^{-1}, *trans*-$CH{=}CH-$ 968 cm^{-1}, *cis*-$CH{=}CH-$

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* Isomeric 1-phenylbutenes are readily separated, even on a preparative scale, on a Carbowax 20 M column.

699 cm^{-1}. The decylmagnesium chloride was prepared in the conventional manner in tetrahydrofuran solution. In the following deuterolytic experiments, controls were carried out using the decyl-Grignard, quantitative yields of monodeuterodecane of purities (97.0, 95.3 and 93%) were obtained*.

Identification of products

In expts. 2 and 8 (Table 1) the hydrocarbons were isolated by gas chromatography. The decane, 1-decene and *trans*-2-decene were identified by mass spectroscopy and by a comparison of their infra-red and NMR spectra with those of authentic specimens. The *cis*-2-decene was identified by its infrared spectrum and gas chromatographic retention time. In all other experiments the hydrocarbons present were identified by their gas chromatographic retention times. Any further individual controls are mentioned in the *Experimental Section*.

Decylmagnesium chloride, $CrCl_3(THF)_3$, ratio 1 : 1, in THF

A solution of decylmagnesium chloride (10 ml, 8.24 mmoles) in tetrahydrofuran was added to a briskly stirred suspension of $CrCl_3(THF)_3$ (3 g, 8.2 mmoles) in tetrahydrofuran (50 ml) at −70°. After ½ h at this temperature the reaction mixture was heterogeneous and dark brown in color. On warming to −40 then −20° a homogeneous green solution was slowly formed (14 h). The Gilman color test No. 1 was negative.

(*a*). *Reaction with mercuric chloride*, was effected by treating the homogeneous solution of the organochromium compound with a solution of mercuric chloride (8.59 g, 33 mmoles) in tetrahydrofuran. After stirring for 24 h most of the solvent was removed by distillation under reduced pressure. The crude material was washed thoroughly with water, dried and crystallized from xylene. In this way n-decylmercuric chloride (2.203 g, 70%), m.p. and mixed m.p. 113–114°, was obtained.

(*b*). *Methanolysis at* −20°. Methanol (10 ml) was added to the reaction mixture prepared above, and the hydrocarbons (Table 1, expt. 2), extracted with ether. They were subsequently isolated by gas chromatography and identified as decane and 1-decene by infrared and NMR spectroscopy.

(*c*). *Deuterolysis at* 20°, was effected by treating the solution of organochromium compound with D_2O (10 ml). The hydrocarbons, identified by gas chromatography, are given in Table 1, expt. 3. The decane and 1-decene isolated by preparative scale gas chromatography were shown by mass spectrometry to have the isotopic composition* given in Table 1, expt. 3. The decane had ν_{max} 2175 cm^{-1}, alkyl C–D.

(*d*). *Deuterolysis of solid solvated monodecylchromium dichloride*. The homogeneous solution of the organochromium compound, in tetrahydrofuran was cooled to −30°, and treated with dry oxygen-free hexane (200 ml). The resulting lime green solid** was filtered at −30°, washed with hexane and redissolved in fresh tetrahydrofuran (50 ml). The resulting solution was treated at −10° with D_2O (10 ml) and allowed to warm slowly to room temperature. The quantities of decane and 1-decene thus formed, together with the isotopic composition of the decane (ν_{max} 2175 cm^{-1}) are given in Table 1, expt. 4.

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* The isotopic compositions were very kindly determined mass spectrometrically by Dr. W. E. Koerner and his associates of Monsanto Company, Research Center, St. Louis, Mo., U.S.A.

** All attempts to dry this solid under vacuum, even at low temperatures, led to extensive decomposition.

(*e*). *Thermal stability.* A solution of the organochromium compound, prepared under (*a*) above, was heated under reflux for 4 h. During this time the reaction mixture went colorless and a copious off-white precipitate was formed. The cooled reaction mixture was filtered. The filtrate was hydrolyzed and the hydrocarbons thus formed are given in Table 1, expt 5. The solid, insoluble chromium salt was shown by potentiometric titration to reduce Fe^{3+} to Fe^{2+}.

Tridecylchromium system

(*a*). *Deuterolysis at* $-40°$. Decylmagnesium chloride (60 ml, 44 mmoles) was added to a briskly stirred suspension of $CrCl_3(THF)_3$ (5.4 g, 14.4 mmoles) in tetrahydrofuran (100 ml) at $-70°$. The stirred solution was allowed to warm, over a period of 3 h, to $-40°$. The resulting brown solution was treated with MeOD (5 g) and kept at $-40°$ for a further four hours. The clear green solution was allowed to warm to room temperature, and then diluted with water. The total reaction mixture was thoroughly extracted with ether. The hydrocarbons isolated in this way, together with their isotopic composition are given in Table 1, expt. 7. The infrared spectrum of the decane had ν_{max} 2175 and that of the 1-decene showed only olefinic adsorption for $-CH{=}CH_2$.

(*b*). *Hydrolysis at* 20°. In a similar experiment with decylmagnesium chloride (26 mmoles) and $CrCl_3(THF)_3$ (8.6 mmoles), the heterogenous red-brown reaction mixture was allowed to warm to 20°. The flask containing the reaction mixture was connected to a high-vacuum line, and all the non-condensable gases removed by pumping (liquid-nitrogen temperature). Water (10 ml) was distilled into the reaction vessel and the whole allowed to warm, in vacuum, to room temperature. The hydrolysis products consisted of hydrogen (134 ml, 6.0 mmoles) and the hydrocarbons given in Table 1, expt. 8. The latter were isolated by gas chromatography and identified as described above (Identification of products).

(*c*). *Deuterolysis at* 20°. Two parallel experiments (9 and 10) similar to that described under (*b*) above were carried out with decylmagnesium chloride (26 mmoles) and $CrCl_3(THF)_3$ (8.6 mmoles). In one case (expt. 9) the reaction mixture was allowed to stand only 2.5 h at 20°, in the other (expt. 10) 20 h. In both experiments D_2O (10 ml) was distilled into the cooled, degassed, reaction mixture. The deuterolysis products were: expt. 9, a mixture of H_2 (3.4%), HD (15.8%), D_2 (80.8%) (141.25 ml, 6.30 mmoles) and the hydrocarbons given in Table 1, expt. 9; expt. 10, a mixture of H_2 (2.2%), HD (10.9%), D_2 (86.9%) (104.6 ml, 4.67 mmoles) the hydrocarbons listed in Table 1, expt. 10, and small quantities of three other hydrocarbons having the same gas chromatographic retention times as *trans*-5-, -4- and -3-decene respectively.

(*d*). *With 1-dodecene, deuterolysis.* In an experiment similar to that described under (*a*) above with decylmagnesium chloride (44 mmoles) and $CrCl_3(THF)_3$ (14.4 mmoles), dry oxygen-free 1-dodecene was added to the reaction mixture at $-40°$. The whole was allowed to warm to room temperature and after 20 h was treated with D_2O (10 ml). The hydrocarbons isolated with the aid of ether and preparative scale gas chromatography were: decane (98% D_0), 1-decene and *trans*-3-decene (98.7% D_0)*, *trans*-2-decene (96% D_0), 1-dodecene (99.2% D_0, infrared only $-CH{=}CH_2$), *trans*-2-dodecene [98.7% D_0, infrared *trans*$-CH{=}CH-$; NMR δ 0.93 (mult., 3 protons

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* These were not separable in the present preparative scale work.

CH_3), 1.25 (sing., 14 protons $(CH_2)_7$), 1.6 (mult., 3 protons $CH_3C{=}C{-}$), 1.9 (mult., 2 protons $-CH_2-C{=}$), 5.3 (sextet, 2 protons $-CH{=}CH-$)]. Gas chromatographic analysis of the total hydrocarbon mixture indicated the presence of small quantities of other isomeric decenes and dodecenes. The amounts of dodecane, 1-dodecene and *trans*-2-dodecene in the total dodecene/dodecane mixture were 9, 25 and 51% respectively.

4-Phenylbutyl bromide

Phosphorus tribromide (8 g) was slowly added to briskly stirred 4-phenylbutanol (34 g)* at 0°. When the addition was complete the whole was allowed to warm over a period of 2 h to 20° and subsequently heated on a water bath until the reaction mixture separated into two layers. The total contents of the flask were poured on to crushed ice and the organic halide isolated with hexane. The hexane layer was washed thoroughly with NaOH (5%) water and finally dried over calcium chloride. Subsequent fractional distillation of the dried extract gave 4-phenylbutyl bromide (42 g) as a colorless liquid, b.p. 62–64°/0.04 mm, n_D^{20} 1.5400; NMR spectrum δ 7.12 (5 protons C_6H_5). 3.29 (2 protons CH_2Br), 2.57 (2 protons $PhCH_2$), 1.8 (4 protons $-CH_2-CH_2-$).

Tris(4-phenylbutyl)chromium system

(*a*). *Analysis of the 4-phenylbutyl-Grignard solution.* An aliquot of the 4-phenylbutylmagnesium bromide solution used in the following experiments was hydrolyzed at 0°, and the resulting hydrocarbons extracted with ether. Gas chromatographic analysis of the extract showed the presence of 1-phenylbutane (97.4%), 4-phenyl-1-butene (2.1%) and tetralin (0.5%). The infrared and NMR spectra of the three isolated hydrocarbons were identical with those of authentic specimens.

(*b*). *4-Phenylbutylmagnesium bromide and $CrCl_3(THF)_3$, ratio 3:1.* In two parallel experiments a solution of 4-phenylbutylmagnesium bromide (50 ml, 37 mmoles) was added to a briskly stirred suspension of $CrCl_3(THF)_3$ (4.62 g, 12.3 mmoles) in tetrahydrofuran at −70°. When the addition was complete both solutions were allowed to warm over a period of one hour to −40°. In one case the resulting red-brown suspension was allowed to warm, over a period of 2 h to 0° and then hydrolyzed. In the other it was allowed to warm over a period of 4 h to 20° and then hydrolyzed. In both cases the resulting hydrocarbons were isolated with the aid of ether. Gas chromatographic analysis of the extracts showed them to contain: 0°/2h: 1-phenylbutane (81.2%), 4-phenyl-1-butene (13.8%), *trans*-1-phenyl-2-butene (3.2%), *cis*-1-phenyl-2-butene (1.15%), *trans*-1-phenyl-1-butene (0.3%) and tetralin (0.4%); 20°/4h: 1-phenylbutane (69.1%), 4-phenyl-1-butene (1.6%), *trans*-1-phenyl-2-butene (23.1%), *cis*-1-phenyl-2-butene (4.3%), *trans*-1-phenyl-1-butene (1.4%) and tetralin (0.4%).

In the first experiment the 1-phenylbutane and 4-phenyl-1-butene were isolated and identified by a direct comparison of their infrared and NMR spectra with those of authentic specimens, similarly with the 1-phenylbutane and *trans*-1-phenyl-2-butene in the second experiment. The *cis*-1-phenyl-2-butene in the second experiment

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* 4-Phenylbutanol (b.p. 72°/0.02 mm, n_D^{20} 1.5209) was prepared by the reduction of ethyl 4-phenylbutyrate (50 g) with $LiAlH_4$ (5 g) in diethyl ether.

was isolated and identified by infrared and NMR spectroscopy [δ 7.51 (5 protons $-C_6H_5$), 5.54 (2 protons $-CH{=}CH-$), 3.33 (2 protons $PhCH_2-$), 1.7 (3 protons $CH_3-C{=}$)].

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