

ALKYL-TRANSITION METAL COMPOUNDS V*. n- AND sec-ALKYLCHROMIUM SYSTEMS: REACTION WITH DIENES

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SUMMARY

Tri-n- and -sec-butylchromium react with conjugated and non-conjugated dienes to give hydrogenation and isomerization products. The former arise by hydrogen transfer processes within the alkylchromium/diene complex. The latter are geometric and positional isomers of the starting dienes. The alkylchromium systems are thus excellent catalysts for the selective rearrangement of linear dienes.

INTRODUCTION

Tri-n- and -sec-alkylchromium compounds furnish catalyst systems which will isomerize and hydrogenate terminal olefins and cyclic dienes^{1,2}. The former are converted, selectively, to *trans*- and *cis*-2-alkenes plus traces of other internal olefins and alkanes, the latter to the conjugated cyclic diene. More detailed examination of the catalyst system revealed that both the formation of the catalyst and its subsequent reactions involved hydrogen transfer processes within the alkylchromium and alkylchromium/olefin complexes¹⁻⁴. It therefore seemed opportune to extend these isomerization studies to other unsaturated substrates, in particular linear dienes. The n- and sec-butylchromium systems were usually used since their volatile fragmentation products are readily separated from the other products. The dienes used were: butadiene, 1,5-hexadiene, *cis,trans*-2,4-hexadiene, 1,5-heptadiene and 1,7-octadiene.

RESULTS AND DISCUSSION

With butadiene

The final hydrolysis products from the interaction of the tri-n-decylchromium system and butadiene, consisted of butenes, decane and decenes and a viscous polymer**. The marked difference in alkane/alkene ratio in the present experiment (60/40) as compared to the usual ratio (70/30)⁴ illustrates the influence of the diene on the

* For Part IV see ref. 1.

** The formation of polymeric material from butadiene and the triethylchromium system has been reported⁵.

fragmentation of the alkylchromium system. With respect to the butadiene, part is reduced to butene, and part is polymerized. There was no evidence for isomerization to methylallene or butyne.

With hexadienes

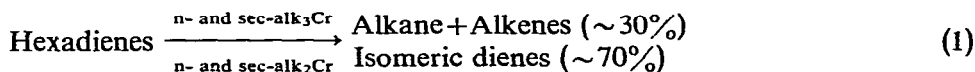
In a series of experiments, 1,5-hexadiene or *cis,trans*-2,4-hexadiene was added to the tributylchromium(III) or dibutylchromium(II) systems at -70° and the whole was allowed to warm to $+20^{\circ}$. The total reaction mixtures were then hydrolyzed. The results summarized in Table 1 (expts. 1-8) show that all the organochromium

TABLE 1
ISOMERIZATION OF DIENES BY BUTYLCHROMIUM SYSTEMS^a

No.	System	Alkenes	Dienes					
			1,5	1,4	<i>t,t</i> -2,4	<i>c,t</i> -2,4	<i>c,c</i> -2,4	
<i>1,5-Hexadiene</i>			1,5	1,4	<i>t,t</i> -2,4	<i>c,t</i> -2,4	<i>c,c</i> -2,4	
1	n-Bu ₃ Cr	28.1	11.7	8.3	22.5	23.6	5.6	
2	sec-Bu ₃ Cr	29.2	6.4	3.7	33.5	22.9	4.3	
3	n-Bu ₂ Cr	27.3	0.8	0.0	23.2	12.5	36.2	
4	sec-Bu ₂ Cr	11.6	21.6	11.0	27.2	24.0	4.5	
<i>cis,trans</i> -2,4 Hexadiene			1,5	1,4	<i>t,t</i> -2,4	<i>c,t</i> -2,4	<i>c,c</i> -2,4	
5	n-Bu ₃ Cr	26.1	0.0	0.0	14.0	55.0	5.0	
6	sec-Bu ₃ Cr	35.5	0.0	0.0	37.9	24.5	2.1	
7	n-Bu ₂ Cr	13.2	0.0	1.9	20.1	61.1	3.7	
8	sec-Bu ₂ Cr	35.0	0.0	0.0	39.1	22.0	1.9	
<i>1,5-Heptadiene</i>			1,5	2,5 ^b			Conjd.	
9	n-Bu ₃ Cr	28	4.0	41.2			26.8	
10	sec-Bu ₃ Cr	22	8.5	60.1			9.5	
<i>1,7-Octadiene</i>			1,7	?	<i>t,t</i> -2,6	<i>c,t</i> -2,6	<i>c,c</i> -2,6	Conjd.?
11	n-Bu ₃ Cr	29.6	1.1	1.0	36.3	26.3	3.0	2.7
12	sec-Bu ₃ Cr	30.6	0.2	1.6	39.8	20.4	3.2	4.0

^a Percentage product distribution after hydrolysis. ^b Total of *t,t*, *c,t* and *c,c*.

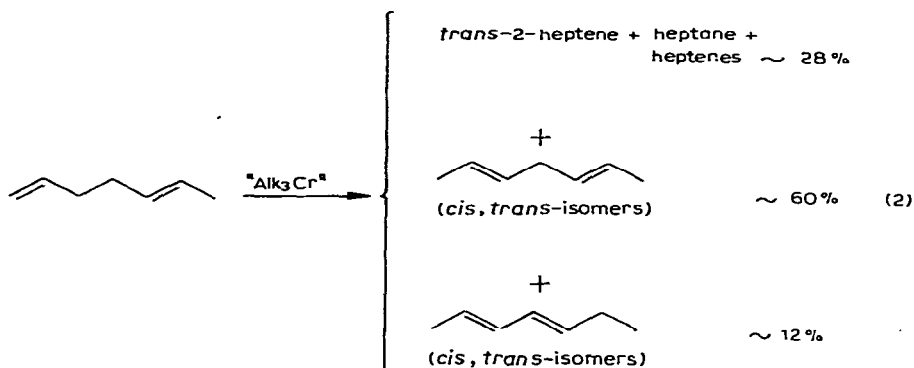
systems consistently react with the dienes to give *hydrogenation* and *isomerization* products (eqn. 1). The alkenes consisted of isomeric hexenes, and the dienes consisted of the more stable conjugated *trans,trans*- and *cis,trans*-2,4-hexadienes.



With 1,5-heptadiene

Both the tri-n- and -sec-butylchromium systems react with 1,5-heptadiene to give, again, hydrogenation and isomerization products (Table 1 expts. 9, 10),

eqn. (2). The hydrogenation products consisted of *trans*-2-heptene, together with heptane and isomeric heptenes.

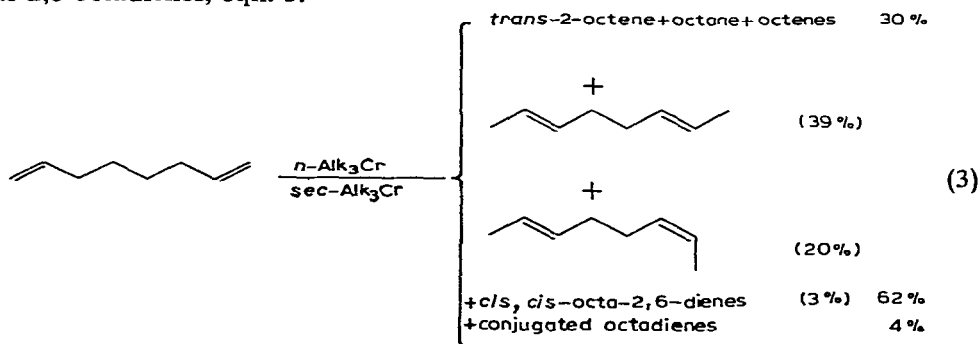


In order to determine the source of the hydrogen required for the conversion of the diene to alkene, the final reaction mixture was treated with deuterium oxide. The resulting alkene fraction contained very little deuterioalkene and the diene fraction, none. Therefore, though some of the alkene is formed at the deuterolysis step (deuterolysis of an alkylchromium intermediate) the majority is formed at some stage prior to the deuterolysis. The inference being that the hydrogenation products involve hydrogen transfer processes, from an alkyl group bonded to chromium and complexed diene*.

The *isomerization products* consisted mainly of the geometric isomers of 2,5-heptadiene, eqn. (2).

With 1,7-octadiene

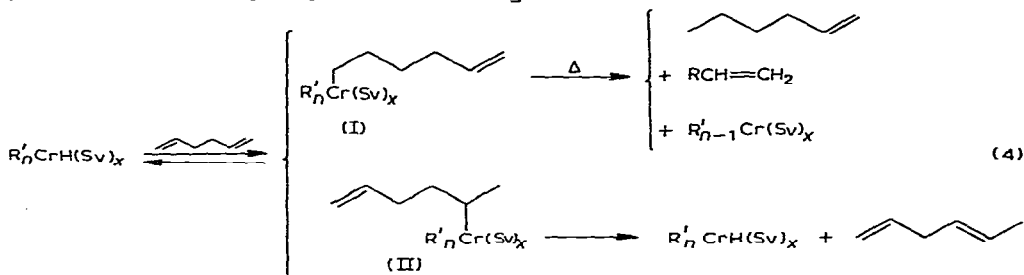
The products from the interaction of the tri-*n*- and -*sec*-butylchromium compounds with the bis-terminal diene, 1,7-octadiene, again consisted of hydrogenation and isomerization products (Table 1, expts. 11 and 12). In the experiment with the tri-*n*-butylchromium system the major hydrocarbon products, isolated by preparative scale gas-chromatography, were identified as *trans*-2-octene, *trans,trans*- and *cis,trans*-2,6-octadienes, eqn. 3.



* Corroboration of this is found in the earlier observation that in the presence of butadiene the amount of alkene formed in the fragmentation of the tridecylchromium system is considerably greater than in its absence. That is, the hydrogen lost in alkene formation is transferred to butadiene to give butene.

Clearly, both tri-*n*- and -*sec*-alkylchromium systems will react with linear dienes to give consistently hydrogenation and isomerization products.

The formation of these products can be explained in terms of the hydrogen transfer processes now known to be characteristic of the fragmentation of *n*- and *sec*-alkylchromium compounds^{1,3}. Thus the complexed diene could react with a hydridochromium species to give two new mixed alkylchromium complexes, eqn. 4 [(I) or (II), R' = RCH₂CH₂ and *n* = 1 or 2]*.



These can undergo fragmentation either homolytically or by metal hydride elimination. In the former case two *olefins* are formed, one corresponding to hydrogenation of the diene, the other to hydrogen abstraction from one of the alkyl groups originally bonded to chromium. In the latter case the products are the hydridochromium species and either one of two dienes; the one, starting material, the other corresponding to an isomerization product.

The selectivity observed in the isomerization of the dienes studied is analogous to that observed in the isomerization of terminal alkenes to *trans*- and *cis*-2-alkenes², and must be ascribed to steric effects in the diene/hydridochromium complex.

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

The general techniques used in the preparation and handling of the organometallic compounds have already been described¹⁻³. Gas chromatographic analyses (GLC) were carried out on an F and M model 5750 equipped with an 18 ft. 20% bis-(methoxyethyl)adipate (BMEA) column (C₆, C₇, C₈ dienes and acetylenes), a 9 ft. 20% Carbowax 20 M column (decenes) and a 2 ft. Silicone Gum Rubber column (aromatic hydrocarbons and high boiling alkanes).

The butadiene was from Fluka, Buchs, Switzerland and was freshly distilled under argon prior to use. The 1,5- and *cis,trans*-2,4-hexadienes and 1-decene were from Fluka; the 1,5-heptadiene from Chemical Samples Co., Columbus, Ohio; the 1,7-octadiene from Aldrich Chemicals, Milwaukee, Wisconsin. All olefins were 99% pure (GLC) and all were filtered through alumina and de-oxygenated before use. The CrCl₂ was from K&K Laboratories, Plainview, New York, and was degassed under vacuum (argon) before use.

Interaction of tri-*n*-decylchromium and butadiene

Butadiene (10 ml) was distilled into a suspension of tri-*n*-decylchromium

* It has recently been proposed that hydrido-Ni, -Co, -Cr and -Fe^{II} react with butadiene to give the corresponding π -crotyl complexes⁶.

[from alkyl-Grignard (100 ml, 52 mmole) and $\text{CrCl}_3(\text{THF})_3$ (6.5 g, 17.3 mmole)] in tetrahydrofuran (100 ml) at -70° . The reaction mixture was allowed to warm to -10° (Gilman test now positive green) and kept at this temperature for 15 h. At the end of this period the Gilman test was still positive green. Water (150 ml) was added (gas evolution) and the organic material isolated with the aid of ether (green ether extract). The volatile material, removed by distillation (up to $100^\circ/12$ mm), was shown (GLC) to consist only of butenes, decane (60.3%), 1-decene (17.5%), *trans*-2-decene (14.3%) and *cis*-2-decene (8.8%) the non-volatile material consisted of a pale yellow viscous liquid which set, slowly, to a mush.

Interaction of n- and sec-butylchromium(III) and -(II) compounds with 1,5- and cis,trans-2,4-hexadiene

In a series of experiments oxygen-free 1,5-hexadiene or *cis,trans*-2,4-hexadiene (Table 2) was added to a freshly prepared suspension, or solution of the alkylchromium compound (from the reagents given in Table 2) in tetrahydrofuran at -70° .

TABLE 2

STOICHIOMETRY OF REAGENTS FOR REACTION OF *n*- AND *sec*-BUTYLCHROMIUM(III) AND -(II) WITH HEXADIENES

Expt. No. ^a	Diene ^b (ml)	BuMgBr		sec-BuMgBr		$\text{CrCl}_3(\text{THF})_3$		CrCl_2		THF (ml)
		(ml)	(mmole)	(ml)	(mmole)	(g)	(mmole)	(g)	(mmole)	
1	3	50	22.5			2.81	7.5			25
2	3			50	18.5	2.31	6.16			25
3	5	53	33					2.08	16.5	50
4	5			22.3	10.2			0.62	5.1	50
5	2.5	50	22.5			2.81	7.5			25
6	2.5			50	18.5	2.31	6.16			25
7	5	72	39.0					2.4	19.5	50
8	5			85	40.8			2.5	20.4	50

^a The numbers of the experiments correspond with those in Table 1 (products). ^b For diene used, see Table 1 (expts. 1-8).

When the addition was complete the whole was allowed to warm to $+20^\circ$ and left at this temperature for 24 h. After this time the clear black solutions were hydrolyzed (gas evolution) and the hydrocarbons, isolated with the aid of ether. On the basis of comparative gas chromatographic retention times the relative percentages of the hydrocarbons thus isolated are given in Table 1 expts. 1 to 8.

Interaction of tri-n- or -sec-butylchromium with 1,5-heptadiene

Dry oxygen-free 1,5-heptadiene (4 ml) was added to suspensions of the title compounds [from *n*-alkyl-Grignard (50 ml, 26.5 mmole) and $\text{CrCl}_3(\text{THF})_3$ (3.3 g 8.8 mmole) and *sec*-alkyl-Grignard (50 ml, 24 mmole) and $\text{CrCl}_3(\text{THF})_3$ (2.98 g, 8 mmole) respectively] in tetrahydrofuran (50 ml) at -70° . When the additions were complete, both reaction mixtures were allowed to warm to 20° and kept at this temperature for 30 h. After this time water (50 ml) was added (gas evolution) and the organic material extracted with isopentane. The hydrocarbon extract was washed

thoroughly with water (12×30 ml) to remove tetrahydrofuran*, and subsequently dried (MgSO_4). The hydrocarbons thus formed are listed in Table 1 (expts. 9 and 10). In both experiments the "cis,trans-mixtures of 2,5-dienes" were isolated and shown from ^1H NMR spectroscopy ($\delta = 1.6$, 6 protons $=\text{C}-\text{CH}_3$; 2.63, 2 protons $=\text{CCH}_2\text{C}=\text{C}$; 5.33, 4 protons $-\text{CH}=\text{CH}-$) to consist of geometric isomers of 2,5-heptadiene.

Interaction of tri-sec-butylchromium with 1,5-heptadiene followed by deuterolysis

In an analogous experiment, 1,5-heptadiene (10 ml) was added to tri-sec-alkylchromium [from sec-alkyl-Grignard (100 ml, 46 mmole) and $\text{CrCl}_3(\text{THF})_3$ (5.72 g, 15.3 mmole)] in tetrahydrofuran (25 ml) at -70° . The final reaction mixture was deuterolyzed (D_2O , 10 ml), the hydrocarbons, isolated with isopentane, were separated by preparative scale gas chromatography. In this way the following three main products were isolated:

(1). *Heptene fraction*. $\delta = 5.3$, 1.99 protons $-\text{CH}=\text{CH}-$; 1.91, 2.2 protons $=\text{C}-\text{CH}_2-$; 1.58, 2.2 protons $=\text{C}-\text{CH}_n\text{D}_{3-n}$; 0.8 to 1.41 broad, 6.8 protons $-\text{CH}_2-\text{CH}_3$. ν_{max} 2160 cm^{-1} , alkyl C-D; 968 cm^{-1} , *trans*- $\text{CH}=\text{CH}$; no absorption at 992 and 909 cm^{-1} , i.e. no terminal olefin. GLC indicated heptane, 1- or -3-heptene, *trans*- and *cis*-2-heptene. The above data indicate that the major constituent of this heptene fraction is slightly deuterated ($\sim 20\%$)** *trans*-2-heptene.

(2). *2,5-Diene mixture*. $\delta = 1.6$, 6 protons $=\text{C}-\text{CH}_3$; 2.63, 2 protons $=\text{CCH}_2\text{C}=\text{C}$; 5.33, 4 protons $-\text{CH}=\text{CH}-$. ν_{max} , no adsorption in alkyl or olefinic C-D region. GLC, three components. These data indicate that the mixture consists of *trans,trans*-, *cis,trans*- and *cis,cis*-2,5-heptadiene.

(3). *Conjugated dienes*. $\delta = 0.97$, triplet, $J = 7$ Hz, 3 protons $-\text{CH}_2-\text{CH}_3$; 1.70, doublet, $J = 6$ Hz, 3 protons $=\text{CH}-\text{CH}_3$; 2.03, multiplet, 2 protons $=\text{C}-\text{CH}_2-$; 5.7, multiplet, 3.85 protons $-\text{CH}=\text{CH}-$. ν_{max} , no absorption in alkyl or olefinic C-D region. GLC, two components. The two compounds are thus undeuterated *trans*- and *cis*-2,4-heptadienes.

Interaction of tri-n- and -sec-butylchromium with 1,7-octadiene

Dry oxygen-free 1,7-octadiene (4 ml) was added to suspensions of the title compounds [from n-alkyl-Grignard (50 ml, 18.5 mmole) and $\text{CrCl}_3(\text{THF})_3$ (2.31 g, 6.16 mmole) and sec-alkyl-Grignard (50 ml, 26.5 mmole) and $\text{CrCl}_3(\text{THF})_3$ (3.3 g, 8.8 mmole) respectively] in tetrahydrofuran (50 ml). The subsequent reaction and product isolation procedures were the same as those described, above, for the experiments with 1,5-heptadiene. The final hydrocarbons isolated are listed in Table 1 (Expts. 11 and 12). In both instances the bulk octadienes were separated by fractional distillation and shown by ^1H NMR spectroscopy ($\delta = 5.33$, 4 protons $-\text{CH}=\text{CH}-$; 1.98, 4 protons $=\text{C}-\text{CH}_2$; 1.58, 6 protons $=\text{C}-\text{CH}_3$; also signals at 1.23, 2 protons; 0.91, 1.8 protons) to consist essentially of geometric isomers of 2,6-octadiene.

In a similar experiment, 1,7-octadiene (7 ml) was added to a suspension of tri-n-butylchromium [from alkyl-Grignard (50 ml, 31 mmole) and $\text{CrCl}_3(\text{THF})_3$

* The washing was continued until such a time as there was no tetrahydrofuran detectable by gas chromatographic analysis.

** The presence of heptane ($M+2$) in the present mixture of olefins (M), precludes the use of mass spectrometry for determining the concentration of deutoalkenes ($M+2$).

(3.86 g, 10.3 mmole)] in tetrahydrofuran (50 ml). The final hydrocarbon mixture was separated by preparative scale gas chromatography into

(1). *Octene fraction*. $\delta = 5.3$, 2 protons $-\text{CH}=\text{CH}-$; 1.91, 2.31 protons $=\text{C}-\text{CH}_2-$; 1.58, 2.5 protons $=\text{C}-\text{CH}_3$; 1.24, 5.7 protons $-\text{CH}_2-$; 0.93, 4.2 protons $-\text{CH}_3$. It would appear to consist of a mixture of 2- and 3-octenes.

(2). *First diene peak*. $\delta = 5.33$, multiplet, 4 protons $-\text{CH}=\text{CH}-$; 1.97, broad singlet, 4 protons $=\text{C}-\text{CH}_2-$; 1.59, triplet $J = 3$ Hz, $=\text{C}-\text{CH}_3$, consists of *trans, trans*-2,6-octadiene.

(3). *Second diene peak*. $\delta = 5.33$, multiplet, 4 protons $-\text{CH}=\text{CH}-$; 2.00, multiplet, 4 protons $=\text{C}-\text{CH}_2-$; 1.59, multiplet, 6 protons $=\text{C}-\text{CH}_3$. It consists of *cis,trans*-2,6-octadiene.

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