Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

ALKYL–TRANSITION METAL COMPOUNDS
VIII*. HYDROGEN TRANSFER REACTIONS

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(Received September 17th, 1970)

SUMMARY

The interaction of tris(2,2-dideutero-4-phenylbutyl)chromium and -iron with 1,7-octadiene and 3-phenylpropene, respectively, results in the formation of hydrogenation products (deutero-2-octene and 1,2-dideutero-3-phenylpropane) and isomerization products. These results prove the intermolecular transfer of hydrogen (deuterium) from the β-position of an alkyl group bonded to the metal to diene (olefin) substrate.

INTRODUCTION

It had been shown earlier[2-4] that alkylchromium and -iron compounds react in the absence of added hydrogen with olefins, dienes and acetylenes to give hydrogenation products (alkanes and alkenes respectively). The results further implied a direct transfer of hydrogen from the alkyl group bonded to the metal, to complexed olefin (diene or acetylene). In view of the significance of such intermolecular hydrogen transfer reactions to many catalytic processes (*e.g.* hydrocarbon cracking, isomerization, etc.) the present experiments, to prove the origins of the hydrogen involved, were undertaken. In order to facilitate experimental procedures the two systems chosen were the non-deuterated an specifically deuterated tris(4-phenylbutyl)chromium and -iron with 1,7-octadiene and 3-phenylpropene respectively.

RESULTS AND DISCUSSION

(1). *Alkylchromium system with 1,7- octadiene*

A control experiment with the non-deuterated (4-phenylbutyl)chromium system and 1,7-octadiene established that the final hydrolysis products contained the C_8 hydrogenation and isomerization products listed in Table 1 (expt. 1).

In a second experiment with the non-deuterated alkylchromium system, the final reaction mixture was deuterolyzed. The isotopic composition of the main C_8

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* For Part VII see ref. 1.

TABLE 1

ALKYLCHROMIUM SYSTEM WITH 1,7-OCTADIENE

Exp. No.	Products (%)			Composition of *trans*-2-octene (%)			
	Hydrogenation	Isomerization					
	Alkane+Alkene[a]	2,6-Dienes	Other dienes	D_0	D_1	D_2	D_3
1	19.7[b]	72.0	8.3	100	0.0	0.0	0.0
2	19.6	73.1	7.2	100	0.0	0.0	0.0
3	13.9	78.4	7.7	56.0	35.0	9.0	0.0

[a] Mainly *trans*- and *cis*-2-octene (see Experimental). [b] This C_8 fraction was used as reference standard in subsequent GLC/mass spectrometric analyses.

hydrogenation product (*trans*-2-octene) (Table 1, expt. 2) indicate that it was not enriched in deuterium.

It is therefore evident that the majority of the hydrogen transfer processes involved in the formation of the hydrogenation products are completed before the hydrolysis (deuterolysis) step.

When the specifically deuterated tris(2,2-dideutero-4-phenylbutyl)chromium system[5] was used, the recovered *trans*-2-octene contained appreciable quantities of monodeutero and some dideutero species (Table 1, expt. 3). This hydrogenation product has therefore been formed in part, by the intermolecular transfer of the hydrogen (deuterium) originally associated with the β-position of the alkyl group bonded to chromium to complexed diene. It was not possible to locate the deuterium within the octene molecule with any certainty, therefore the following experiment with the alkyliron system was carried out.

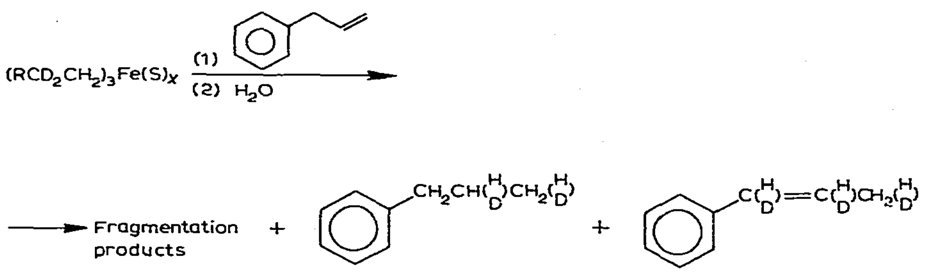
TABLE 2

FRAGMENTATION PRODUCT FROM 4-PHENYLBUTYLCHROMIUM SYSTEMS

Exp. no.	Alkane	1-Alkene	*trans*-2-Alkene	*cis*-2-Alkene	3-Alkene
1	57.0	1.4	28.2	6.7	6.7
2	55.4	1.4	29.4	7.6	6.2
3	59.6	1.3	25.5	6.4	7.2

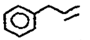
(2). *Alkyliron system with 3-phenylpropene*

Previous studies on the interaction of alkyl–transition metal compounds with olefins revealed that the alkyliron system produced more hydrogenated material than the corresponding chromium system[2]. In the present work therefore the interaction of the tris(2,2-dideutero-4-phenylbutyl)iron system and 3-phenylpropene was studied since moderate yields of alkane (deuteroalkane) were to be anticipated; and the structure of this alkane is such that the location of the deuterium atoms could be made with certainty. The isotopic composition of the resulting 3-phenylpropane (see Experimental) and its NMR spectrum indicated that it was a mixture of non-, mono- and *dideutero species* with the deuterium located on C_1 and C_2, eqn. (1) ($R = PhCH_2$-



(1)

CH_2–). Once again the hydrogenation product has been formed by the intermolecular transfer of hydrogen (deuterium) from the β-position of an alkyl group bonded to the metal to complexed olefin. This intermolecular hydrogen transfer can be interpreted in terms of the fragmentation processes already demonstrated for the alkylchromium system[1,6]. Thus fragmentation of the (deuteroalkyl)iron compound gives an iron deuteride, which subsequently reacts with olefin substrate to give mixed (monodeuteroalkyl)metal species, eqn. (2) ($R = PhCH_2CH_2CD_2CH_2$–). These can subsequently undergo fragmentation via β-hydrogen (deuterium) transfer to give a *dideutero species* with the deuterium on adjacent carbon atoms, eqn. (3) ($R = PhCH_2CH_2CD_2CH_2$–).



$$R_nFe(S)_x \xrightarrow{\Delta} PhCH_2CH_2CD{=}CH_2 + DFeR_{n-1} \longrightarrow$$
$$\rightarrow PhCH_2CHDCH_2FeR_{n-1} + PhCH_2CH(CH_2D)FeR_{n-1} \quad (2)$$

$$\left.\begin{array}{l} PhCH_2CHDCH_2FeR_{n-1} \\ PhCH_2CH(CH_2D)FeR_{n-1} \end{array}\right] \xrightarrow{\Delta}$$
$$\rightarrow PhCH_2CHDCH_2D + PhCH_2CH_2CD{=}CH_2 + FeR_{n-2} \quad (3)$$

The present results together with those involving the tris(deuteromethyl)chromium system[7,8] clearly prove the transfer of both the α- and the β-hydrogen from the alkyl group bonded to the metal to the complexed unsaturated substrate.

EXPERIMENTAL (with Miss U. FEISST)

The present results together with those involving the tris(deuteromethyl)-moisture sensitive organometallic compounds have already been described[3]. The gas liquid chromatography (GLC) both preparative and analytical was carried out on a F and M Model 5750 equipped with a Carbowax 20M column for phenylbutanes and -butenes and phenylpropane and -propenes; a bis(methoxyethyl)adipate column (BMEA) for the C_8 compounds.

Alkylchromium system with 1,7-*octadiene*

In three parallel experiments (Table 1, expts. 1–3) 1,7-octadiene (7 ml) was added to a briskly stirred suspension of the alkylchromium system [from (4-phenylbutyl)magnesium bromide (50 ml, 30.5 mmoles) and $CrCl_3(THF)_3$ (3.80 g, 10.2

mmoles), expts. 1 and 2; and (2,2-dideutero-4-phenylbutyl)magnesium bromide[5] (35 ml, 19.6 mmoles) and $CrCl_3(THF)_3$ (2.44 g, 6.53 mmoles), expt. 3] in tetrahydrofuran at −70°. The reaction mixtures were allowed to warm to room temperature and after 14 h at 20° they were either hydrolyzed (expts. 1 and 3) or deuterolyzed (expt. 2). The hydrocarbons, isolated with the aid of isopentane were shown by GLC analysis to consist of the C_8 compounds given in Table 1* and the fragmentation products given in Table 2. In each case the bulk C_8 compounds were isolated by preparative scale GLC. The IR spectra of the total C_8 fractions showed: expts. 1 and 2, no alkyl C–D; expt. 3, ν_{max} 2160, 2190 (sh) and 2230 cm^{-1}, alkyl and olefinic C–D. The isotopic composition of the *trans*-2-octene fractions (GLC/mass spectrometry**) are given in Table 1, in expt. 3 the *cis*-2-octene had the isotopic composition D_0 62.0, D_1 36.0, D_2 2.0, D_3 0.0**.

Alkyliron system with 3-phenylpropene

Dry, oxygen-free 3-phenylpropene (5 ml) was added to a briskly stirred suspension of the specifically deuterated alkyliron system [from (2,2-dideutero-4-phenylbutyl)magnesium bromide[5] (35 ml, 19.6 mmoles) and $FeCl_3$ (1.02 g, 6.3 mmoles)] in tetrahydrofuran at −70°. The whole was allowed to warm to +20°, and after 14 h, hydrolyzed. The resulting hydrocarbons, isolated with the aid of ether consisted of the following C_{10} and C_9 compound.

C_{10}. The "4-phenylbutane" (57.4%), D_0 3.3, D_1 6.5, D_2 70.7, D_3 18.9, D_4 0.6, D_5 0.0%; NMR, δ_{TMS} 7.07 (5.0 protons), 2.55 (1.83 protons), 1.55 (1.85 protons), 0.89 ppm (2.64 protons); ν_{max} 2110, 2170, 2180 (sh) and 2220 cm^{-1} (alkyl C–D) consisted mainly of 2,2-dideutero-4-phenylbutane together with some 1,2,2-trideutero species. The "1-phenyl-1-butene" (42.5%), D_0 42.3, D_1 40.6, D_2 14.6, D_3 2.5, D_4 0.0%; NMR, δ_{TMS} 7.15 (5 protons), 6.15 (1.91 protons), 2.17 (1.66 protons), 1.05 ppm (2.64 protons); ν_{max} 2170, 2140 (sh), 2210 and 2220 cm^{-1} (alkyl C–D and possibly some olefinic C–D) consisted of a mixture on non-deuterated and deuterated 1-phenyl-1-butene with the deuterium on C_3 and C_4.

C_9. The "1-phenylpropane" (17.8%), D_0 57.1, D_1 32.7, D_2 8.9%, D_3 1.3%; NMR, δ_{TMS} 7.07 (5 protons), 2.55 (1.97 protons), 1.65 (1.78 protons), 0.90 ppm (2.78 protons); ν_{max} 2170, 2150 cm^{-1} (alkyl C–D) consisted of a mixture of non-deuterated and deuterated 1-phenylpropane with the deuterium on C_2 and C_3.

The 1-phenyl-1-propene (82.0%), D_0 76.4, D_1 20.8, D_2 2.8, D_3 0.0%; NMR, δ_{TMS} 7.14 (5.0 protons), 6.13 (1.82 protons), 1.83 ppm (2.79 protons); ν_{max} 2235 and 2160 cm^{-1} (olefinic and alkyl C–D) consisted of non-deuterated and deuterated 1-phenyl-1-propene with the deuterium on C_1, C_2 and C_3.

ACKNOWLEDGEMENTS

The authors thank Mr. F. Bangerter of MRSA, Zürich for measuring all the ^1H NMR spectra.

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* A detailed analysis and identification of the C_8 fraction has already been described[3].

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

REFERENCES

1 R. P. A. Sneeden and H. H. Zeiss, *J. Organometal. Chem.*, 26 (1971) 101.
2 R. P. A. Sneeden and H. H. Zeiss, *J. Organometal. Chem.*, 22 (1970) 713.
3 R. P. A. Sneeden and H. H. Zeiss, *J. Organometal. Chem.*, 19 (1969) 93.
4 J. R. C. Light and H. H. Zeiss, *J. Organometal. Chem.*, 21 (1970) 517.
5 R. P. A. Sneeden and H. H. Zeiss, *J. Label. Compounds*, 5 (1969) 54.
6 R. P. A. Sneeden and H. H. Zeiss, *Angew. Chem. Int. Ed. Engl.*, 7 (1968) 951.
7 M. Michman and H. H. Zeiss, *J. Organometal. Chem.*, 13 (1968) P23.
8 M. Michman and H. H. Zeiss, *J. Organometal. Chem.*, 25 (1970) 167.