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π-COMPLEXES OF THE TRANSITION METALS

XIX*. BENZYLCHROMIUM, DEUTEROLYSIS

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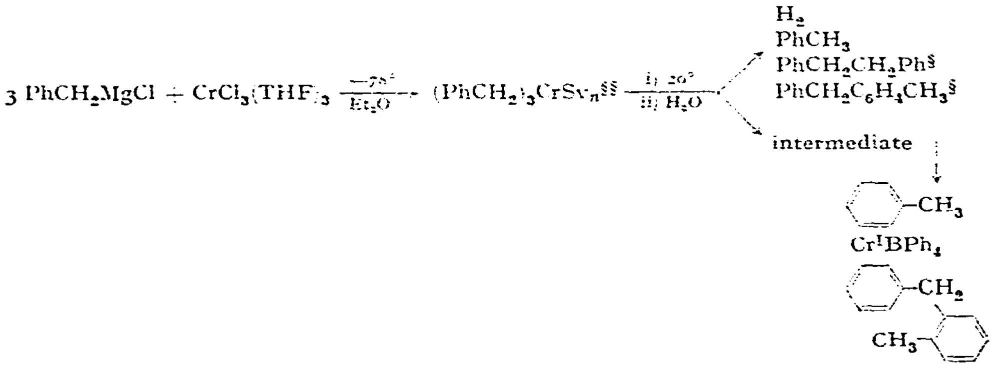
The products of the reaction between benzylmagnesium chloride and chromium(III) chloride tristetrahydrofuranate depend critically on reactant ratio, the mode of their addition, the temperature and the solvent or solvent mixture[2]. In the present work, benzylmagnesium chloride and $CrCl_3(THF)_3$, ratio 3:1, were allowed to react in diethyl ether at −78°, warmed to 20° and then hydrolyzed (or deuterolyzed). A series of these reactions, preceded by a careful analysis of the benzylmagnesium chloride reagent prior to use, have confirmed the products under these conditions to be hydrogen, toluene, a mixture of bibenzyl and 2-benzyltoluene***, and π-(2-benzyltoluene)-π-toluenechromium(I), isolated as its tetraphenylboron salt.

The first step of reaction at −78° is the formation of a solvated tribenzylchromium[2]. Its subsequent decomposition to toluene and 2-benzyltoluene involves the acquisition of hydrogen by benzyl groups initially bonded to chromium. Further, the bis-arene-π-complex can only arise by the acquisition of two hydrogen atoms by an intermediate resulting from the coupling of two benzyl species within the benzylchromium complex. These "hydrogens" could originate from the water used in the hydrolysis step, assuming that a σ-bonded organochromium intermediate is stable



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[***] The *trans*-stilbene also found in the products[2] is already present in the ethereal benzylmagnesium chloride.

[§] Gas chromatography did not separate bibenzyl and 2-benzyltoluene. However, it was possible by infrared and NMR spectroscopy to detect the one in the presence of the other.

[§§] The solvating species Sv throughout the paper is either diethyl ether or tetrahydrofuran.

under the reaction conditions and only undergoes heterolysis. However, in view of the evidence that such compounds can also undergo homolysis[1,2], such an assumption cannot be lightly made. Therefore the possibility exists that in the present reaction the toluene and 2-benzyltoluene, both free and in the bis-arene-π-complex, arise not by the simple hydrolysis of an organochromium intermediate but by hydrogen abstraction or transfer over chromium. Deuterolytic studies were undertaken to resolve this point.

Deuterolysis of tribenzylchromium(III) gives mainly monodeuterated toluene[3]. Consequently, the ultimate deuterolytic products of the reaction under investigation here should be *monodeuterotoluene* and *monodeutero-2-benzyltoluene*, both free and in the π-complex, *if* the source of "hydrogen" in the products derives from the final step. However, should "hydrogen" be acquired by internal abstraction or transfer processes, then the ultimate deuterolytic products must contain *deuterium-free* species.

Aliquots of ethereal benzylmagnesium chloride reagent were deuterolyzed under several conditions including those of the actual reaction runs. The results given in Table 1 show not only that the deuterolysis of benzylmagnesium chloride proceeds consistently to monodeuterotoluene but also that no hydrogen–deuterium exchange occurs either during the deuterolysis in the presence of magnesium salts or under the conditions of preparative scale gas chromatography.

TABLE 1

DEUTEROLYSIS OF BENZYLMAGNESIUM CHLORIDE

Reaction conditions	*Purification*	*Toluene, composition*[a]		
		C_7H_8	C_7H_7D	$C_7H_6D_2$
$D_2O/0°$	Distillation	1.6	97.9	0.3
$D_2O/0°$	Preparative VPC	2.3	97.4	trace
$D_2O/20°$[b]	Preparative VPC	1.5	98.2	0.3

[a] Composition is expressed in relative percentage and corrected for natural abundance isotopes. [b] The ethereal benzylmagnesium chloride was subjected to the operations normally employed in the reactions involving benzylmagnesium chloride and $CrCl_3(THF)_3$ (see EXPERIMENTAL).

Ethereal benzylmagnesium chloride and chromium trichloride tristetrahydrofuranate were allowed to react under the conditions described earlier (−78° to 20°). The resulting mixture was deuterolyzed and the products separated into *non-condensable* gases, D_2, HD and H_2, *organic products** consisting of "toluene", "bibenzyl", "2-benzyltoluene", and "*π-(2-benzyltoluene)-π-toluenechromium(I)*" isolated from the aqueous layer as its tetraphenylboron salt. The π-complex was pyrolyzed, and the "toluene" and "2-benzyltoluene" were isolated from the pyrolyzate by preparative scale gas chromatography. The isotopic composition of the products isolated is given in Table 2. Since the deuterolyses were carried out with 99.8% pure deuterium oxide, it is evident from these results that other reactions besides that of simple deuterolysis have taken place. The possibilities are that (*i*) the hydrogen deuteride

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* Throughout the text the compounds between quotation marks are those which have been isolated from deuterolytic experiments, and whose isotopic composition has been established by mass spectroscopy.

TABLE 2

PERCENTAGE COMPOSITION OF DEUTEROLYSIS PRODUCTS[a]

		Organic	From π-complex
Toluene	C_7H_8	58	17.2
	C_7H_7D	26	65.3
	$C_7H_6D_2$	8.7	8.5
	$C_7H_5D_3$	7.5	9.0
2-Benzyltoluene	$C_{14}H_{14}$	74[b]	21
	$C_{14}H_{13}D$	17[b]	57
	$C_{14}H_{12}D_2$	5[b]	15
	$C_{14}H_{11}D_3$	3[b]	6
	$C_{14}H_{10}D_4$	1[b]	1
Gaseous products:	D_2, 81.0; HD, 18.2; H_2, 0.8		

[a] Composition expressed in relative percentages and corrected for natural abundance isotopes. [b] Owing to technical difficulties these values are only approximate and are not corrected for possible undeuterated bibenzyl content.

TABLE 3

REACTION OF $PhCH_2MgCl$ (45 MMOLES) WITH $CrCl_3(THF)_3$ (15 MMOLES) IN THE ABSENCE OF DIHYDROANTHRACENE (*1*) AND IN THE PRESENCE OF DIHYDROANTHRACENE (*2*)

Compound	(*1*)	(*2*)
"Toluene"[a]	22.3 (49%)	19 (42%)
C_7H_8[b]	64.5	65.0
C_7H_7D[b]	15.9	13.0
$C_7H_6D_2$[b]	10.2	10.8
$C_7H_5D_3$[b]	8.8	10.6
$C_7H_4D_4$[b]	0.6	0.6
"π-Complex" as BPh_4salt[a]	1.3	1.1

[a] Expressed in mmoles. [b] Expressed in relative percentages and corrected for natural abundance isotopes.

arises from the deuterolysis of a chromium hydride, implying the transfer of hydrogen to chromium at some stage during the reaction; (*ii*) the undeuterated toluene and 2-benzyltoluene are formed by a process of hydrogen abstraction; and (*iii*) the presence of two and three deuterium atoms in the "toluene" and "2-benzyltoluene" both free and in the bis-arene-π-complex are the result of a hydrogen/deuterium exchange reaction. However, before attributing these reactions to some special property of an organochromium center, it must first be ascertained whether they may be due to the presence of "free benzyl radicals" in solution.

Dihydroanthracene is an excellent reagent for detecting organic "free radicals", since it acts as a hydrogen source for the "free radical", thereby forming characteristic and easily isolable side products[4]. The present reaction was therefore repeated both in the presence and in the absence of dihydroanthracene. The final reaction mixtures were deuterolyzed and both the "toluene" and "bis-arene-π-complex" isolated. From the results (Table 3), it is evident that the presence of dihydroanthracene affects neither the yield nor the composition of the "toluene". Furthermore since none of the characteristic side products (*i.e.*, 9,9′,10,10′-tetrahydrobianthryl-9,9′) could be isolated from the remaining organic material, it is unlikely that benzyl radicals are produced "free" in solution.

Waters[5] has shown that anthracene is an efficient reagent for trapping "free radicals", since even in diethyl ether solution radicals combine with anthracene to give easily identifiable products. For example the cobalt chloride-catalyzed reaction of benzylmagnesium chloride and benzyl chloride in its presence leads to the isolation of 9,10-dibenzylanthracene (and other products), showing that the reaction proceeds via the generation of "free" benzyl radicals in solution. Since these conditions are analogous to ones used in the present work, the reaction of benzylmagnesium chloride with chromium trichloride tristetrahydrofuranate, ratio 3:1, was repeated in the presence of anthracene. Analysis of the final hydrolytic products (see EXPERIMENTAL) reveals that the amount of toluene isolated (54%)* is virtually the same as that formed in the presence of dihydroanthracene (42%)* and in the blank run (49%)*. The anthracene originally introduced is recovered. None of the products which would be formed by the action of benzyl radicals on anthracene was detected among the non-volatile organic material. Finally, the bis-arene-π-complex consisted of π-(2-benzyltoluene)-π-toluenechromium(I), and no anthracene could be detected in its pyrolyzate.

The results of the reactions carried out in the presence of anthracene and in the presence of dihydroanthracene demonstrate that no benzyl radicals are released into solution. Therefore the processes of hydrogen abstraction and hydrogen transfer involved in the formation of the organic products and the bis-arene-π-complex must all occur within the confines of an organochromium intermediate.

The formation of the observed products may be explained by assuming that in the initially formed tribenzylchromium compound one of the benzyl–chromium bonds undergoes homolysis. The benzyl radical thus produced remains within the confines of the organochromium complex attacking either coordinated solvent to form undeuterated toluene, or an adjacent benzyl group giving ultimately 2-benzyltoluene, bibenzyl and the bis-arene-π-complex.

It appears probable that the hydrogen/deuterium exchange reaction also takes place within the confines of an organochromium intermediate. Further deuterolytic studies are in progress to clarify these points.

EXPERIMENTAL

For general reaction conditions and gas chromatographic techniques see earlier papers[1,2]. Preparative-scale gas chromatography was carried out on an Aerograph "Autoprep" Model A 700, equipped with a 12 ft. silicone SE-30/firebrick column. All column chromatography separations were carried out on silica gel. Concentrations of organomagnesium halides were determined by acid/base titrations, and concentrations of "toluene" in ethereal extracts were determined by gas chromatography.

Analysis of benzyl Grignard solution

An aliquot of the solution used (300 ml, 165 mmoles), was hydrolyzed, and the organic products, isolated by ether extraction, consisted of toluene (162 mmoles);

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* These values are based on the benzyl groups introduced as benzylmagnesium chloride.

bibenzyl (0.8 g, 4.5 mmoles), isolated by column chromatography, m.p. and mixed m.p. 52–53°; benzyl alcohol (0.9 g, 8.5 mmoles) isolated by preparative-scale gas chromatography, and column chromatography, and identified by a direct comparison of its IR spectrum with that of an authentic specimen; *trans*-stilbene (0.6 mmoles), isolated by preparative scale gas chromatography, and identified by a direct comparison of its IR spectrum with that of an authentic specimen.

Deuterolysis of benzyl Grignard solution

(*a*) *Isolation of "toluene" by distillation.* An aliquot of ethereal $PhCH_2MgCl$ (50 ml, 52 mmoles) was cooled to 0° and treated with D_2O (5 ml). The dried ethereal layer, which contained "toluene" (44 mmoles) gave on fractional distillation: diethyl ether; "toluene" which after further purification had the composition: C_7H_8, 1.6; C_7H_7D, 97.9; $C_7H_6D_2$, 0.3; $C_7H_5D_3$, 0.2%; residue which on column chromatography gave bibenzyl (0.1 g, 0.5 mmoles), m.p. and mixed m.p. 52–53°, and an oil (0.1 g) which was not further investigated.

(*b*) *Isolation of "toluene" by preparative scale gas chromatography.* A solution of $PhCH_2MgCl$, in diethyl ether (40 ml, 60.7 mmoles), was cooled to 0° and treated with D_2O (5 ml). The dried ethereal layer, which contained "toluene" (60.5 mmoles), was concentrated by fractional distillation. The "toluene", isolated from the concentrate (9.6 ml) by preparative-scale gas chromatography, had the composition: C_7H_8, 2.26; C_7H_7D, 97.4%; $C_7H_6D_2$, traces: its infrared spectrum had a strong band at 2180 cm^{-1} (alkyl C–D).

(*c*) *Under reaction conditions.* An aliquot of the ethereal benzylmagnesium chloride solution used (50 ml, 45 mmoles) was added slowly to diethyl ether (30 ml) which had been precooled to −78°. After 0.5 h at this temperature the whole was allowed to warm to room temperature, and after 3 h was re-cooled to 0°, treated with a mixture of diethyl ether (100 ml) and D_2O (10 ml), and allowed to stand overnight. The organic products, isolated in the usual way were "toluene" (44 mmoles), composition: C_7H_8, 1.5; C_7H_7D, 98.2; $C_7H_6D_2$, 0.3%; bibenzyl (0.117 g, 0.6 mmoles), m.p. and mixed m.p. 52–53°; a yellow oil (0.1 g) which was not further investigated.

Benzylmagnesium chloride, $CrCl_3(THF)_3$, ratio 3:1, in diethyl ether; deuterolysis

(*a*) *Isolation of "2-benzyltoluene".* Ethereal $PhCH_2MgCl$ (200 ml, 244 mmoles) was added, over 15 min to a briskly stirred suspension of $CrCl_3(THF)_3$ (29.6 g, 78.8 mmoles) at −78°. After 30 min at this temperature, the dark reaction mixture was allowed to warm to 20° (Gilman color test No. I negative). Three hours later the whole was cooled to 0°, treated with D_2O (20 ml) and allowed to stand overnight at room temperature. The heterogeneous product was filtered through a sinter disc, with nitrogen pressure, the residue being washed with ether, water and hot acetone until the respective filtrates were colorless. The ethereal layers which were combined, washed with water and dried (Na_2SO_4) were shown by gas chromatography to contain "toluene" (123.5 mmoles), a mixture of "bibenzyl" and "2-benzyltoluene" and *trans*-stilbene. The residue obtained on evaporation of the ethereal solution gave by chromatography: bibenzyl, m.p. and mixed m.p. 52–53°; "2-benzyltoluene" (5 g, 27.4 mmoles), further purified by preparative scale gas chromatography and its percentage composition shown by mass spectroscopy to be $C_{14}H_{14}$, 74; $C_{14}H_{13}D$, 17; $C_{14}H_{12}D_2$, 5; $C_{14}H_{11}D_3$, 3; $C_{14}H_{10}D_4$, 1%; *trans*-stilbene, m.p. and mixed m.p.

117–120°. The acetone extract was concentrated by distillation under reduced pressure, and the residue was combined with the water washings. This clear solution was treated with excess sodium tetraphenylboron (32 g, in H_2O, 100 ml) thereby giving crude* "π-(2-benzyltoluene)-π-toluenechromium(I)" tetraphenylboron (4.4 g, 6.83 mmoles), m.p. 189–190° (*ex* acetone).

(*b*) *Isolation of "toluene"*. In a repeat experiment with $PhCH_2MgCl$ (250 ml, 257 mmoles) and $CrCl_3(THF)_3$ (31.2 g, 83.1 mmoles) in diethyl ether (175 ml). The ether extract was concentrated by fractional distillation, and the "toluene isolated from the residue by distillation. After further purification by preparative-scale gas chromatography the "toluene" was shown by mass spectroscopy to have the composition: C_7H_8, 58; C_7H_7D, 26; $C_7H_6D_2$, 8.7; $C_7H_5D_3$, 7.5 %. Treatment of the combined aqueous phases with sodium tetraphenylboron (42 g, in H_2O, 100 ml) gave crude "π-(2-benzyltoluene)-π-toluenechromium(I)" tetraphenylboron as a yellow solid, m.p. 185–190° (π-complex A).

(*c*) *Examination of non-condensable gases*. The experiment was repeated with $PhCH_2MgCl$ (30 ml, 63 mmoles) and $CrCl_3(THF)_3$ (7.9 g, 21 mmoles) in a vacuum line apparatus. The non-condensable gases evolved during the deuterolysis (22.9 ml at S.T.P.) were shown by mass spectroscopy, to consist of D_2, 81; HD, 18.2; H_2, 0.8 %.

In a duplicate run the gases formed were led into a vacuum line. After an initial purification the non-condensable gases were shown by mass spectroscopy to consist of D_2, 82.7; HD, 12.6; H_2, 0.26; N_2, 3.6; O_2, 0.49; C_2H_4, less than 0.01 %.

(*d*) *Isolation of "toluene" and "2-benzyltoluene" from bis-arene-π-complex*. The tetraphenylboron salt of the crude "π-(2-benzyltoluene)-π-toluenechromium(I)" obtained above [experiment (*b*), π-complex A] was pyrolyzed as described earlier[2]. The "toluene" and "2-benzyltoluene" were isolated and purified by preparative-scale gas chromatography. The "toluene" was shown by mass spectroscopy to be composed of C_7H_8, 17.2; C_7H_7D, 65.3; $C_7H_6D_2$, 8.5; $C_7H_5D_3$, 9.0 %. The "2-benzyltoluene" had the following composition: $C_{14}H_{14}$, 21; $C_{14}H_{13}D$, 57; $C_{14}H_{12}D_2$, 15; $C_{14}H_{11}D_3$, 6; $C_{14}H_{10}D_4$, 1 %.

Benzylmagnesium chloride, $CrCl_3(THF)_3$, ratio 3:1, with dihydroanthracene; deuterolysis

(*a*) *Blank run*. The reaction between $PhCH_2MgCl$ (50 ml, 45 mmoles) and $CrCl_3(THF)_3$ (5.62 g, 15 mmoles) was carried out as described above. The "toluene (22.3 mmoles) was isolated by fractional distillation and purified by preparative-scale gas chromatography. The composition, established by mass spectroscopy was C_7H_8, 64.5; C_7H_7D, 15.9; $C_7H_6D_2$, 10.2; $C_7H_5D_3$, 8.8; $C_7H_4D_4$, 0.6 %. A sample of this "toluene" was oxidized with neutral potassium permanganate and the "benzoic acid", m.p. and mixed m.p. 120–122° was shown by mass spectroscopy ($C_7H_6O_2$, 100 %, corrected for natural abundance) to contain no deuterium.

The combined aqueous solutions from the above reaction was treated with sodium tetraphenylboron (6.2 g, in H_2O, 40 ml) and gave "π-(2-benzyltoluene)-π-toluenechromium(I)" tetraphenylboron (0.86 g, 1.33 mmoles), m.p. 189–190°.

(*b*) *In the presence of dihydroanthracene*. The reaction between $PhCH_2MgCl$ (50 ml, 45 mmoles) and $CrCl_3(THF)_3$ (5.62 g, 15 mmoles), in the presence of dihydro-

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* The presence of small quantities of other π-bisarenechromium(I) tetraphenylboron salts in this crude salt cannot be excluded.

anthracene (8.11 g, 45 mmoles), in diethyl ether (30 ml) was carried out analogously to the previous reaction. After deuterolysis the mixture was filtered, the residue being washed thoroughly with ether, water and finally hot acetone. The *ether solution* which contained "toluene" (19 mmoles) was fractionally distilled, and the fraction b.p. 73–110° further purified by preparative-scale gas chromatography. The "toluene" obtained in this way was shown by mass spectroscopy to consist of C_7H_8, 65; C_7H_7D, 13.0; $C_7H_6D_2$, 10.8; $C_7H_5D_3$, 10.6; $C_7H_4D_4$, 0.6 %. The residue from the above distillation gave by chromatography: bibenzyl, m.p. and mixed m.p. 52–53°; an oily fraction consisting of a mixture of bibenzyl and "2-benzyltoluene", which was not further investigated; traces of *trans*-stilbene; dihydroanthracene (7.9 g), m.p. and mixed m.p. 107–109°; anthracene (0.12 g), m.p. and mixed m.p. 215–217°; anthraquinone (0.1 g), m.p. and mixed m.p. 285–287°.

The *aqueous solution* from the above reaction when treated with sodium tetraphenylboron (6.2 g, in H_2O, 40 ml) gave "π-(2-benzyltoluene)-π-toluenechromium(I)" tetraphenylboron, m.p. 189–190°, (0.7 g, 1.08 mmoles).

Benzylmagnesium chloride, $CrCl_3(THF)_3$, ratio 3:1, with anthracene; hydrolysis

(*a*) *Analytical*. An ethereal solution of $PhCH_2MgCl$ (100 ml, 57 mmoles) was added to a suspension of $CrCl_3(THF)_3$ (7.12 g, 19 mmoles) and anthracene (10 g, 56.2 mmoles) in diethyl ether (60 ml) at −78°. After 30 min at this temperature, the dark reaction mixture was allowed to warm to 20° (Gilman color test No. I negative). Three hours later the whole was cooled to 0°, treated with water (50 ml), allowed to stand overnight at room temperature and filtered. The residue was washed with ether, hot benzene, water and finally hot acetone, until the respective filtrates were colorless. The dried *ether layer* contained toluene (30.6 mmoles) and a residue (5.4 g). The latter gave by chromatography: a mixture of bibenzyl and 2-benzyltoluene (0.9 g) and anthracene (2.9 g), m.p. and mixed m.p. 216–218°. The dried *benzene layer* on concentration under reduced pressure gave anthracene (6.4 g, m.p. and mixed m.p. 216–217°, (total anthracene recovered 9.3 g). The *acetone layer* was concentrated, and the residue combined with the *aqueous* washings. This clear solution on treatment with sodium tetraphenylboron (7.6 g, in H_2O, 50 ml) gave π-(2-benzyltoluene)-π-toluenechromium(I) tetraphenylboron (1.36 g, 2.11 mmoles) m.p. 182–187°. Pyrolysis of this unrecrystallized bis-arene-π-complex gave a mixture containing benzene, biphenyl (from BPh_4 anion), toluene and 2-benzyltoluene. No significant traces of anthracene could be detected in the pyrolyzate.

(*b*) *Duplicate run*. The above reaction was repeated with $PhCH_2MgCl$ (500 ml, 285 mmoles), $CrCl_3(THF)_3$ (33.7 g, 90 mmoles) and anthracene (20 g) in diethyl ether (300 ml). The total anthracene recovered, m.p. and mixed m.p. 216–217° was 19.3 g. The crude bis-arene-π-complex isolated as described above was pyrolyzed; benzene, toluene, 2-benzyltoluene and biphenyl but no anthracene could be detected among the pyrolysis products.

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SUMMARY

The products obtained from deuterolysis of the reaction of benzylmagnesium chloride with chromium trichloride tristetrahydrofuranate, ratio 3:1, in diethyl ether, either alone or in the presence of dihydroanthracene or anthracene have been isolated and analyzed. The processes of hydrogen abstraction and hydrogen transfer involved in the formation of the organic products and the bis-arene-π-complex according to the evidence must all occur within the confines of intermediate organochromium complexes.

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