

Preliminary communication

Hydroboration, followed by water addition of benchrotrenic alkenes. Formal dihydrogen addition

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Abstract

The reaction of the BH_3 -THF reagent with benchrotrenic alkenes, followed by a water addition and the formation of hydrogenated products are described. This formation and the regioselectivity observed is a consequence of the electron withdrawing effect of the $\text{Cr}(\text{CO})_3$ group.

Keywords: Chromium; Boron; Carbonyl; Dihydrogen; Hydroboration; Benchrotrenic alkenes

1. Introduction

Carbon–carbon double bond hydroboration is one of the most well-known reactions in organic synthesis [1]. It has been applied to a great variety of organometallic compounds [2]. Curiously, no extensive report in this field concerns the chromium tricarbonyl complexes. In 1972, Pauson and coworkers [3] reported the unusual formation of ethylbenzene tricarbonylchromium (20% yield) during the attended hydroboration, followed by alkaline oxidation, of styrene complex. Today, the real origin of this unexpected formation remains unclear. We extend this result to other chromiumtricarbonyl alkenes, and we show that, at room temperature, simple water addition produces the hydrolysis of the benzylic carbon–borane bond. This evolution should be the consequence of the electron withdrawing effect of the tricarbonyl group [4].

2. Results and discussion

Treatment of 1-phenylpropene tricarbonylchromium **1a** (Scheme 1, $\text{R}_1 = \text{H}$, $\text{R}_2 = \text{CH}_3$) with BH_3 -THF followed by a room temperature water addition gave a 60% yield (after chromatography) of propylbenzene

complex **2a**. Under the same conditions, the 1-methoxy-2-phenylpropene complex **1b** ($\text{R}_1 = \text{H}$, $\text{R}_2 = \text{OCH}_3$) gave the reduced complex **2b** in 37% yield, together with a great amount of the styrene complex **5b** (43% yield). In contrast, the α carbon methyl substitution (2-phenylpropene complex **1c** case, $\text{R}_1 = \text{CH}_3$, $\text{R}_2 = \text{H}$) allowed the formation of the boronic acids **3c** (40% yield) and **4c** (44% yield) [5] in which the boron atom is bonded to the β carbon.

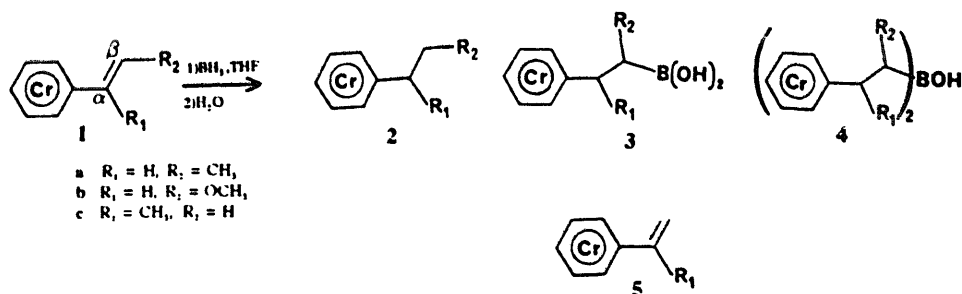
In cyclic series (Scheme 2), the 3,4-dihydronaphthalene **6a** ($\text{R}_1 = \text{H}$, $\text{R}_2 = \text{H}$, $n = 1$) and the 2-methyl-3,4-dihydronaphthalene **6c** ($\text{R}_1 = \text{H}$, $\text{R}_2 = \text{H}$, $n = 1$) complexes produced respectively the tetrahydronaphthalene **7a** (87% yield) and the 2-endo-methyl-tetrahydronaphthalene **7c** (64% yield) complexes [6]. Again the α substitution of the double bond by a methyl group in **6b** ($\text{R}_1 = \text{CH}_3$, $\text{R}_2 = \text{H}$, $n = 1$) allowed the formation of a small amount of the boronic acid **8b** (17% yield) together with the 1-methyltetralin complex **7b** (57% yield).

In these two products, the methyl group is on the same side of the tricarbonyl group. The observed stereochemistry is consistent with a BH_3 attack via the exo face of the cyclic complex **6b**.

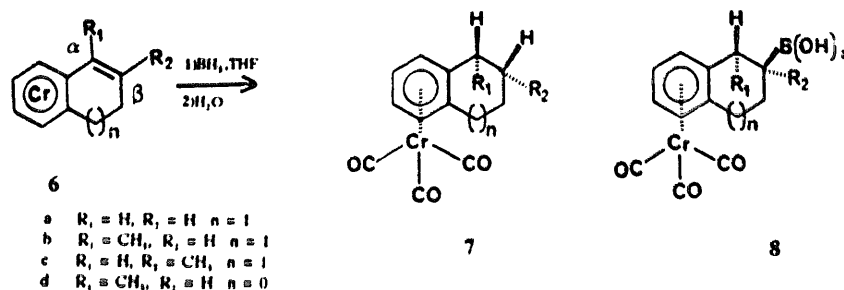
Finally, the same reaction with the 1-methylindene complex **6d** ($\text{R}_1 = \text{CH}_3$, $\text{R}_2 = \text{H}$, $n = 0$) provides a 62% yield of the boronic acid **8d**.

It is to be noted that the hydroboration of **6b** followed by the action of D_2O leads to 1-exo-deutero, 1-endo-methyltetralin $\text{Cr}(\text{CO})_3$.

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Scheme 1.



Scheme 2.

The lack of boronic acids formation derived from the boron attack to the α carbon of the double bond suggests an easy hydrolysis of these acids or the intermediate benzylboranes.

The $\text{Cr}(\text{CO})_3$ group controls the stereochemistry of the BH_3 attack, and by its electron withdrawing effect promotes the hydrolysis of the benzylic carbone–borane bond to give the hydrogenated products with retention of configuration (Scheme 3). In the case of **1b**, (Scheme 1), an elimination process competes with the $\text{C}\alpha\text{--B} \rightarrow \text{C}\alpha\text{--H}$ transformation.

On the contrary, the lack of formation of 1-endo-methyl, 2-exo-deuterotetralin $\text{Cr}(\text{CO})_3$ during the hydroboration– D_2O experiment performed with **6b**, and the isolation of the boronic acids **3c**, **4c**, **8b** and **8d**

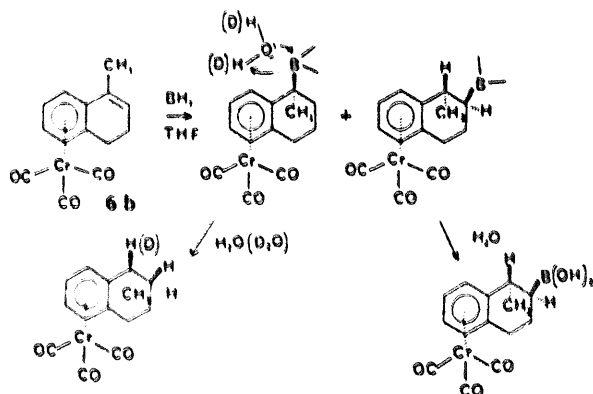
show that, in our experimental conditions the $\text{C}\beta\text{--B} \xrightarrow{\text{H}_2\text{O}} \text{C}\beta\text{--H}$ transformation is not operative.

It has been observed previously that organoboranes of benzylic type are susceptible to hydrolysis, under the influence of aqueous alkali, under mild conditions. For example, Brown and Sharp [7] have reported the isolation of ethylbenzenes during the hydroboration–alkali hydroperoxide oxidation of electron attracting substituted styrenes. However, this formation is minor at room temperature.

Weinheimer and Marsico [8] have found that *cis* α, α' dimethylstilbenes are converted into *meso* 2,3-diphenylbutane by hydroboration and subsequent treatment with 3N sodium hydroxide. However the formation of the diphenyl alkane failed when the hydroborated products was treated with water alone or with diluted acetic acid. Finally note that hydrogenated products have been produced when triene $\text{Fe}(\text{CO})_5$ complexes was hydroborated [9].

In Refs. [7] and [8] it was suggested that the alkali fission of the carbon–borane bond depends on the ability of the benzylic substrate to stabilize a negative charge, a property well illustrated in the benchrotronic series [10].

Finally, a comparison with the literature results, concerning the hydroboration–oxidation of non complexed alkenes (Table 1), shows that, without α methyl substitution, the $\text{Cr}(\text{CO})_3$ group tends by its electron withdrawing effect [4] to shift the regioselectivity of the boron attack towards the α carbon [7].



Scheme 3.

Table 1

		1a	1b	1c	6a	6d
Complexed alkenes	Styrene $\text{Cr}(\text{CO})_3$					
% α/β [11]	100/0 [3]	100/0	100/0	0/100	100/0	0/100
Uncomplexed alkenes	Styrene					
% α/β [12]	20/80 [7]	85/15 [13]	100/0 [14]	0/100 [13]	92/8 [15]	0/100 [16]

The steric effect of the α methyl group in **1c** and **6d** far outweigh the electronic influence. However, the result observed in the case of **6b** seems surprising [17].

3. Experimental details

3.1. General procedures

A solution of BH_3 -THF (3.75 ml of 1M in THF) was added to the benchrotrenic alkene ($2.5 \cdot 10^{-3}$ mol) in dry THF at 0°C . The reaction mixture was warmed to room temperature, stirring was carried out for 1 h and water was slowly added. During this operation the temperature did not exceed 22°C .

3.2. Deuteriation experiment (formation of 1-exo-deutero, 1-endo-methyltetralin $\text{Cr}(\text{CO})_3$)

The same experimental protocol is used. D_2O was added, instead of H_2O , to the reaction mixture. ^1H NMR spectroscopy indicated essentially complete deuterium incorporation. The measurement was based on the integration of the aromatic and benzylic multiplets.

Typical NMR and IR data. **2b** ^1H NMR, 60 MHz, (CDCl_3), δ (ppm): 5.31 (m, 5H, H BCT); 3.59 (t, 2H, OCH_2 , $J = 6$ Hz); 3.35 (s, 3H, $\text{O}-\text{CH}_3$, $J = 6$ Hz); 2.61 (t, 2H BCT- CH_2). **3a** ^1H NMR, 300 MHz, (acetone d_6), δ (ppm): 6.87 (s, 2H, OH), 5.60–5.62 (m, 5H, H BCT); 2.86–2.74 (m, 1H, BCT- $\text{CH}(\text{CH}_3)\text{CH}_2$); 1.27 (d, 3H, CH_3 , $J = 6$ Hz); 1.14 (dd, 1H, $J = 4.4$ Hz, $J = 9.9$ Hz, $-\text{CH}_2-\text{B}$); 0.99 (dd, 1H, $J = 9.6$ Hz, $J = 9.9$ Hz, $-\text{CH}_2-\text{B}$). ^{11}B , NMR δ (ppm) (acetone $d_6/\text{Et}_2\text{OBF}_3$): 32.55 (broad). ^{13}C , NMR 75.469 Hz, (acetone d_6), δ (ppm): 235.07 ($\text{C}=\text{O}$); 123.98, 95.24, 94.87, 93.67 (C BCT), 35.35 ($-\text{CH}(\text{CH}_3)-$); 26.80 (broad CH_2-B); 22.81 (CH_3). IR (KBr): ν OH 3380 cm^{-1} ; $\nu\text{C}=\text{O}$, 1900, 1860 cm^{-1} . **4a** (mixture of isomers), ^1H NMR, 300 MHz (acetone d_6), δ (ppm): 5.61–5.58 (m, 6H, H BCT + O-H); 2.88 (m, CH); (decoupling experiment at 1.25 ppm gives two singlets) 1.32–1.21 (m, $\text{CH}_3 + \text{CH}_2$). ^{11}B NMR (acetone $d_6/\text{Et}_2\text{OBF}_3$) δ (ppm): 53.59 (broad). ^{13}C NMR 75.469 MHz (acetone d_6), δ (ppm): 235.00 ($\text{C}=\text{O}$); 123.95, 94.94, 93.97, 93.75 (C BCT); 35.02, 34.92, ($-\text{CH}(\text{CH}_3)$), 32.94 (broad, CH_2-B); 23.36 (CH_3). IR (KBr): νOH , 3585 cm^{-1} , 3400 cm^{-1} ; $\nu\text{C}=\text{O}$, 1870 cm^{-1} , 1960 cm^{-1} .

7b, ^1H , NMR 60 MHz, (CDCl_3), δ (ppm): 5.68–5.30 (m, 2H, CH BCT); 5.20–4.77 (m, 2H, CH BCT); 2.93–2.40 (m, 3H, $\text{CH}_2 + \text{CH}-\text{CH}_3$); 2.10–1.36 (m, 3H, $\text{CH}_2 + \text{CH}_2$); 1.34–(d, 3H, $J = 7$ Hz, CH_3); 5.63–5.30 (m, 2H, H, BCT); 5.16–4.83 (m, 2H, CH, BCT); 2.80–2.40 (m, 2H, CH_2); 2.06–1.50 (m, 4H); 1.31 (s, 3H, CH_3). **8b** ^1H NMR, 60 MHz (acetone d_6) δ (ppm): 6.85 (s, 2H, OH); 6.60–5.55, (m, 2H, H, BCT); 5.50–5.15, (m, 2H, H, BCT); 3.06–2.50 (m, 3H $\text{CH}_2 + \text{CH}-\text{CH}_3$); 1.98–1.55 (m, 3H, $\text{CH}_2 + \text{CH}-\text{B}$); 1.33 (d, CH_3 , $J = 6.6$ Hz). IR (KBr): νOH 3640 cm^{-1} , 3200 cm^{-1} ; $\nu\text{C}=\text{O}$, 1950 cm^{-1} , 1860 cm^{-1} . **8d** ^1H NMR, 60 MHz (acetone d_6), δ (ppm): 6.95 (s, 2H, OH); 5.95–5.10 (m, 4H, BCT); 3.46–2.71 (m, 3H, $\text{CH}_2 + \text{CH}-\text{CH}_3$); 1.27 (d + m, $\text{CH}-\text{B} + \text{CH}_3$, $J = 6$ Hz). IR (KBr): νOH 3620 cm^{-1} , 3300 cm^{-1} ; $\nu\text{C}=\text{O}$, 1950 cm^{-1} , 1870 cm^{-1} . **7c** ^1H NMR, 60 MHz (CDCl_3), δ (ppm): 5.33–5.03 (m, 4H, H BCT); 2.87–2.23 (m, 4H, CH_2 , CH_2); 2.03–1.36 (m + d, (6H), $\text{CH}-\text{CH}_3 + \text{CH}_2$, $J = 5$ Hz).

Tetralin $\text{Cr}(\text{CO})_3$ and propylbenzene $\text{Cr}(\text{CO})_3$ complexes (**7a** and **1a**) have been characterised by comparison with samples obtained by direct complexation with $\text{Cr}(\text{CO})_3$ (See Caro et al., *Tetrahedron*, 44 (12) (1988) 3565). The styrene $\text{Cr}(\text{CO})_3$ complex has been characterised by comparison with samples obtained by Watts and coworkers synthesis [3].

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