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Syntheses with Organoboranes. VII. Monohydroboration of Conjugated Dienes with Catecholborane Catalyzed by Complexes of Nickel(II) Chloride and Cobalt(II) Chloride with Diphosphines

Marek Zaidlewicz* and Jerzy Meller

Faculty of Chemistry, Nicolaus Copernicus University, 87-100 Toruń, Poland

Abstract: The monohydroboration of representative conjugated dienes **1-7** with catecholborane in the presence of SmI_3, *t*-$BuOSmI_2$, LaI_3, $Ti(OPr^i)_4$, iron(II), nickel(II) and cobalt(II) chloride complexes with dppe, dppp and dppb was examined. $NiCl_2$(dppe), $NiCl_2$(dppp) and $CoCl_2$(dppp) showed catalytic activity. The 1,2-addition products were obtained, no 1,4-addition was observed. The reactivity in the presence of $NiCl_2$(dppe) decreased in the order acyclic dienes > cyclic dienes >>1-decene.
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Catalytic hydroboration is a new methodology of great synthetic potential.[1-4] The reaction is usually carried out with catecholborane and is catalyzed by rhodium, palladium, iridium or ruthenium compounds. Regio- and stereoselectivity of the catalyzed and uncatalyzed hydroboration are often different.

In contrast to olefins, very little is known on catalytic hydroboration of conjugated dienes. Two reports published to date indicate interesting possibilities. Thus, Suzuki and Miyaura[5] described a 1,4-addition of catecholborane to acyclic 1,3-dienes catalyzed with tetrakis(triphenylphosphine)palladium(0). The catalyst was not active with conjugated cyclic dienes and hydroboration of 1,3-cyclohexadiene was catalyzed with tetrarhodium dodecacarbonyl to give the corresponding allylic organoborane which could be formed either by 1,2- or 1,4- addition. An interesting Markovnikov type regioselectivity was observed in the enantioselective dihydroboration of (E)-1-phenyl-1,3-butadiene with catecholborane catalyzed by chiral rhodium complexes.[6] However, the scope of these reactions is not well delineated and the choice of catalysts is very limited.

Our earlier studies on the uncatalyzed monohydroboration of conjugated dienes,[7] and a recent report on the hydroboration of 1-decene with catecholborane catalyzed by lanthanide iodides[8] prompted us to search for transition metal catalysts other than rhodium and palladium compounds for monohydroboration of conjugated dienes.

We started with lanthanide iodides monitoring by ^{11}B NMR analysis the stability of 1 M catecholborane solutions in tetrahydrofuran containing 10 molar % of SmI_3, *t*-$BuOSmI_2$ and LaI_3. For all three iodides additional signals to catecholborane at higher field were observed already in the first hour. After 24 h, the signal corresponding to catecholborane integrated as approximately 60 % of the total area of all signals. The signal corresponding to borane-tetrahydrofuran (quartet at 0.5ppm) was also present integrating 10-16 %. The ^{11}B NMR spectrum of 1 M catecholborane solution in benzene containing 10 molar % of LaI_3 taken after 3 h showed the catecholborane signal at 28 ppm and an additional signal at 22.5 ppm integrating 15 %. The picture remained unchanged after 24 h.

The hydroboration of 1,3 butadiene, isoprene and 2,3-dimethyl-1,3-butadiene with catecholborane at 1:1 molar ratio in the presence of 10 molar % of SmI_3 and *t*-$BuOSmI_2$ in tetrahydrofuran was very sluggish taking 80-100 h. Oxidation of the reaction mixture with alkaline hydrogen peroxide gave the corresponding diols in 31-62 % isolated yields. No monohydroboration products were isolated. The hydroboration of isoprene in tetrahydrofuran in the presence of 10 molar % of lanthanium iodide was still slower proceeding to 20 % in 24 h, and no reaction was observed in benzene.

Catecholborane was also not stable in the presence of 10 molar % of titanium(IV) isopropoxide. In tetrahydrofuran the ^{11}B NMR spectrum taken after 30 min showed 7 % of borane-tetrahydrofuran, the amount increasing to 14 % after 3 h. Signals at 24 ppm and 18.5 ppm corresponding to i-PrOBO$_2$C$_6$H$_4$ and a trialkoxyborane, respectively, indicated disproportionation. In benzene, the disproportionation was slower, nevertheless after 24 h the catecholborane signal integrated for only 43 % of the total area of signals. Hydroboration of isoprene with catecholborane at 1:1 molar ratio in the presence of 10 molar % of titanium(IV) isopropoxide in tetrahydrofuran and benzene was completed in 32 h. The ^{11}B NMR spectrum showed a signal at 37.2 ppm corresponding to the hydroboration product and signals of disproportionation products at 24 and 18 ppm. The presence of the hydroboration product does not necessarily mean that it was formed by catalytic hydroboration. Extensive disproportionation of catecholborane in the presence of titanium (IV) isopropoxide, long reaction time and earlier observations of the reaction with 1-decene,[9] suggest that it might be formed by the redistribution reaction. For comparison, 1-hexene was hydroborated under the same conditions in benzene. The ^{11}B NMR spectrum taken after 24 h showed in addition to signals at 36, 24 and 18 ppm, small signals at 55.09 and 86 ppm corresponding to a borinate ester and a trialkylborane, respectively. Clearly, the lanthanide iodides and titanium(IV) isopropoxide are not suitable catalysts for hydroboration of conjugated dienes.

Then, we turned to nickel(II), iron(II) and cobalt(II) chloride complexes with diphosphines.[10] The stability of catecholborane in the presence of NiCl$_2$(dppe) is much better as compared to the lanthanide iodides and titanium(IV) isopropoxide. No signal corresponding to borane-tetrahydrofuran was observed in the ^{11}B NMR spectrum after 24 h. Only one signal at 18.5 ppm in addition to the catecholborane signal at 26 ppm was present. Hydroboration of isoprene with catecholborane at 1:1 molar ratio in tetrahydrofuran in the presence of 10 molar % of NiCl$_2$(dppe) at room temperature was completed in 6 h. The amount of catalyst could be lowered to 1 molar % with no effect on the reaction time. It is very interesting to note that 1-decene reacted slower than isoprene under these conditions. In a competitive experiment at 1:1:1 molar ratio of 1-decene, isoprene and catecholborane, 87 % of 1-decene remained unreacted. It is the first observation of higher reactivity of 1,3-diene as compared to 1-alkene in the hydroboration reaction. It is also an indirect indication that borane is not involved in the reaction since acyclic conjugated dienes are less reactive than 1-alkenes toward borane.[11]

Hydroboration of representative acyclic and cyclic conjugated dienes **1-7** in the presence of NiCl$_2$(dppe) was carried out on a preparative scale and the results are shown in Table 1. The monohydroboration products were isolated by distillation and oxidized to the corresponding unsaturated alcohols. The regioselectivity observed in these reactions is shown on Figure 1.

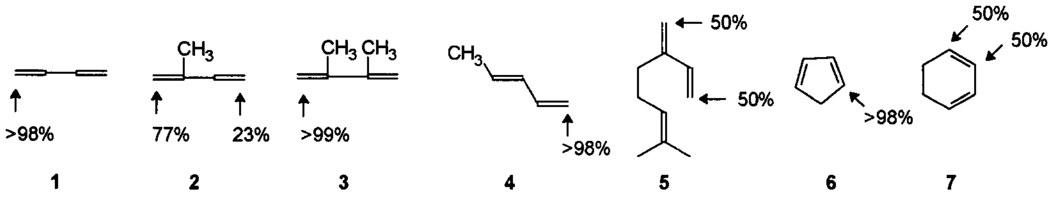

Figure 1. Regioselectivity of Hydroboration with Catecholborane in the Presence of NiCl$_2$(dppe)

In all the cases examined the 1,2-addition products were obtained. In contrast to palladium and rhodium catalyzed monohydroboration, no 1,4-addition products were found. The boron atom was placed on the terminal position of dienes **1-5**. Isoprene showed higher reactivity of the more substituted double bond but no difference in the reactivity of both terminal double bonds was observed for myrcene. Regioselectivity of the addition to 1,3-cyclopentadiene was the same as in the uncatalyzed hydroboration. 1,3-Cyclohexadiene gave a

1:1 mixture of the allylic and homoallylic addition product. In the uncatalyzed hydroboration the allylic addition product is formed preferentially by dialkylboranes and also by borane.[12]

The acyclic dienes reacted faster (6 h) and gave higher yields of the corresponding organoboranes than the cyclic dienes. Although the reactivity of cyclic dienes was lower, nevertheless both acyclic and cyclic dienes could be hydroborated in the presence of $NiCl_2$(dppe). However, styrene containing a conjugated double bond was unreactive.

Encouraged by the results described above we also used $NiCl_2$(dppp) and $NiCl_2$(dppb) complexes. Catecholborane in tetrahydrofuran was stable in the presence of these complexes. The reaction with 1-decene was very sluggish and only a few percent of the hydroboration product was formed in 24 h. In contrast, isoprene reacted in 6 h in the presence of 1 molar % of $NiCl_2$(dppp). The reaction in the presence of $NiCl_2$(dppb) was slower taking 24-26 h.

Table 1. Hydroboration-oxidation of Conjugated Dienes with Catecholborane in the Presence of $NiCl_2$(dppe) in Tetrahydrofuran at Room Temperature [a]

		Hydroboration product CB–R [b]			Oxidation product [c]	
Diene	Time h	R	Bp °C/0.3 mmHg	Yield [d] %	Alcohol [e]	Yield [d] %
1,3-Butadiene	6	3-Butenyl	50-53	79	3 -Butenol	76
Isoprene	6	2-Methyl-3-butenyl 3-Methyl-3-butenyl	60-62	80	2-Methyl-3-butenol (77%) 3-Methyl-3-butenol (23%)	79
2,3-Dimethyl-1,3-butadiene	6	2,3-Dimethyl-3-butenyl	75-78	76	2,3-Dimethyl-3-butenol	71
(E)-1,3-Pentadiene	6	E-3-Pentenyl	66-70	82	(E)-3-Pentenol	60
Myrcene	6	2-Ethenyl-6-methyl-5-heptenyl 3-Methylene-7-methyl-6-octenyl		f	2-Ethenyl-6-methyl-5-heptenol (50%) 3-Methylene-7-methyl-6-octenol (50%)	74
1,3-Cyclopentadiene	24	3-Cyclopentenyl		f	3-Cyclopentenol	30
1,3-Cyclohexadiene	48	2-Cyclohexenyl 3-Cyclohexenyl	104-110	54	2-Cyclohexenol 3-Cyclohexenol	32

[a] Experimental procedure is described in note 13. [b] CB–R = B-alkenylbenzo[1.3.2]dioxaborole. [c] Obtained by standard oxidation of the hydroboration products with alkaline hydrogen peroxide. [d] Isolated yield. [e] Identified by comparison (GC, ^{1}H NMR) with authentic samples. [f] Not isolated.

The effect of $FeCl_2$(dppe), and cobalt(II) chloride complexes with dppe, dppp and dppb on the hydroboration of 1-decene and isoprene with catecholborane under the some conditions as described for $NiCl_2$(dppe) was also examined. Catecholborane was stable in the presence of these complexes. The iron complex neither catalyzed the reaction with 1-decene nor isoprene. $CoCl_2$(dppb) was inactive in the hydroboration of 1-decene, $CoCl_2$(dppe) and $CoCl_2$(dppp) showed low activity, the reaction proceeding to 20 % and 30 % in 24 h, respectively. Isoprene reacted slowly in the presence of $CoCl_2$(dppe) and $CoCl_2$(dppb), 50 % and 86 % of catecholborane remaining unreacted after 24 h. However, in the presence of $CoCl_2$(dppp) the reaction was completed in 24 h.

In conclusion, $NiCl_2$(dppe), $NiCl_2$(dppp) and $CoCl_2$(dppp) are the first transition metal complexes other than rhodium and palladium compounds catalyzing the monohydroboration of conjugated dienes with catecholborane. The reactions proceed by an anti-Markovnikov 1,2-addition. Lower reactivity of 1-decene as compared to isoprene indicates the possibility of selective hydroboration of a conjugated diene in the presence of a terminal double bond, the selectivity opposite to the uncatalyzed hydroboration. Nickel(II) and cobalt(II) chloride complexes with chiral diphospines are now under study as catalysts for the enantioselective monohydroboration of conjugated dienes.

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13. Representative procedure. Catecholborane (3.00 g, 25 mmol) was added to a mixture of $NiCl_2$(dppe) (0.132 g, 0.25 mmol), (E)-1,3-pentadiene (1.70 g, 25 mmol) and tetrahydrofuran (25 mL). The mixture was stirred under argon atmosphere and monitored by ^{11}B NMR analysis. After 6 h the catecholborane signal at 28.8 ppm disappeared. The solvent was removed and B-(E-3-pentenyl)benzo[1.3.2]dioxoborole was isolated by distillation, 3.87 g, 82 % yield, bp. 66-70/0.3 mm Hg, ^{11}B NMR ($CDCl_3$), δ 36.93 ppm; ^{1}H NMR ($CDCl_3$) δ ppm, 1,40 (t, J = 6.8 Hz, 2H, CH_2B), 1.66 (d, J = 5.0 Hz, 3H, CH_3), 2.34 (q, J = 6.6 Hz, 2H, CH_2), 5.55 (m, 2H, =CH), 7.08 (m, 2H, CH), 7.22 (m, 2H, CH).

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