(100 mL), washed with water (2 × 50 mL), dried (Na_2SO_4), and concentrated at 60 °C (1 mm) for 16 h to give a yellow rubberlike product: 2.2 g; IR ($CDCl_3$) 1760 cm^{-1} (s); ^1H NMR ($CDCl_3$) δ 4.8 (broad s, 1 H), 4.28 (q, 2 H, J = 6 Hz), 1.9 (broad s, 2 H), 1.35 (t, 3 H, J = 6 Hz); 0.85 DS.

Acknowledgment. We are grateful to Dr. J.-P. Senet for useful discussions. We also thank SNPE of France for the funds used to perform this investigation.

Registry No. **3**, 124820-66-2; **3** (R = H), 492-61-5; **4**, 125333-92-8; **5**, 124781-64-2; **5** (R = H), 138-52-3; **6**, 124781-65-3; **6** (R = H), 488-81-3; **7**, 106766-23-8; **7** (R = H), 57-50-1; **8**, 124820-67-3; **9**, 102198-10-7; **9** (R = H), 50-89-5; **10**, 124781-66-4; ethyl fluoroformate, 461-64-3; 1-adamantyl fluoroformate, 62087-82-5; isopropyl fluoroformate, 461-71-2; octyl fluoroformate, 104483-19-4; indole-3-carboxaldehyde, 487-89-8; isopropenyl fluoroformate, 74601-07-3; cellulose, 9004-34-6; poly(vinyl alcohol), 9002-89-5; poly(vinyl ethyl carbonate), 113150-73-5.

Regioselective Hydrogenation of Conjugated Dienes Catalyzed by Hydridopentacyanocobaltate Anion Using β-Cyclodextrin as the Phase-Transfer Agent and Lanthanide Halides as Promoters

Jong-Tae Lee and Howard Alper*

Ottawa-Carleton Chemistry Institute, Department of Chemistry, University of Ottawa, Ottawa, Ontario, Canada K1N 6N5

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β-Cyclodextrin is a useful phase-transfer agent for the hydrogenation of conjugated dienes to monoolefins catalyzed by the in situ generated hydridopentacyanocobaltate anion. This reaction, which usually proceeds by 1,2-addition to the diene, is promoted by cerium or lanthanum chloride. Polyethylene glycol (PEG-400), with or without added lanthanide, can also be used as the phase-transfer agent for the reduction process.

β-Cyclodextrin, a cyclic oligomer of D-glucose, has been employed as a phase-transfer agent in several nucleophilic substitution reactions.[1,2] This cycloamylose has also been useful in metal-catalyzed oxidation and reduction reactions. In particular, β-cyclodextrin is an effective phase-transfer catalyst for the palladium chloride catalyzed oxidation of both terminal and internal olefins (eq 1).[3] A subsequent publication has confirmed these findings.[4] Aryl alkyl ketones and aromatic aldehydes can be converted to hydrocarbons in high yields using hydrogen and catalytic amounts of the dimer of chloro(1,5-hexadiene)rhodium (I) and β-cyclodextrin.[5] The heterogeneous hydrogenation of acylpyridines catalyzed by 10% palladium on carbon has also been investigated in the presence of stoichiometric quantities of β-cyclodextrin.[6]

$$RCH{=}CH_2 + O_2 \xrightarrow[\beta\text{-cyclodextrin, 65 °C}]{PdCl_2,\ CuCl_2,\ H_2O} RCOCH_3 \quad (1)$$

One of the useful phase-transfer reduction processes is the hydrogenation of conjugated dienes catalyzed by the hydridopentacyanocobaltate anion, generated in situ by treatment of cobalt chloride with potassium cyanide, potassium chloride, and a quaternary ammonium salt in aqueous base. It is believed that $[R_4N]_3HCo(CN)_5$ is transferred to the organic phase where it usually catalyzes 1,4-addition of hydrogen to a diene.[7] In contrast, use of neutral surfactants which function as micelles instead of quaternary ammonium salts can result in selective 1,2-addition in some cases with reaction here occurring in the aqueous phase.[8]

Table I. Phase Transfer Catalyzed Hydrogenation of 1 Using β-Cyclodextrin[a]

NaOH, N	$LnCl_3{\cdot}7H_2O$, Ln =	yield,[b] %	product distribution 2	product distribution 3
0.055		87	24	76
0.25		91	44	56
0.50		85	64	36
1.0		71	70	30
3.0		59	90	10
5.0		55	91	9
0.25	La	95	44	56
0.5	La	100	64	36
1.0	La	100	75	25
1.0	Ce	100	79	21
5.0	Ce	95	98	2
5.0	Yb	69	90	10
2.0[c]	Ce	90	97	3

[a] Reaction conditions: 1 [5.0 mmol], base [10 mL], C_6H_6 [5 mL], β-cyclodextrin [0.55 mol], $LnCl_3{\cdot}7H_2O$ [0.55 mmol, if used], $CoCl_2$ [0.55 mmol], KCN [2.85 mmol], KCl [1.2 mmol]; H_2, room temperature, 1 atm., 24 h. [b] Yields and product ratios were determined by gas chromatography and by ^1H NMR. Products were identified by comparison of GC and NMR data with those of authentic materials. [c] Using a 7/1 ratio of $KCN/CoCl_2$.

Since it is known that β-cyclodextrin can bind a conjugated diene such as cyclopentadiene,[9] it seemed conceivable that the bound diene could be transferred to the aqueous phase where it would be hydrogenated in the presence of $HCo(CN)_5^{3-}$. It is also possible that β-cyclodextrin can serve as a second-sphere ligand[10] for HCo-

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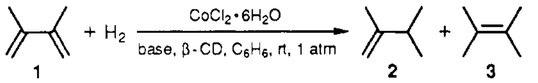
$(CN)_5^{3-}$, transferring it to the organic phase where diene hydrogenation would take place. We now report that β-cyclodextrin is an effective phase-transfer agent for the diene hydrogenation reaction, a process which usually occurs by 1,2-addition to the unsaturated reactant.

Results and Discussion

When a benzene solution of 5.0 mmol of 2,3-dimethyl-1,3-butadiene (**1**, eq 2) was treated with 0.55 mmol of hydrated cobalt chloride, 2.85 mmol of potassium cyanide (i.e. 5.2/1.0 ratio of CN^-/Co), and 1.2 mmol of potassium chloride in 3 N sodium hydroxide, under an atmosphere of hydrogen at room temperature, 2,3-dimethyl-1-butene (**2**) and 2,3-dimethyl-2-butene (**3**) were formed in a ratio of 86/14, the total yield being 22%. However, by repetition of the experiment in the presence of 0.55 mmol of β-cyclodextrin (β-CD), the yield of monoolefins increased substantially (to 59%) with the distribution of **2**/**3** being 9/1. The results in Table I indicate that the base concentration has a significant influence on the yield and proportion of formed monoolefins, with higher base concentration favoring the 1,2-addition product (**2**). No reaction occurs using water instead of base, or α- as a substitute for β-cyclodextrin.



1 **2** **3** (2)

One of us recently reported that lanthanide halides such as cerium chloride can accelerate the rate of phase transfer catalyzed carbonylation of benzylic chlorides catalyzed by nickel cyanide.[11] It is believed that interaction occurs between the lone pair of the nitrogen atom of the cyano ligand with the lanthanide reagent. In principle, such adduct formation can also result when $HCo(CN)_5^{3-}$ is used as the catalyst. Indeed, either hydrated lanthanum or cerium chloride [0.55 mmol, equimolar with respect to cobalt (ytterbium chloride is less effective)] is capable of converting **1** to **2** and **3** in very high yields, irrespective of the concentration of base [i.e. 0.25–5.0 N NaOH], when a 5.2/1.0 ratio of $KCN/CoCl_2{\cdot}6H_2O$ is used in these reactions. However, the product distribution of **2** and **3** is, in most cases, similar to or identical with that realized in the absence of the lanthanide reagent. At a 7/1 $KCN/CoCl_2{\cdot}6H_2O$ ratio, the influence of the lanthanide reagent is modest (e.g. using 2 N KOH results in a 96/4 ratio of **2**/**3**, the yield being 97% without lanthanide; with $CeCl_3{\cdot}7H_2O$ the ratio is 97/3: **2**/**3** and the yield is 98%). In order to determine whether the observations made with the lanthanide compounds were restricted to β-cyclodextrin or of broader scope, an examination was also made of the use of PEG-400, a polyethylene glycol, as a phase-transfer agent for the hydrogenation reaction effected in the absence or presence of lanthanide reagents. Polyethylene glycols[12] are valuable phase-transfer agents for a number of metal-catalyzed processes including oxidation[13] and carbonylation[14,15] reactions. The behavior pattern observed, with and without lanthanide reagent, mirrors that found using β-cyclodextrin (Table II). It should be noted that use of 0.055 mmol [90% yield of products] or 0.20 mmol [92% yield] of lanthanide reagent, instead of 0.11 mmol, in the reaction has no effect on the product distribution although the yield is somewhat reduced. Also, KCl is not required for the lanthanide-promoted process.

Table II. Phase Transfer Catalyzed Hydrogenation of 1 Using PEG-400[a]

KOH, N	$LnCl_3{\cdot}7H_2O$, Ln =	yield,[b] %	product distribution **2**	**3**
0.50		70	71	29
1.0		56	79	21
1.5		29	86	14
5.0		17	94	6
0.50	Ce	100	71	29
1.0	Ce	100	83	17
2.0	Ce	100	86	14
2.0[c]	Ce	89	97	3
5.0	Ce	98	93	7

[a] Reaction conditions are the same as those for β-cyclodextrin except for the use of PEG-400 and KOH instead of NaOH. [b] Yields and product ratios were determined by capillary GC and by ^1H NMR. Products were identified by comparison of gc and NMR with those for authentic materials. [c] Using a 7/1 ratio of $KCN/CoCl_2$.

Table III. Phase Transfer Catalyzed Hydrogenation of Conjugated Dienes Using β-CD[a]

diene	reaction time, h	products,[b] %
1,3-pentadiene	24	*trans*-2-pentene, 96 1-pentene, 2
isoprene	10	3-methyl-1-butene, 67 2-methyl-1-butene, 21 2-methyl-2-butene, 12
4-methyl-1,3-pentadiene	50	2-methyl-2-pentene, 58 *trans*-4-methyl-2-pentene, 23
2-methyl-1,3-pentadiene	50	2-methyl-2-pentene, 58 *trans*-4-methyl-2-pentene, 22
1,3-heptadiene	50	*trans*-3-heptene, 10 *trans*-2-heptene, 4
1,3-heptadiene[c]	48	*trans*-3-heptene, 36 *trans*-2-heptene, 12
1,3-heptadiene[d]	48	*trans*-3-heptene, 49 *trans*-2-heptene, 34
1,3-octadiene	48	*trans*-3-octene, 46 *trans*-2-octene, 8
sorbic acid	48	*trans*-2-hexenoic acid, 75[d] *trans*-3-hexenoic acid, 13[d]
1-vinylcyclohexene	48	1-ethylcyclohexene, 56 ethylidenecyclohexane, 3
cycloheptatriene	36	1,3-cycloheptadiene, 57 cycloheptene, 30 1,4-cycloheptadiene, 13
1,4-cyclohexadiene	70	–

[a] Reaction conditions: diene (5.0 mmol), 2 N KOH (10 mL), C_6H_6 (5 mL), β-CD (0.55 mmol), $CoCl_2{\cdot}6H_2O$ (0.55 mmol), KCN (3.85 mmol), KCl (1.20 mmol), H_2, room temperature, 1 atm. [b] Yields of products were determined by NMR and by GC. [c] Reaction effected without C_6H_6. [d] Using 5.2/1.0 ratio of $KCN/CoCl_2{\cdot}6H_2O$, and $CeCl_3{\cdot}7H_2O$. [e] Isolated yields. Previous attempts to hydrogenate sorbic acid by $HCo(CN)_5^{3-}$ under phase-transfer or micellular conditions failed [Reger, D. L.; Habib, M. M. *J. Mol. Catal.* **1980**, *7*, 365].

The hydrogenation of a series of conjugated dienes was examined using a 7:1 ratio of $KCN/CoCl_2$, β-CD as the phase-transfer agent, and 2 N KOH as the base, and the results are listed in Table III. Note that olefin isomerization does not occur under the reaction conditions, e.g. use of a 47:53 mixture of 1-heptene and *trans*-3-heptene,

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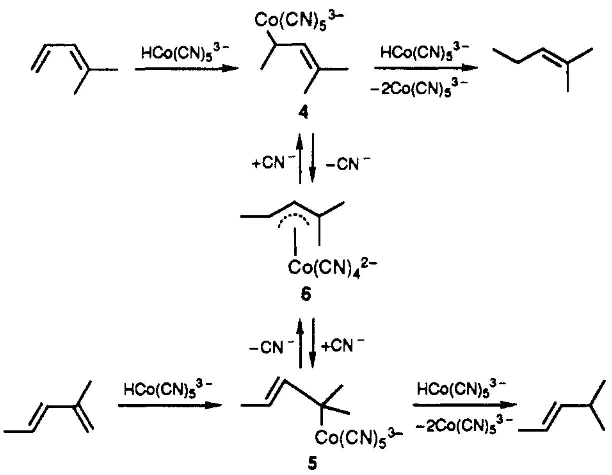
Scheme I



instead of a conjugated diene, in the hydrogenation reaction gave recovered olefins in a 48:52 ratio. All of the internal olefinic products formed in the diene hydrogenation reactions were of trans stereochemistry. The major pathway, except for 2-methyl-1,3-butadiene, involves 1,2-addition of the cobalt hydride to the diene. For dienes having substituents at the 2-position (2,3-dimethyl-1,3-butadiene, isoprene), 1,2-addition apparently occurs to the more substituted double bond of the diene with the cobalt becoming attached to the more substituted carbon atom. For dienes with terminal substituents (4-methyl-1,3-pentadiene, 1,3-heptadiene, 1,3-octadiene) addition takes place at the less substituted double bond. The anionic cobalt hydride adds to the less substituted double bond of a 1,2-disubstituted diene (1-vinylcyclohexene) and, in the case of a 1,4-disubstituted diene, adds to the double bond having the more electron-donating substituent (sorbic acid). Finally, for a 1,3-disubsituted diene (2-methyl-1,3-pentadiene), addition occurs to the double bond having the substituent group at an internal position. The fact that 2-methyl-1,3-pentadiene and 4-methyl-1,3-pentadiene give the same product distribution suggests that the initial σ-allyl intermediates (**4** and **5**) can interconvert via a π-allyl complex **6** (Scheme I).

In conclusion, β-cyclodextrin and PEG-400 are useful phase-transfer agents for the hydrogenation of conjugate dienes to monoolefins catalyzed by the hydridopentacyanocobaltate anion. Furthermore, cerium and lanthanum chlorides can promote the reaction.

Experimental Section

General. All reactants, solvents, and catalysts were commerical materials whose purity was checked prior to use (distillation or recrystallization if necessary). The following instrumentation was used in this research: capillary gas chromatography (Varian 3300 using a DB-1 10 m length column), nuclear magnetic resonance spectroscopy (Varian Gemini 200 MH_z, XL-300 MHz) and mass spectrometry (VG 7070E).

General Procedure for the Hydrogenation of Conjugated Dienes Catalyzed by $HCo(CN)_5^{3-}$, β-Cyclodextrin, and $LnCl_3 \cdot 7H_2O$. A solution of aqueous base [5 mL, see Tables I–III for base concentration] containing cobalt chloride hexahydrate [0.131 g, 0.55 mmol], β-cyclodextrin [0.624 g, 0.55 mmol], and $LnCl_3 \cdot 7H_2O$ [0.55 mmol, if used] was placed in a 50-mL three-necked flask equipped with a gas inlet, a condenser, and a pressure-equalizing dropping funnel. Into the latter was added a mixture of potassium cyanide [0.186 g, 2.85 mmol] and potassium chloride [0.089 g, 1.20 mmol] dissolved in 5 mL of aqueous base. The apparatus was purged three times with hydrogen, and then the cyanide solution was added rapidly to the efficiently stirred solution containing the catalysts. After 30 min, the substrate [5.0 mmol] in benzene [5 mL] was added, and the reaction mixture was stirred under hydrogen at ambient temperature and pressure [see Tables I–III for reaction times, reaction was monitored by GC]. After completion, the phases were separated and the organic phase was subjected to GC and NMR analyses. The aqueous phase was also checked for the presence of any organic products. In the case of sorbic acid, the reaction mixture was carefully acidified with 10% HCl and extracted with ether. The ether extract was dried ($MgSO_4$) and concentrated by rotary evaporation to give *trans*-2-hexenoic acid in 75% yield and *trans*-3-hexenoic acid in 13% yield (ratio determined by ^1H NMR, products could also be distilled).

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Registry No. **1**, 513-81-5; **2**, 563-78-0; **3**, 563-79-1; β-CD, 7585-39-9; PEG-400, 25322-68-3; $LaCl_3$, 10099-58-8; $CeCl_3$, 7790-86-5; $CoCl_2$, 7646-79-9; KCN, 151-50-8; 1,3-pentadiene, 504-60-9; isoprene, 78-79-5; 4-methyl-1,3-pentadiene, 926-56-7; 2-methyl-1,3-pentadiene, 1118-58-7; 1,3-heptadiene, 1002-26-2; 1,3-octadiene, 1002-33-1; sorbic acid, 110-44-1; *trans*-2-pentene, 646-04-8; 1-pentene, 109-67-1; 3-methyl-1-butene, 563-45-1; 2-methyl-1-butene, 563-46-2; 2-methyl-2-butene, 513-35-9; 2-methyl-2-pentene, 625-27-4; *trans*-4-methyl-2-pentene, 674-76-0; *trans*-3-heptene, 14686-14-7; *trans*-2-heptene, 14686-13-6; *trans*-3-octene, 14919-01-8; *trans*-2-octene, 13389-42-9; *trans*-2-hexenoic acid, 13419-69-7; *trans*-3-hexenoic acid, 1577-18-0; 1-vinylcyclohexene, 2622-21-1; cycloheptatriene, 544-25-2; 1-ethylcyclohexene, 1453-24-3; ethylidenecyclohexane, 1003-64-1; 1,3-cycloheptadiene, 4054-38-0; cycloheptene, 628-92-2; 1,4-cycloheptadiene, 7161-35-5.