Rhodium-Catalyzed Carbonylation of Norbornene under Water–Gas-Shift Reaction Conditions. Selective Formation of Co-dimeres with Lactone Terminus

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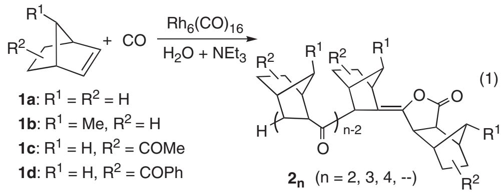
Carbonylation of norbornene in the presence of a rhodium carbonyl catalyst under water–gas-shift reaction conditions gave a norbornene–carbon monoxide co-dimer having an enol–lactone structure in a high yield.

Carbonylations of unsaturated hydrocarbons such as alkenes and alkynes have provided useful methods for the production of a variety of carbonyl compounds such as aldehydes and carboxylic acid derivatives.[1] Cobalt and rhodium complexes are effective catalysts for the carbonylation of alkenes. We previously showed that alkynes are also carbonylated by the catalysis of a rhodium complex to give a cyclocarbonylation product, lactone, under water–gas-shift reaction (WGSR) conditions.[2] Recently we have focused our interest on the carbonylation of cycloalkenes and showed that the carbonylation of norbornadiene gives an alternating co-polymer, polyketones.[3] Now we have found that norbornene undergoes carbonylation to afford an oligomerized and cyclocarbonylated product in a high yield by the catalysis of a rhodium complex under WGSR conditions (Eq 1).



Carbonylation of cycloalkenes is known generally to give aldehydes and alcohols,[4] however the carbonylation of norbornene catalyzed by rhodium carbonyls under WGSR conditions interestingly gave co-oligomerized and cyclocarbonylated products **2**, which have a polyketone main chain with a lactone terminus. Thus, norbornene was treated with carbon monoxide (80 atm) in the presence of water, triethylamine and $Rh_6(CO)_{16}$ (0.3 mol %) in THF at 80 °C. The analysis with GC–MS showed the product to be a mixture of $\mathbf{2a_2}$ (co-dimer, m/z 244, relative intensity 100%), $\mathbf{2a_3}$ (co-trimer, 366, 38%), $\mathbf{2a_4}$ (co-tetramer, 488, 24%), $\mathbf{2a_5}$ (co-pentamer, 610, 20%), and $\mathbf{2a_6}$ (co-hexamer, 732, 13%) (Eq 1). Co-dimer $\mathbf{2a_2}$ was isolated by column chromatography and the mass number of 244 is consistent with a product composed of each two molecules of norbornene and carbon monoxide. The structure was identified to be enol lactone $\mathbf{2a_2}$ by IR and NMR spectra as well as a chemical reaction. The IR spectrum of $\mathbf{2a_2}$ exhibited sharp absorptions at 1786 and 1723 cm^{-1} assignable to γ-lactone with an exocyclic double bond. The ^{13}C NMR spectrum was consistent with the reported data of the enol lactone[5] and showed each pairs of signals due to E and Z isomers in a ratio of ca. 1:3.

In the literature there have already appeared some reports on the formation of enol lactones from the carbonylation reaction of norbornene in the presence of stoichiometric or catalytic amounts of transition metal complexes such as cobalt carbonyl[6] and palladium–phosphine complexes.[5,7] In those reactions, however, a mixture of products containing several oligomers and in some cases hydroformylation products were formed, and the selectivity of the catalytic reactions was low. There have been so far no reports on the selective formation of enol lactones, for example, $\mathbf{2a_2}$.

Table 1. Rhodium-catalyzed carbonylation of norbornene under WGSR conditions[a]

Entry	Solvent/mL	Conv./%	Yield/%[b] of $\mathbf{2a_2}$
1	THF(15)	100	62
2	benzene (15)	100	36
3	toluene (15)	100	50
4	CH_2Cl_2 (15)	100	52
5	dioxane (15)	100	53
6	THF (10)	100	42
7	THF (50)	100	92 (83[c])

[a]Reaction conditions: norbornene, 5 mmol; $Rh_6(CO)_{16}$ 0.015 mmol; NEt_3, 14 mmol; H_2O, 56 mmol; CO, 80 atm; 60 °C. [b]Determined by GC. [c]Isolated yield.

Then, to improve the selectivity of our system we examined the effect of reaction conditions and found that solvents exhibited a somewhat influence, while the concentration of substrate significantly affects the selectivity for $\mathbf{2a_2}$ (Table 1). As a solvent THF is of best choice among the solvents tested, and the carbonylation at a substrate concentration of 0.33 $mol\,dm^{-3}$ gave $\mathbf{2a_2}$ in 62% yield. Use of the same concentration in other solvents such as toluene and dichloromethane gave almost the same result except benzene which showed a low selectivity in the present reaction although it is the best solvent for the copolymerization of norbornadiene with CO.[3] Increase in the substrate concentration resulted in decrease of the selectivity (Entry 6), whereas decrease in the concentration greatly improved the selectivity, and adoption of a substrate concentration of 0.1 M gave 92% selectivity for $\mathbf{2a_2}$. It would be reasonably understood because intermolecular propagation reactions leading to higher oligomers must be depressed at a lower substrate concentration (vide infra).

Norbornene derivatives **1b**–**1d** were also carbonylated under the same reaction conditions to give co-dimers $\mathbf{2b_2}$–$\mathbf{2d_2}$ in good yields. The spectral data indicated the product to be co-dimers, but the chemical sequence in respect to the position of substituent R^2 in **2c** and **2d** has not yet been clear. It should be noted that the carbonylation of 7-methylnorbornene[9] (**1b**, a 1:1 mixture of *syn*- and *anti*-isomers, **1b**–**1** and **1b**–**2**) gave a product ($\mathbf{2b_2}$) derived from the *anti*-isomer (**1b**–**2**), and *syn*-isomer **1b**–**1** was recovered intact after the reaction probably owing to the steric effect of a methyl substituent at the 7-position (Eq 2).

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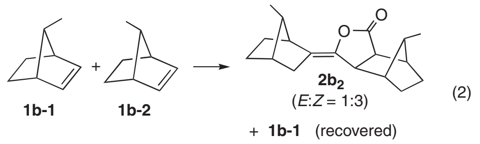
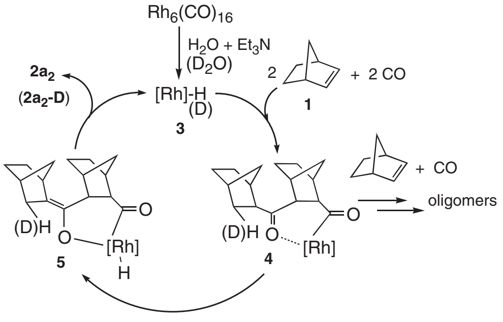
Table 2. Rhodium-catalyzed carbonylation of norbornene derivatives under WGSR conditions[a]

Entry	R^1	R^2	Conv. /%	Yield[b]/% Dimer	Yield[b]/% Oligmer
1	H	H	100	92	0
2	Me	H	100	90[c]	0
3	H	COMe	100	76	24
4	H	COPh	100	85	15

[a]Reaction conditions: substrate, 5 mmol; $Rh_6(CO)_{16}$, 0.015 mmol; NEt_3, 14 mmol; H_2O, 56 mmol; THF, 50 mL; CO, 80 atm; at 60 °C. [b]Determined by GC. [c]The yield is based on the *anti*-**1b** used.



To obtain mechanistic information of the present carbonylation, we carried out the reaction of **1a** in D_2O. The mass spectrum of the product showed an m/z of 245 which is corresponding to monodeuterated co-dimer **$2a_2$-D** and the structure was assigned by the NMR spectra. On the basis of the deuterium experiment as well as the experimental results obtained previously,[3] a plausible reaction mechanism is proposed in Scheme 1. Under WGSR conditions, the Rh carbonyl catalyst is transformed to a hydrido-rhodium species (**3**) by the attack of a hydroxy nucleophile to a carbonyl ligand,[10] followed by successive insertions of norbornene and CO to give intermediate **4**. The intermediate may be transformed to Rh-enolate **5**, and then reductive elimination of co-dimer **2_2** re-generates hydrido-rhodium species **3**. The transformation of **4** to **5** may compete with further insertion of norbornene leading to the formation of oligomers. Although in the carbonylation of norbornadiene an intermediate corresponding to **4** may be considerably stabilized by coordination of an olefinic moiety[3] and the stabilization prevents the transformation to an enolate, resulting in further insertion of norbornadiene and carbon monoxide to form co-polymers. Instead a weak interaction between the Rh and ketonic group in **4** would preferentially transform to enolate **5** at a low substrate concentration, leading to selective formation of **$2a_2$**. The reaction in the presence of D_2O gave products consisting of 60% of **$2a_2$-D** and 4% of **$2a_2$**, suggesting an H–D exchange between Rh–H and D_2O for intermediate **3** or **5**.



Scheme 1. A possible reaction mechanism.

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