

Results and Discussion

All complexes were prepared in a way similar to the preparation of the unsubstituted pyridine complex, $[\text{Co}(\text{C}_5\text{H}_5\text{N})_2\text{Br}_2]$,⁸ which was also used as a substance for the comparison of the catalytic activity of the Co(II) complexes.

The oxidations of α -pinene were performed in non-solvent conditions at 50 °C, 60 °C and 68 °C by bubbling neat oxygen through the mixture of α -pinene and the catalyst.

The catalytic action of monomethyl substituted, di- and trimethylsubstituted and N,N-dimethylamino substituted Co(II) pyridine complexes was separately related to the activity of the unsubstituted one and the most active complexes of each group were related to one other. Each pair of catalyst was studied as side by side reactions, having an equal reaction temperature and flow of oxygen. Typical results are presented in Table 1.

Table 1. Relative Catalytic Action of Cobalt(II) Complexes of Some Pyridine Derivatives in the Allylic Oxidation of α -Pinene at 68 °C by O_2 Flow 38 ml/min.

$[\text{Co}(\text{C}_5\text{H}_5\text{N})_2\text{Br}_2] < [\text{Co}(2\text{-MeC}_5\text{H}_4\text{N})_2\text{Br}_2] < [\text{Co}(3\text{-MeC}_5\text{H}_4\text{N})_2\text{Br}_2] < [\text{Co}(4\text{-MeC}_5\text{H}_4\text{N})_2\text{Br}_2]$
$[\text{Co}(2,6\text{-Me}_2\text{C}_5\text{H}_3\text{N})_2\text{Br}_2] < [\text{Co}(\text{C}_5\text{H}_5\text{N})_2\text{Br}_2] < [\text{Co}(2,4\text{-Me}_2\text{C}_5\text{H}_3\text{N})_2\text{Br}_2] < [\text{Co}(3,5\text{-Me}_2\text{C}_5\text{H}_3\text{N})_2\text{Br}_2]$
$[\text{Co}(\text{C}_5\text{H}_5\text{N})_2\text{Br}_2] < [\text{Co}(2,4,6\text{-Me}_3\text{C}_5\text{H}_2\text{N})_2\text{Br}_2]$
$[\text{Co}(\text{C}_5\text{H}_5\text{N})_2\text{Br}_2] < [\text{Co}(4\text{-N,N-Me}_2\text{NC}_5\text{H}_4\text{N})_2\text{Br}_2]$
$[\text{Co}(2,4,6\text{-Me}_3\text{C}_5\text{H}_2\text{N})_2\text{Br}_2] < [\text{Co}(3,5\text{-Me}_2\text{C}_5\text{H}_3\text{N})_2\text{Br}_2] < [\text{Co}(4\text{-MeC}_5\text{H}_4\text{N})_2\text{Br}_2]$
$[\text{Co}(4\text{-N,N-Me}_2\text{NC}_5\text{H}_4\text{N})_2\text{Br}_2] < [\text{Co}(4\text{-MeC}_5\text{H}_4\text{N})_2\text{Br}_2]$

A higher reaction temperature with the same catalyst mainly accelerated the reaction, but for the most part the relative reactivity order of the catalysts remained the same at different temperatures. However, α -pinene oxidized at 50 °C faster with $[\text{Co}(3,5\text{-Me}_2\text{C}_5\text{H}_3\text{N})_2\text{Br}_2]$ than with $[\text{Co}(4\text{-MeC}_5\text{H}_4\text{N})_2\text{Br}_2]$.

With all the catalysts, the allylic oxidation was very sensitive to changes of the flow rate of O_2 . When the amount of oxygen was diminished the reaction slowed down markedly and when the flow of O_2 was doubled the reaction time was halved. Additionally, the shorter reaction time reduced the amount of side products. The reactions were followed by gas chromatography (GC) and by combined GC-mass spectrometer. α -Pinene seemed to oxidize first to a mixture of alcohols (each component had the molecular ion m/z 152 and they experienced the loss of M-18) and in a smaller amount to verbenone (the molecular ion m/z 150). Subsequently, the alcohols further oxidized to verbenone. Among the side products with a low yield, myrtenal was recognized by using the mass library.

As the most active catalyst among the studied ones, $[\text{Co}(4\text{-MeC}_5\text{H}_3\text{N})_2\text{Br}_2]$ was chosen for the macro scale allylic oxidation of (-)- and (\pm)- α -pinene. The amount of the catalyst was 0.13 mol %. The increase of the amount of the catalyst (to 1 mol %) did not have any significant effect to the rate of oxidation. Enantiopure (-)- α -pinene yielded (-)-verbenone and the racemic α -pinene [(-)/(+), 3:5] yielded racemic verbenone in the

corresponding ratio. The total reaction time was dependent on the rate of oxygen flow. The reaction was stopped when GC showed that α -pinene had been fully consumed. During the long reaction time, the first formed alcohols had oxidized to the only major product, verbenone (76 %). The side products in the reaction constituted each <2 % of the product mixture.

The purification of verbenone was performed by Tiemann's method.⁹ The crude verbenone was dissolved in ether and vigorously shaken with an aqueous solution of NaHSO₃ and NaHCO₃ overnight at room temperature. The two phases were separated and the organic phase was checked by GC. It confirmed that all verbenone was converted into a bisulfite adduct. The water phase was extracted twice with ether before cleavage of the bisulfite adduct. Cleavage was performed by steam distillation in neutral, mildly acidic or basic conditions. The yield and composition of the distillate were dependent on the conditions. The bisulfite adduct of verbenone seemed to be rather stable one and verbenone distilled with steam slowly. Cleavage of the addition compound took place best when boiled with 10 % NaCO₃ solution and the liberated verbenone (98 % pure) was simultaneously steam distilled off. The yield of verbenone was about 35 % from the total amount of verbenone subjected to the purification process. The steam distillation under acidic conditions (1 - 2.5 M HCl solution) increased the amount of the distillate, but the product contained also other compounds. The more acidic conditions during the steam distillation, the more side products were observed. Cleavage in 1 M HCl solution produced a mixture of 77 % of verbenone. Steam distillation directly from the bisulfite solution (pH ca. 7) yielded pure verbenone, but with a low yield.

Purification by distillation caused dimerization.

From the eight Co(II) catalysts of pyridine derivatives studied, [Co(4-Me(C₅H₄N)₂Br₂)] showed the strongest catalytic action in the allylic oxidation of α -pinene by molecular oxygen. This practically wasteless oxidation occurred smoothly under non-solvent conditions with verbenone as the sole product. Purification through the bisulfite adduct yielded the enantiomerically pure product.

Experimental

All complexes were prepared similarly to the unsubstituted pyridine complex.⁸ They were bright blue and their yield varied from 35 - 67 %. The complexes were used as catalysts without recrystallisation, which can be done from absolute ethanol. The complexes could be stored without decomposition in a desiccator.

Reactions comparing the catalytic activity of Co(II) complexes were performed with 10 g of (1S)-(-)- α -pinene (98 %, Aldrich Chemical Co.) in gas wash bottles connected in a chain to each others. Between the reaction vessels there were an empty flask and the first and last reaction bottle contained the catalyst for comparison, [Co(C₅H₅N)₂Br₂]. The catalysts were added either directly to α -pinene or α -pinene which was warmed and saturated with O₂. Oxygen was bubbled through the bottles for 20 min before the immersion of the reaction vessels into a glycol bath. The flow of oxygen was measured at the beginning of the reaction. The progress of the parallel reactions was followed by GC (column CP cyclodextrin-B-236-M-19, length 25 m, i.d. 0.25 mm, phaselayer 0.25 μ m).

The macro scale allylic oxidation was performed with 103.8 g (0.763 mol) of (\pm)- α -pinene (Veitsiluoto Co., Oulu, Finland) 407 mg (0.13 mol %) of [Co(4-Me(C₅H₄N)₂Br₂)] as the catalyst. A constant oxygen flow (60 ml/min) was passed through the reaction mixture in a glycol bath at 72 °C. After seven days all α -pinene had

converted and the crude product contained 76 % of (\pm)-verbenone. The catalyst was removed from the viscous product mixture by dissolving the product first in ether and then by filtering it. Some α -pinene had evaporated with the O₂ flow and the total yield of the crude product was 98.5 g. The purification through bisulfite addition compound⁹ can also be done without the removal of the catalyst, because the aqueous reaction conditions destroy it.

Acknowledgements

Material support from Veitsiluoto Co and financial support from TEKES (Technology Development Centre, Finland) are gratefully acknowledged.

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(Received in UK 14 March 1994; accepted 29 April 1994)