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HOMOGENEOUS SELECTIVE HYDROGENATION OF CYCLODODECATRIENE, CYCLOOCTADIENE, AND 1,6-DIENES TO THE CORRESPONDING MONOENES CATALYZED BY $RuCl_2(PPh_3)_3$

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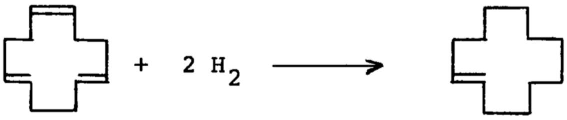
Cyclododecatriene was hydrogenated to cyclododecene with a high selectivity by using $RuCl_2(PPh_3)_3$ as catalyst at room temperature. Selective hydrogenation of cyclooctadiene to cyclooctene was also achieved. Ethyl 2-acetyl-4,9-decadienoate was converted to 2-acetyl-4-decenoate with 100% selectivity at room temperature.

In recent years there has been considerable interest in selective hydrogenation of various substrates catalyzed by homogeneous transition metal complexes.[1] The most well-studied catalyst for this purpose is $RhCl(PPh_3)_3$. In comparison, less extensive studies have been carried out with ruthenium complexes. Wilkinson showed that internal olefins are reduced more slowly than terminal olefins with $RuCl_2(PPh_3)_3$.[2] Selective hydrogenation of 1,4-androstadiene-3,17-dione to 4-androstene-3,17-dione catalyzed by the same complex under the hydrogen pressure of 150 atm was also carried out by Nishimura.[3,4]

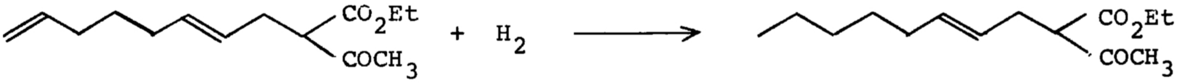
From a preparative point of view, we have investigated selective hydrogenation of 1,5,9-cyclododecatriene (CDT), 1,5-cyclooctadiene (COD), and several 1,6-dienes, and have found that $RuCl_2(PPh_3)_3$ is a very satisfactory catalyst for the selective hydrogenation of these di- and trienes to the monoenes under mild conditions. The selective hydrogenation of CDT to cyclododecene (CDE) was reported by Misono and Ogata by using $Co_2(CO)_8$ coordinated by tributylphosphine at 140°C under the hydrogen pressure of 30 atm.[5] $RuCl_2(CO)_2(PPh_3)_2$ was used as catalyst by Fahey for the same purpose at 135-160°C under the hydrogen pressure of 100-200 psig.[6] We found that the hydrogenation of CDT to CDE proceeded smoothly under mild conditions with $RuCl_2(PPh_3)_3$.



In a typical example, to a solution of *cis,trans,trans*-CDT (4.05 g, 25 mmol) in benzene-ethanol (20 ml each) in an autoclave was added $RuCl_2(PPh_3)_3$ (120 mg, 0.5 mol%), prepared by the Wilkinson's method.[7] Triethylamine (12.6 mg) was added as an activator. The reaction was carried out at room temperature under 10 atm of hydrogen with stirring for 30 hr. The absorption of two molar equivalents of hydrogen was observed. Gas chromatographic analysis of the reaction mixture showed complete conversion of CDT to CDE. Distillation of the product gave *trans*-CDE at 115°C/18 Torr (3.6 g, 87.4%). NMR spectrum shows two olefinic protons at δ 6.50 and four allylic protons at δ 2.15. A strong IR band at 970 cm^{-1} shows that the double bond has a trans configuration.

The hydrogenation of COD was slower than that of CDT, but proceeded smoothly by warming. Thus, a mixture of COD (4.33 g, 40 mmol), the ruthenium complex (115 mg, 0.12 mmol, 0,3 mol%), and triethylamine (20.2 mg, 0.2 mmol) in benzene-ethanol (25 ml each) was placed in the autoclave. The autoclave was charged with 10 atm of hydrogen. The hydrogenation was carried out at 45°C for 12 hr, and cyclooctene (COE) was isolated by distillation at 44°C/20 Torr (3.94 g, 89.2%). Gas chromatographic analysis showed the 100% selectivity of the reaction. NMR (CCl_4): δ 3.5 (m, 2H, olefin), 2.15 (m, 4H, allylic), 1.50 (m, 8H). Fahey reported that the selective hydrogenation of COD to COE was not possible with $RuCl_2(CO)_2(PPh_3)_2$.[6]

In our natural product synthesis, the selective hydrogenation of the terminal double bond of ethyl 2-acetyl-4,9-decadienate became necessary, and again the ruthenium complex was found to be a good catalyst.[8] The ester (4.35 g, 18.3 mmol) was hydrogenated with $RuCl_2(PPh_3)_3$ (96 mg, 0.1 mmol) in benzene-ethanol (20 ml each) at room temperature under 29 atm of hydrogen. Absorption of hydrogen virtually stopped after 6 h. Distillation of the reaction mixture gave ethyl 2-acetyl-4-decenoate at 135°C/3 Torr (4.07 g, 93%). Gas chromatographic analysis and NMR spectrum showed that the selectivity to the monoene was complete. NMR (CCl_4): δ 5.40 (m, 2H, olefin), 4.20 (q, 2H), 3.35 (t, 1H), 2.5 (m, 2H), 2.1 (s, 3H), 2.0 (m, 2H), 0.9-1.4 (m, 12H). When the hydrogenation was carried out at temperatures higher than 50°C, a slow hydrogenation of the internal double bond was observed and hence the selectivity became lower.



Under the same conditions, the 1,6-diene systems of butyl 3,8-nonadienoate, ethyl 4,9-decadienoate, and 2,7-octadienyl acetate were hydrogenated to give the internal monoenes with high selectivity.

Thus, these studies clearly show that $RuCl_2(PPh_3)_3$ is a very satisfactory catalyst for selective hydrogenation under mild conditions and the method can be used for preparative purpose.

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