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Preliminary communication

CATALYTIC HYDROGENATION OF α-TERPINENE AND 2,3-DIHYDROANISOLE BY A PHENANTHRENECHROMIUM TRICARBONYL COMPLEX

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Summary

The hydrogenation of α-terpinene and 2,3-dihydroanisole catalysed by phenanthrenechromium tricarbonyl is described and discussed.

Arenechromium tricarbonyl complexes are very effective catalysts for the regioselective 1,4-hydrogenation of dienes to monoenes [1]. The substitution of a carbonyl group by a chiral ligand would be of interest in connection with asymmetric synthesis. We previously reported our results on the activities of a series of arene-$Cr(CO)_2L$ compounds in catalytic hydrogenation [2]. The replacement of a CO ligand in the $Cr(CO)_3$ group by the *N*-benzoyl isocyanide (L = CNCOPh) and the trifluorophosphine (L = PF_3) ligands led to satisfactory catalytic properties for the hydrogenation of bicyclo[2.2.1]hepta-2,5-diene. In continuation of this work, we now report preliminary studies of the catalytic hydrogenation of two prochiral dienes, 2,3-dihydroanisole and α-terpinene. Attempts to induce asymmetric catalytic activity by adding chiral ketones to the hydrogenation mixture are also described.

The 2,3-dihydroanisole contaminated with approximately 20% of the 2,5-dihydroanisole was first chosen as a substrate because of its commercial availability and because the hydrogenation products can be readily identified. The results are listed in Table 1 and show that while 2-methoxycyclohexene is the major reduction product (75%), an appreciable amount of 1-methoxycyclohexene and traces of 3-methoxycyclohexene are also formed. If 1,4-addition is the main reduction path as previously reported [1], the distribution of methoxycyclohexene isomers can be accounted for in terms of the various modes of conjugation of the double bonds in the 2,5-dihydroanisole isomer before reduction. Additional information about the stereoselectivity and regioselectivity of the reaction should be obtained from planned studies with deuterium.

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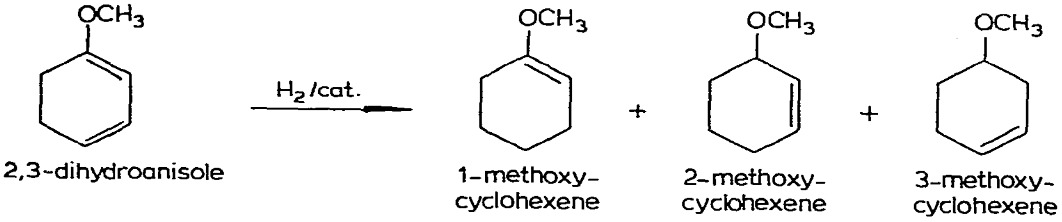
TABLE 1

HYDROGENATION OF 2,3-DIHYDROANISOLE CATALYSED BY PHENANTHRENE-$Cr(CO)_3$ [a]

Solvent (volume)	Reaction time (h)	Hydrogenation product distribution [b]		
		1-methoxy-cyclohexene	2-methoxy-cyclohexene	3-methoxy-cyclohexene
Cyclohexane (50 ml)	28	20	76	4
Acetone (50 ml)	2	21	75	4
Cyclohexane (50 ml) Acetone (3 ml)	6	20	73	7
Cyclohexane (50 ml) (+)-3-methyl cyclohexanone (3 ml) [c]	6	18	78	4

[a] The reaction involved 3×10^{-2} *M* of 2,3-dihydroanisole (± 0.6×10^{-2} *M* of 2,5-dihydroanisole) and 0.5×10^{-3} *M* of catalysts at 80°C under 7 atm of H_2. [b] The reduction was continued until a 99% yield was obtained. [c] Two other chiral ketones, *l*-carvone and *l*-menthone, were also examined, but without success.

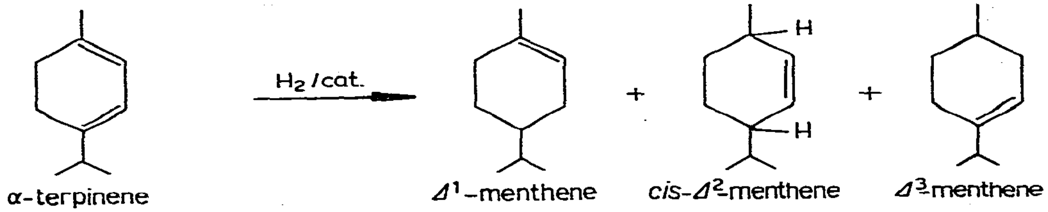
SCHEME 1



Of particular interest is the observation that the catalytic reaction is greatly accelerated when minute quantities of ketone are added to the cyclohexane solution. Facilitation of the catalytic reaction by the use of coordinating solvents such as tetrahydrofuran or acetone instead of cyclohexane has been reported previously [4]. As can be seen from Table 1, this effect is evident even when only small quantity of a ketone is added to the cyclohexane. In order to induce asymmetric synthesis, chiral ketones such as (+)-3-methylcyclohexanone or *l*-carvone were added to the cyclohexane solution, but all attempts to detect optical activity in the 2-methoxycyclohexene were unsuccessful.

We chose α-terpinene as a second diene for the reduction because large amounts are available from natural oils [5]. Furthermore substrates having alkyl substituants in the 1 and 4 positions of the diene undergo hydrogenation less readily [6]. Consequently the study of the hydrogenation should give more information on the preparative utility of this catalytic reaction. Stereospecific hydrogenation of α-terpinene catalysed by phenanthrene-chromium tricarbonyl [7] in cyclohexane at 120°C (under 20 atm of H_2) leads to *cis*-Δ^2-menthene [8]. The regioselectivity of the 1,4-addition of hydrogen was found to be 81% and two other isomers, Δ^1-menthene and Δ^3-menthene, were present in 11 and 8% yield, respectively. α-Terpinene was reduced slowly and the reaction required 9 h for completion. Raising the temperature from 120 to 170°C increased the rate (reaction time: 3 h) but re-

SCHEME 2



sulted in a mixture of Δ^1- and Δ^3-menthene as main products (99% reduction). The activity of phenanthrene-$Cr(CO)_3$ in catalyzing isomerization of terpenes was studied to see whether this reaction might explain the change in selectivity on raising the temperature. No isomerization of α-terpinene [9] was detected under a nitrogen pressure of 20 atm. at 175°C after 6 h, while *cis*-Δ^2-menthene is isomerized slowly to a mixture of the Δ^1- and Δ^3-menthene (respectively 45/55), the yield being 68% under the same conditions [7]. Therefore, the preponderant formation of Δ^1- and Δ^3-menthene under the hydrogenation conditions at 175°C can be attributed to isomerization of the *cis*-Δ^2-isomer.

The reduction of other natural dienes are currently under investigation.

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