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Preliminary communication

Photo-induced hydrogenation of conjugated dienes catalyzed by chromium hexacarbonyl★

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Various arene- and cyclopentadienyl-chromium complexes have been used as catalysts for the thermal hydrogenation of conjugated dienes[2]. The amounts of metal complexes needed are relatively large, elevated temperatures and sometimes high pressures are necessary. Mixtures of various isomers are generally obtained.

Chromium hexacarbonyl has been found to be a good catalyst for the light-induced hydrogenation of 2,3-dimethylbutadiene and 1,3-cyclohexadiene, yielding respectively 2,3-dimethyl-2-butene and cyclohexene. It is noteworthy that hydrogenation occurred exclusively on the 1–4 positions, isomer-free 2,3-dimethyl-2-butene being obtained.

Preliminary experiments with norbornadiene chromium tetracarbonyl show that this complex catalyzes the hydrogenation of norbornadiene. The mechanisms of this reaction is being investigated.

EXPERIMENTAL

(*a*) A 10 ml solution of 1,3-cyclohexadiene ($7 \cdot 10^{-2} M$) and chromium hexacarbonyl ($1.5 \cdot 10^{-3} M$) in decalin (free aromatic compounds), was degassed by freeze-pump-thaw cycles (10^{-4} mm), and the Pyrex reaction cell was connected to a hydrogen tank with a by-pass system maintaining 1 atmosphere pressure. The reaction mixture was stirred to achieve the gas-solution equilibrium before irradiation with 360 nm light from a high pressure mercury arc fitted with a Baush & Lomb grating monochromator. Total transformation into cyclohexene was observed after 2.5 hours irradiation.

The extent of reaction was followed by gas chromatography on a Carbowax 10% or tricresylphosphate column, using helium as carrier gas. Blank experiments showed that light and chromium hexacarbonyl were both necessary.

(*b*) A 10 ml decalin solution containing 2,3-dimethylbutadiene ($0.16 M$) and chromium hexacarbonyl ($2 \cdot 10^{-4} M$) was irradiated under one atmosphere H_2 pressure.

★See also ref. 1.

After 2¼ h, approximately 30% of the diene was converted into 2,3-dimethyl-2-butene. Hydrogenation proceeded further on additional irradiation. Gas-chromatography on a diisodecylphthalate column or a Carbowax 10% column allowed identification of the reaction product since authentic mixtures of 2,3-dimethyl-2-butene and 2,3-dimethyl-1-butene were perfectly separated. The NMR spectrum allowed unambiguous assignment of the product.

(*c*) The usefulness of the method as a synthetic tool was shown when a mixture of 2 ml pure 2,3-dimethylbutadiene and 0.002 g chromium hexacarbonyl was irradiated (with the full spectral range of a Philips HPK 125 W medium-pressure mercury lamp) under one atmosphere H_2 pressure. Three hours photolysis yielded 13% conversion and hydrogenation went further on additional irradiation.

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