# Stepwise and Catalytic *cis*-Hydrogenation of an Alkyne under Single Phase Conditions, including the Isolation of an Intermediate, an Alkyne–Transition Metal Hydride Adduct

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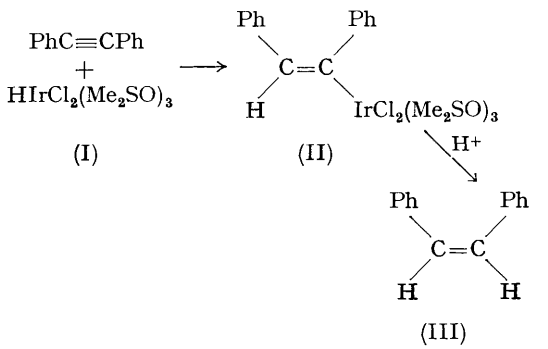
*cis*-ALKENES are the main products first formed in the reduction of alkynes by molecular hydrogen in the presence of metals[1] or certain complexes of ruthenium[2] or rhodium.[3] Such reactions are generally thought to proceed *via* intermediates in which carbon is bonded temporarily to a metal atom. A stable intermediate has now been obtained by keeping a solution of diphenylacetylene (72 mg.) and hydrodichlorotris(dimethyl sulphoxide)iridium (I) (100 mg.) in propan-2-ol (5 ml., containing 2% water) at 73° for 90 minutes. The adduct separates during the reaction; after cooling the yield is 80 mg. Crystallisation from chloroform–pentane gives the adduct as cream needles, m.p. 196—198°, correct analysis for $C_{20}H_{29}Cl_2O_3S_3$ (*cf.* II), H–Ir group absent (i.r. and n.m.r. evidence). Treatment of this compound with boiling methanol containing concentrated hydrochloric acid (10% v/v) for 2 min. gives *cis*-stilbene (> 90%), identified by gas chromatography and by preparation of the methoxychloromercuri-compound, PhCH(OMe)CH(HgCl)Ph, m.p. and mixed m.p. 145—146° (lit.,[4] m.p. 143°). If retention of configuration occurs in the replacement of the iridium-containing group by hydrogen (as is general for the protonolysis of vinyl–metal bonds), the adduct can be formulated as (II); its formation then involves *cis*-addition of the metal hydride to the triple bond.




*cis*-Hydrogenation can be effected in one operation by having acid present in the reaction solution together with the hydride, in catalytic proportion. A reaction starting with a molar ratio of 20 : 1 : 2 of diphenylacetylene : hydride : hydrogen chloride in propan-2-ol (2% water) at 65° gives *cis*-stilbene (*ca.* 35% after 3 hr. and *ca.* 60% after 8 hr., the corresponding yields of *trans*-stilbene being *ca.* 1 and 2%). The adduct (II) can be used in place of hydride to give closely similar results.

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