

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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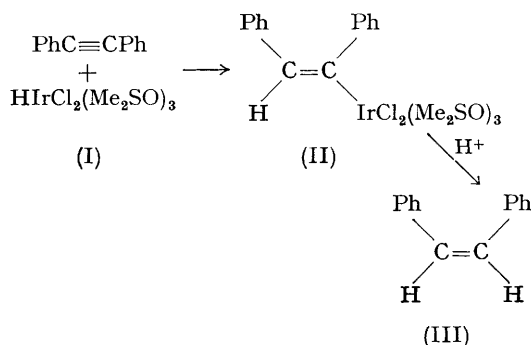
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cis-ALKENES are the main products first formed in the reduction of alkynes by molecular hydrogen in the presence of metals¹ or certain complexes of ruthenium² or rhodium.³ Such reactions are generally thought to proceed *via* intermediates in which 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 $C_{20}H_{20}Cl_2O_3S_3$ (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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