Some Alkyl, Acetyl, Aryl, and Benzoyl Derivatives of Tungsten

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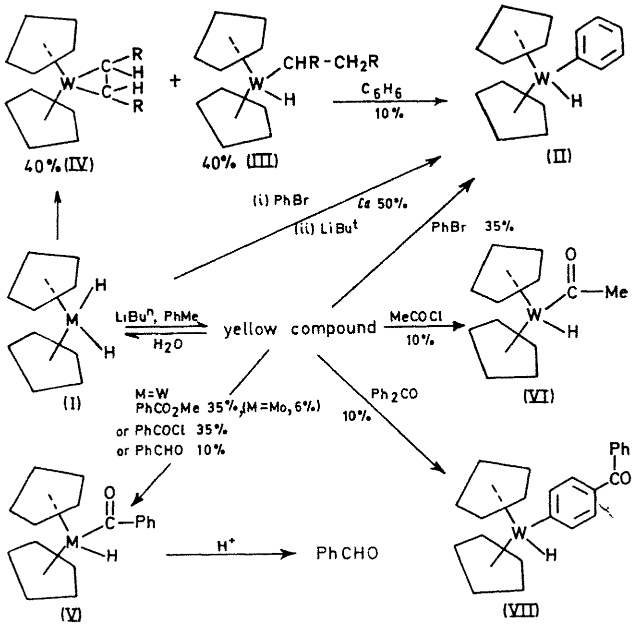
Summary The preparation and properties of the new compounds $(\pi\text{-}C_5H_5)_2WHR$ [where R = $CH(CO_2Et)\cdot CH_2\cdot(CO_2Et)$, COPh, COMe, $p\text{-}C_6H_4\cdot COPh$], $(\pi\text{-}C_5H_5)_2W[CH(CO_2Et)\cdot CH(CO_2Et)]$, and of some molybdenum analogues are described.

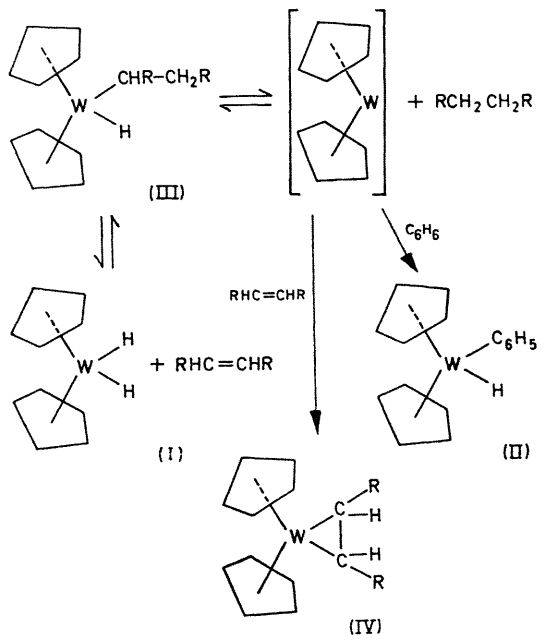
IT was observed recently that the reaction between the dihydride $(\pi\text{-}C_5H_5)_2MH_2$ (I; M = W) and a diene in benzene or toluene led to the formation of the aryl–hydrides $(\pi\text{-}C_5H_5)_2WH(C_6H_4R)$, (II; R = H or Me, respectively).[1] It was suggested that the reaction proceeded *via* homogeneous substitution of the aromatic ring by tungstenocene which was formed as an intermediate.

Further studies on this reaction, described here, show that the dihydride (I; M = W) readily adds to the maleic acid ester RCH=CHR (R = CO_2Et), giving the succinyl derivative (III). Also formed in this reaction is the compound (IV) which the ^1H n.m.r. spectrum shows to have the *trans*-configuration and which may be represented as a tungstenacyclopropane derivative, as shown in the Scheme. The molybdenum analogue of (IV) is similarly prepared.



SCHEME

If the succinyl compound (III) in benzene is heated at 120° for 6 h, then the phenyl–hydride (II) is formed in *ca.* 10% yield, together with some of the cyclic compound (IV), the dihydride (I; M = W) and diethyl succinate; the following equilibria may be envisaged to occur:



In a separate experiment it was found that heating solutions of the phenyl–hydride (II) in deuteriobenzene at 120° for up to two days did not give any pentadeuteriophenyl derivatives. This suggests that the phenyl–hydride (II) is not a good source of the tungstenocene intermediate.

In a search for an improved route to the phenyl–hydride (II) some surprising reactions have been found. For example, addition of butyl-lithium in hexane to the dihydrides (I; M = Mo or W) in toluene gives yellow precipitates. They are very reactive towards both oxygen and water, and have not yet been characterised. However, they behave as though they contain an extremely reactive anion $[(\pi\text{-}C_5H_5)_2MH]^-$. For example, when M = W, the yellow compounds react with PhBr, PhCOX (X = H, OMe or Cl), or MeCOCl giving the derivatives (II), (V), and (VI), respectively; see the Scheme. Higher yields (*ca.* 50%) of the phenyl–hydride (II) are obtained when butyl-lithium is added to a solution of the hydride (I; M = W) in bromobenzene. It is also worth noting that treatment of the benzoyl derivative (V; M = W) with hydrogen chloride gives benzaldehyde in high yield.

We report finally the unexpected observation that treatment of the yellow precipitate (M = W) with benzophenone gives the *p*-benzoylphenyl derivative (VII).

All the new compounds have been fully characterised by analysis, i.r., ^1H n.m.r., and mass spectra.

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[1] M. L. H. Green and P. J. Knowles, *J. Chem. Soc.* (*A*), 1971, 1508.