63-2-4

Office of Naval Research

Contract No. N62558 - - - 2381

Task No. NR051 - - - 417

Technical Report No.5

Reduction by Metal Carbonyls.

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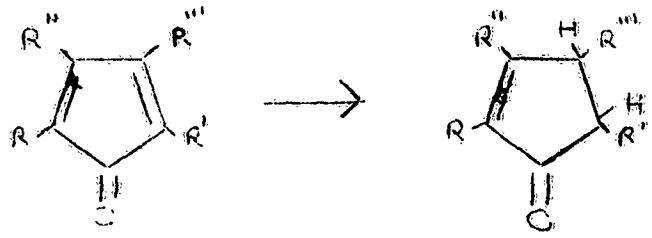
Reduction by metal carbonyl hydrides such as $Fe(CO)_4H_2$ and $Co(CO)_4H$ are well known. Reductions by organometallic complexes apparently involve the transient formation of metal-hydrogen bonds (1,2). We wish to report that Group 6 carbonyls can also act as reducing agents in the presence of moisture but not apparently via their unstable hydrides and hydride ions such as $Cr(CO)_5H^-$ but rather through the reaction of unstable π-complexes. Thus, when a solution (10^{-1}M) of hexacarbonylchromium in isooctane which is also approximately molar with respect to water is refluxed under nitrogen with an organic oxidant, quantitative yields of the reductant are obtained. The reaction proceeds smoothly for oxidants such as tetrasubstituted cyclopentadienones with R=R'=R''=R'''=Ph; R=R'=Me, R''=R'''=Ph; R=R'=Et and R''=R'''=Ph.

In addition, good yields have been obtained of hydroquinone from p-benzoquinone, benzoin from benzil (20%) and quantitative reduction of methylene blue observed. In none of these cases is reduction obtained in the absence of water. The reaction with tetraphenylcyclopentadienone differs from the others in that excess carbonyl forms small quantities (5%) of tricarbonyl-π-2,3,4,5-tetraphenylcyclopenta-2-en-1-one chromium and about 1% of tricarbonyl-π-tetraphenylcyclopentadienone chromium. However, in both complexes the ketonic carbonyl frequency lies higher than in the parent ketone so the phenyl substituents are probably used for forming π-bonds with the $Cr(CO)_3$ moiety.

It is tempting to consider the reducing nature of the above solution as arising from the presence of the unstable $Cr(CO)_5H^-$


R''
R'''
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R'
C
R''
H
R'''
R
H
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anion but there is no evidence for this. The rate of reduction of tetraphenylcyclopentadienone is approximately independent of previous refluxing time and, moreover, the evolution of carbon monoxide from hot solutions of hexacarbonylchromium in both dry and moist isooctane is less than 1% per mole so no appreciable reaction occurs. However, addition of tetraphenylcyclopentadienone or benzoquinone causes a rapid evolution of carbon monoxide which ceases when reduction is complete (3 moles/mole of oxidant). There is also no spectral evidence for chemical change before addition of oxidant. We consider then that reduction proceeds via an unstable π-complex in which the $Cr(CO)_3$ group is bonded to the central ring with subsequent protonation at the metal atom followed by intramolecular hydrogen transfer. Previous molecular-orbital calculations (3) showed that complexes of the type (tetraphenylcyclopentadienone) $M(CO)_3$ would be more stable for M=Fe than Cr because of the occupation of a vacant and slightly bonding π-orbital in the former; this supports the above scheme for the reduction of this ketone. Detailed studies of the kinetics of these reactions are in progress.

(1) Sternberg and Wender, Internat. Conf. Coordination Chemistry, Chem. Soc. Special Publ. No. 13, 1959, p. 35.

(2) Brown, Hargaden and Sloan, above.

(3) Brown, J. Inorg. Nuclear Chem., 1959, 10, 49.

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