939. *Reduction Reactions of Organometallic Compounds. Part I.*

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The reduction of a series of conjugated ketones by moist hexacarbonylchromium solutions is described. It is suggested that reduction proceeds through an unstable π-complex which is sensitive to protonation. Reduction by stable π-complexes, tricarbonylarenechromiums, in acid solution is also described and a similar mechanism is suggested.

HYDRIDO-COMPLEXES of transition metals containing ligands of high field strength are particularly stable owing to the metal's acquiring some metalloid character.[1] The hydridocarbonylcyclopentadienyl-metals, $MH(C_5H_5)(CO)_3$ (M = Cr, Mo, and W), and hydridocarbonylphosphine-metals, $MHClCO(PR_3)$ (M = Os or Ru) [1] are examples. These compounds, in which the hydrogen is firmly bound and may be regarded as anionic, do not act as reducing agents. In marked contrast, hydridocarbonyl-metals such as $H_2Fe(CO)_4$ and $HCo(CO)_4$ are unstable and strong reducing agents; [2,3] for example, they reduce olefins to the alkanes. The anions of these carbonyls, formed by reaction of the parent carbonyl with water or alkali, are also good reducing agents.[3] Similarly, hydrogenation in the presence of carbonyls such as octacarbonyldicobalt is presumed to involve the hydridocarbonyl-metal as intermediate. In these compounds the hydrogen is weakly bound and cationic in character, as shown by their acidity, so that reducing ability may be related to this property. Extension of these ideas suggests that organometallic compounds which can be protonated may also be reducing agents. Sternberg and Wender [2] suggested this to explain the quantitative reduction of azobenzene to benzidine by a solution of dicarbonyl-π-cyclopentadienyliron dimer in ethanolic hydrochloric acid in terms of protonation at the iron atom:

$$PhN{=}NPh + 2HCl + (C_5H_5)_2Fe_2(CO)_4 \longrightarrow 2C_5H_5Fe(CO)_2Cl + H_2N{\cdot}C_6H_4{\cdot}C_6H_4{\cdot}NH_2$$

Wilkinson and his co-workers [4] have criticized the above explanation since there is no direct evidence for the species $(C_5H_5)_2Fe_2(CO)_4H_2^{2+}$. However, it should be stressed, especially in view of the instability of hydridocarbonyl-metals at these temperatures, that the protonated species need have only transient existence to be a reducing agent; for example, ethanolic solutions of tricarbonylarenechromiums decompose rapidly in the presence of acid owing, presumably, to the instability of the protonated species. In this paper, reduction by Group VI carbonyls in the presence of water and by acid solutions of tricarbonylarenechromiums is discussed in terms of protonation of a π-complex as an important step during reduction.

Reduction by Moist Solutions of Hexacarbonylchromium.—Refluxing a solution of hexacarbonylchromium in 2,2,4-trimethylpentane, made molar with respect to water, under nitrogen with an unsaturated compound gives good yields of the reduced compound. Tetrasubstituted cyclopentadienones form the corresponding cyclopent-2-enones; low yields obtained with the 2,5-dimethyl-3,4-diphenyl compound may be related to the high stability of its dimer. Reduction of *p*-benzoquinone to quinol, of benzil to benzoin, and of Methylene Blue also occurs; however, in the case of stilbene only the known mononuclear π-complex [5] was obtained, and no saturated compound.

Tetraphenylcyclopentadienone reacts with an excess (essential) of carbonyl-metal, giving

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[1] Chatt, *Proc. Chem. Soc.*, 1962, 318.

[2] Sternberg and Wender, Internat. Conf. Co-ordination Chem., *Chem. Soc. Special Publ.*, No. 13, 1959, p. 35.

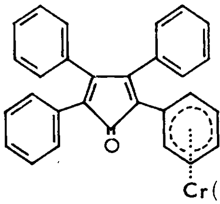
[3] Chatt, Pauson, and Venanzi, "Organometallic Chemistry," Reinhold Publ. Corp., New York, 1960.

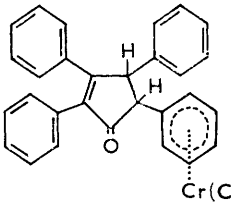
[4] Davison, McFarlane, Pratt, and Wilkinson, *J.*, 1962, 3653.

[5] Calderazzo, Ercoli, and Mangini, *Ricerca Sci.*, 1959, **29**, 2615.

small quantities of a blue and a yellow complex, the former obtained in the absence of water. The first compound was shown to be tricarbonyl-π-(tetraphenylcyclopentadienone)-chromium by analysis and by ultraviolet and infrared spectra. Solutions of this complex in light petroleum were blue, with $\lambda_{\max.}$ 323 mμ; the solution gradually became violet, with $\lambda_{\max.}$ 331 mμ close to that of tetraphenylcyclopentadienone itself ($\lambda_{\max.}$ 335 mμ). The yellow compound was similarly shown to be tricarbonyl-π-(2,3,4,5-tetraphenylcyclopent-2-enone)chromium; it was also synthesised from 2,3,4,5-tetraphenylcyclopent-2-enone and hexacarbonylchromium. In both complexes the ketonic-carbonyl stretching frequency lies close to, or higher than, that in the parent ketone, which is not in accord with molecular-orbital theory[6] if the $Cr(CO)_3$ group is bonded to the central ring. It seems probable, therefore, that the $Cr(CO)_3$ group is bonded to one of the phenyl substituents (cf. I). If this is correct, then two structural isomers could arise, from the bonding of the $Cr(CO)_3$ group to different phenyl substituents. In fact, chromatography of the product obtained by direct synthesis of tricarbonyl-π-(2,3,4,5-tetraphenylcyclopent-2-enone)chromium gave a number of bands from which unfortunately we were not able to isolate any pure structural isomer because of rapid decomposition on elution.

(I)





(II)

Mechanism of Reduction.—Hydrogen abstraction from the solvent can be discounted since no reduction was observed in the absence of water; however, in an aprotic solvent such as carbon tetrachloride reduction still proceeded but gave a lower yield, presumably owing to the lower reaction temperature. The water is then the source of hydrogen. Stable π-complexes are not intermediates and were formed only in the case of tetracyclone in the presence of an excess of carbonyl, and then the major yield was from the reduced compound. No spectral evidence (u.v. or visible) was obtained for any change before reduction although attempts to measure the n.m.r. spectrum of hexacarbonylchromium in hot moist 2,2,4-trimethylpentane were thwarted by the low solubility of the carbonyl. The evolution of carbon monoxide from hot solutions of hexacarbonylchromium in dry or moist trimethylpentane was less than 1 mole %, but addition of tetraphenylcyclopentadienone or of benzoquinone caused an evolution of 3 moles of carbon monoxide per mole of reduced compound formed. The unstable and reducing hydrocarbonyl anion, $HCr(CO)_5^-$, may be discounted.

We suggest then that reduction proceeds through an unstable π-complex in which the $Cr(CO)_3$ group is bonded to the central ring with subsequent protonation (and possibly solvation) at the metal atom, followed by intramolecular hydrogen transfer. The chromium in the unstable complex is oxidized to a chromium(III) entity and eventually to chromic acid or a complex oxide. Previous molecular-orbital calculations[6] 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 views for the reduction of this ketone.

Reductions by Tricarbonylarenechromiums.—It is also possible to observe reductions by the use of stable π-complexes. Solutions of azobenzene and tricarbonylarenechromiums, $RC_6H_5Cr(CO)_3$, in dilute ethanolic hydrochloric acid gave fair yields (up to 30%) of benzidine hydrochloride. The reaction occurred for the substituent range, $R = Me$, Cl, H, NH_2, NHMe, and NMe_2, and was facilitated by electron-repelling groups; this is consistent with

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[6] Brown, *J. Inorg. Nuclear Chem.*, 1959, **10**, 39.

protonation at the chromium atom, assisted by charge transfer, as discussed by two of us previously.[7] No reduction was found in the absence of acid, so some type of protonation seems essential. More dilute solutions (10^{-4}M) of the complexes decomposed rapidly (30—120 minutes) in ethanolic hydrochloric acid with evolution of carbon monoxide and free arene; for example, spectrophotometric studies of tricarbonylanilinechromium gave an immediate fall in intensity of the 315 mμ band followed by further decrease due to decomposition.

In view of these results, it is hardly surprising that Wilkinson and his co-workers[4] found decomposition of tricarbonylarenechromiums in 98% sulphuric acid within a few minutes; however, at the higher concentrations thereby achieved, n.m.r. evidence was obtained for metal–hydrogen bonds, which supports the above views for dilute solutions. In the presence of an unsaturated system, reduction apparently occurs by hydrogen transfer from the protonated complex with, consequently, less direct decomposition. Increase in reaction temperature favours the latter and the yields of benzidine were then correspondingly lower.

The above reductions by carbonyl-metals and organometallic compounds are consistent with the formation of metal–hydrogen bonds as an important step in the process.

EXPERIMENTAL

Ultraviolet spectra were measured for 2,2,4-trimethylpentane, ethanol, or cyclohexane solutions on a Bausch and Lomb 505 recording spectrophotometer. I.r. spectra were measured for potassium bromide discs and carbon tetrachloride solutions on a Beckman, I.R.5 double-beam spectrometer. N.m.r. spectra were taken on the A.E.I. instrument at Sheffield University. Estimation of carbon monoxide evolved during a reaction was carried out by an iodine pentoxide furnace method.[8] It was essential to use silica gel and cold traps line to prevent contamination of the furnace by solvents.

Reaction of Hexacarbonylchromium and Tetraphenylcyclopentadienone in Absence of Water.—A solution of hexacarbonylchromium (1·2 g.) and tetracyclone (1 g.) in 2,2,4-trimethylpentane (25 ml.) was refluxed under nitrogen for 80 hr. A brown amorphous insoluble compound (0·55 g.) was filtered off and when heated with cyclohexane gave tetracyclone. The yellow filtrate was chromatographed on alumina; elution with benzene gave unchanged tetracyclone (0·7 g.) and blue crystals of *tricarbonyl-π-tetraphenylcyclopentadienonechromium*, m. p. 215° (decomp.) (Found: C, 72·9; H, 4·2. $C_{32}H_{20}CrO_4$ requires C, 73·8; H, 3·9%). The i.r. spectrum showed terminal carbonyl absorption at 5·1, 5·3, and 5·35 μ and a ketonic-carbonyl band at 5·84 μ. $\lambda_{max.}$ at 323 and 618 mμ.

Reaction of Moist Hexacarbonylchromium and Tetraphenylcyclopentadienone.—Hexacarbonylchromium (1·2 g.) and tetracyclone (1 g.) in 2,2,4-trimethylpentane (25 ml.) and water (2 ml.) were refluxed under nitrogen for 50 hr. A green insoluble compound was filtered off and the yellow solution chromatographed on alumina. Elution with light petroleum gave unchanged tetracyclone (0·23 g.), and use of benzene gave 2,3,4,5-tetraphenylcyclopent-2-enone (0·80 g.), m. p. 162—163° (Found: C, 89·6; H, 6·0. $C_{29}H_{22}O$ requires C, 90·1; H, 5·7%), and orange *tricarbonyl-*2,3,4,5-*tetraphenylcyclopenta-*2-*enonechromium* (0·1 g.), m. p. 183—187° (Found: C, 73·1; H, 4·7; Cr, 9·9. $C_{32}H_{20}CrO_4$ requires C, 73·6; H, 4·3; Cr, 10·0%), $\lambda_{max.}$ 307 mμ (in EtOH), $\nu_{max.}$ (terminal C=O) 5·09, 5·20, and 5·28 μ, and (C=O) 5·84 μ.

2,3,4,5-*Tetraphenylcyclopent*-2-*enone*.[9]—A solution of tetracyclone (0·5 g.) in glacial acetic acid (175 ml.) was refluxed with slow addition of zinc dust (1 g.). The product, precipitated with water and recrystallized from cyclohexane, had m. p. and mixed m. p. 162—163° (Found: C, 89·5; H, 6·1%), $\lambda_{max.}$ 226—228 and 296 mμ.

*Tricarbonyl-π-*2,3,4,5-*tetraphenylcyclopent-*2-*enonechromium.*—2,3,4,5-Tetraphenylcyclopent-2-eneone (1 g.) and hexacarbonylchromium (1 g.) in 2,2,4-trimethylpentane (40 ml.) were refluxed under nitrogen for 50 hr. Orange crystals of one form of tricarbonyl-π-2,3,4,5-tetraphenylcyclopent-2-enonechromium, m. p. 192—196° (decomp.), were formed (Found: C, 73·3; H, 4·3%). This isomer was insoluble in most solvents; it had $\lambda_{max.}$ 233, 257, and 299 mμ

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[7] Brown and Sloan, *J.*, 1962, 3846.

[8] Adams and Simmons, *J. Appl. Chem.*, 1951, *S.* **20**, 1.

[9] Cf. Sonntag, Linder, Becker, and Spoerri, *J. Amer. Chem. Soc.*, 1953, **75**, 2283.

in EtOH; its i.r. spectrum included terminal-carbonyl frequencies at 5·09, 5·20, and 5·28 μ and a ketonic-carbonyl band at 5·84 μ, with the remainder of the spectrum close to that of the cyclopentenone. Chromatography of the filtrate on alumina and elution with benzene gave unchanged cyclopentenone and an orange *form* of tricarbonyl-π-2,3,4,5-tetraphenylcyclopent-2-enonechromium, m. p. 183—187° (Found: C, 73·1, H, 4·7%) [from light petroleum (b. p. 100—120°)]. This form was soluble in most solvents and had $\lambda_{max.}$ 307 mμ (in EtOH) but $\nu_{max.}$ as above. Further chromatography of this complex on alumina and elution with light petroleum gave six orange bands which decomposed too rapidly for isolation of individual isomers.

Reaction of 2,5-*Dimethyl*-3,4-*diphenylcyclopentadienone and Moist Hexacarbonylchromium.*—Hexacarbonylchromium (3 g.) and 2,5-dimethyl-3,4-diphenylcyclopentadienone in 2,2,4-trimethylpentane (50 ml.) and water (4 ml.) were refluxed under nitrogen for 60 hr. The solution was chromatographed on alumina, and the column was eluted with benzene, giving unchanged dienone (2·5 g.) and a small amount of 2,5-dimethyl-3,4-diphenylcyclopent-2-enone (0·1 g.), m. p. 117—120° (Found: C, 86·45; H, 6·2. $C_{19}H_{18}O$ requires C, 87·0; H, 6·9%), identical in u.v. and i.r. spectra with the sample described below.

2,5-*Dimethyl*-3,4-*diphenylcyclopent*-2-*enone.*—2,5-Dimethyl-3,4-diphenylcyclopentadienone (1 g) in acetic acid (20 ml.) was refluxed with slow addition of zinc dust (~1 g.) until solution became colourless. The hot solution was filtered. Crystals obtained on addition of water recrystallized from ethanol, giving 2,5-dimethyl-2,4-diphenylcyclopent-2-enone, m. p. and mixed m. p. 119—120° (Found: C, 86·4; H, 6·9%).

Reaction of 2,5-*Diethyl*-3,4-*diphenylcyclopentadienone and Moist Hexacarbonylchromium.*—Hexacarbonylchromium (1 g.) and 2,5-diethyl-3,4-diphenylcyclopentadienone (0·8 g.) in 2,2,4-trimethylpentane (25 ml.) and water (2 ml.) were refluxed for 70 hr. Evaporation and sublimation removed the excess of carbonyl. Recrystallization of the residue from ethanol gave 2,5-diethyl-3,4-diphenylcyclopent-2-enone (0·8 g.), m. p. 82—84° (Found: C, 87·7; H, 8·0. $C_{21}H_{22}O$ requires C, 86·9; H, 7·6%).

2,5-*Diethyl*-3,4-*diphenylcyclopent*-2-*enone.*—The corresponding dienone (1 g.) in acetic acid (25 ml.) was refluxed with slow addition of zinc dust (3 g.) until the solution became colourless. Addition of water and recrystallization of the precipitate from ethanol gave 2,5-diethyl-3,4-diphenylcyclopent-2-enone, m. p. and mixed m. p. 82—84° (Found: C, 87·7; H, 8·0%), $\lambda_{max.}$ 216 and 274 mμ in EtOH, $\nu_{max.}$ 5·95 μ (C=O).

Reaction of trans-*Stilbene with Moist Hexacarbonylchromium.*—Hexacarbonylchromium (3 g.) and *trans*-stilbene (2·6 g.) were refluxed in 2,2,4-trimethylpentane (30 ml.) and water (2 ml.) under nitrogen for 80 hr. The solution became orange. Stilbene (1·0 g.) crystallized on cooling. Chromatography of the filtrate on alumina and elution with benzene gave further stilbene (0·3 g.) and tricarbonylstilbenechromium (0·5 g.), m. p. 131—132°. The product was identical with that described by Calderazzo *et al.*[5]

Reduction of Methylene Blue.—The dye (0·02 g.) and hexacarbonylchromium (1 g.) in 2,2,4-trimethylpentane (20 ml.) and water (2 ml.) were refluxed under nitrogen. The solution became colourless in 20 hr. but on exposure to air became blue again.

Reduction of p-*Benzoquinone.*—Hexacarbonylchromium (1 g.) and the quinone (0·3 g.) in 2,2,4-trimethylpentane (50 ml.) and water (2 ml.) were refluxed under nitrogen. The solid formed on cooling was extracted with water and a black residue was filtered off. Extraction of the filtrate with ether gave white crystals (0·3 g.) of quinol, m. p. and mixed m. p. 162—164° (correct i.r. spectrum).

Determination of Carbon Monoxide Evolved during Reaction.—Hexacarbonylchromium (3 g.) was refluxed in 2,2,4-trimethylpentane (50 ml.) and water (2 ml.) under nitrogen, and the carbon monoxide was measured after passage through an iodine pentoxide furnace.[8] About 10^{-3} mole per mole of carbonyl was evolved in 30 min. The solution was cooled and a weighed sample of benzoquinone (0·005—0·007 g.) was added. Reaction ceased after about 2 hr., the rate of evolution had returned to the above, and all the benzoquinone was reduced. After subtraction of total control value it was found that 3 moles of carbon monoxide were evolved per mole of benzoquinone.

Reduction in Carbon Tetrachloride.—Hexacarbonylchromium (1·3 g.) and tetracyclone (1 g.) in carbon tetrachloride (25 ml.) and water (2 ml.) were refluxed under nitrogen for 70 hr. Chromatography on alumina gave tetracyclone (0·95 g.) and 2,3,4,5-tetraphenylcyclopent-2-enone (0·05 g.).

Reactions of Tricarbonylarenechromiums and Azobenzene.—Azobenzene (0·1 g.) and the tricarbonylarenechromium (0·1—0·2 g.) in ethanol (50 ml.) and concentrated hydrochloric acid (0·5 ml.) were kept under nitrogen in the dark for 12—24 hr. Benzidine dihydrochloride (0·04 g.) (Found: C, 56·0; H, 5·6; Cl, 27·3. Calc. for $C_{12}H_{14}Cl_2N_2$: C, 56·0; H, 5·45; Cl, 27·5%). The filtrate was concentrated, diluted with water, and extracted with ether, from which orange crystals of azobenzene (0·06 g.) were obtained. The aqueous layer was green, presumably owing to a chromium(III) entity, but gave no more benzidine.

We thank the U.S. Office of Naval Research, Washington, for a grant, also Dr. Kettle, Sheffield University, for help with the n.m.r. measurements, and the Ethyl Corporation, Detroit, Michigan, for a gift of hexacarbonylchromium.

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[*Received, March 11th*, 1963.]