

CYCLOPENTADIENYL-AROMATIC SANDWICH
COMPLEXES OF MANGANESE AND IRON

Sir:

The isolation of ferrocene^{1,2} initiated extensive research effort on the chemistry of cyclopentadienyl-metal complexes. More recently, a second series of remarkable complexes has been reported in which aromatic molecules, such as benzene, are coordinated with transition metals *via* the π -electrons of the ring. This chemistry came to light with the elucidation of the structure of Hein's³ enigmatic polyphenylchromium compounds by Zeiss,⁴ and the elegant synthesis and characterization of dibenzene chromium by Fischer.⁵

We now wish to report the first synthesis of sandwich complexes of transition metals in which both a cyclopentadiene and an aromatic ring are coordinated to the central metal atom. We also wish to report the first synthesis of an aromatic complex of a Group VIIB metal, specifically, manganese.

Methylcyclopentadienyl manganese benzene has been prepared by allowing phenylmagnesium bromide to react with methylcyclopentadienyl manganese chloride or bis-methylcyclopentadienyl manganese in tetrahydrofuran and under an inert atmosphere. The latter compounds were obtained by allowing one or two equivalents, respectively, of sodium methylcyclopentadienide to react with manganous chloride. Following hydrolysis and evaporation of the Grignard reaction mixture, the product was isolated as ruby-red crystals, m.p. 116–118°, from the residues which were chromatographed and sublimed several times. (*Anal.* calcd. for C₁₃H₁₃Mn: C, 67.9; H, 6.2; Mn, 25.9. Found: C, 67.9; H, 6.2; Mn, 25.9.) The pure crystalline material was relatively stable to air and showed no signs of thermal decomposition up to the melting point. However, thermal degradation at higher temperatures gave benzene and methylcyclopentadiene in good yield.

Treatment of cyclopentadienyl iron dicarbonyl chloride, prepared by the method of Piper,⁶ with aluminum chloride in refluxing mesitylene resulted in the smooth evolution of two equivalents of carbon monoxide. Hydrolysis, followed by saturation of the water layer with potassium iodide gave ionic cyclopentadienyl iron mesitylene iodide as stable ivory needles in 40% yield (*Anal.* calcd. for C₁₄H₁₇IFe: C, 45.7; H, 4.7; I, 34.5; Fe, 15.2. Found: C, 45.3; H, 4.84; I, 34.6; Fe, 14.6). The infrared spectrum supports the assigned structure.

The mesitylene manganese tricarbonyl cation resulted from the reaction of bromomanganese pentacarbonyl⁷ with refluxing mesitylene in the

(1) T. J. Kealy and P. L. Pauson, *Nature*, **168**, 1039 (1951).

(2) S. A. Miller, J. A. Tebboth and J. F. Tremaine, *J. Chem. Soc.*, 632 (1952).

(3) F. Hein, *Ber.*, **52**, 195 (1919); F. Hein, *ibid.*, **54**, 1905 (1921).

(4) H. H. Zeiss and M. Tsutsui, Abstracts of Papers Presented at the 126th Meeting of the American Chemical Society, New York, N. Y., September, 1954, p. 29-O; H. H. Zeiss and W. Herwig, *THIS JOURNAL*, **78**, 5959 (1950).

(5) E. O. Fischer and W. Hafner, *Z. Naturforsch.*, **10b**, 665 (1955).

(6) T. S. Piper, F. A. Cotton and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **1**, 165 (1955).

(7) T. H. Coffield, J. Kozikowski and R. D. Closson, *J. Org. Chem.*, **22**, 598 (1957).

presence of aluminum chloride. After hydrolysis, the cation was isolated as the iodide from the water layer in 90% yield as cream-colored crystals (*Anal.* calcd. for C₁₂H₁₂O₃IMn: C, 37.3; H, 3.1; I, 32.9; Mn, 14.2. Found: C, 37.1; H, 3.0; I, 33.3; Mn, 14.3.) The infrared spectrum showed carbon-hydrogen stretching bands at 3.35, 4.05 and 4.10 μ and bands at 4.80 and 5.00 μ in the metallo-carbonyl region. The toluene and benzene analogs also were prepared.

All of the products described above are diamagnetic⁸ and thus exhibit the inert gas configuration. A complete discussion of the above work will be the subject of a forthcoming publication.

(8) We are indebted to Dr. Stanley Kirschner of Wayne State University for carrying out these measurements.

ETHYL CORPORATION LABORATORIES
DETROIT, MICHIGAN

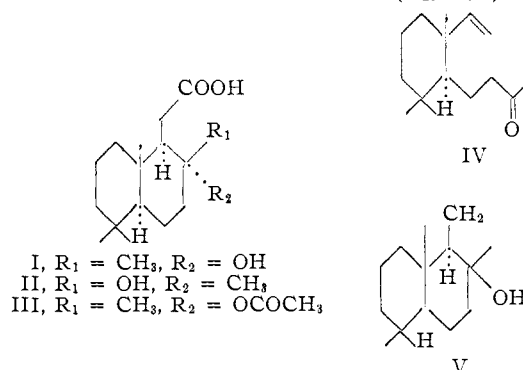
T. H. COFFIELD
V. SANDEL
R. D. CLOSSON

RECEIVED OCTOBER 1, 1957

C β -C γ CLEAVAGE OF A γ -HYDROXY ACID BY
ELECTROLYTIC OXIDATION¹

Sir:

We recently reported the conversion of salts of I and II to tetracyclic triterpenes of the onocerane series by electrolytic oxidation.² The present communication concerns a novel elimination process which occurs concurrently with the previously described coupling during the electrolysis of I and leads to the unsaturated ketone IV (C₁₅H₂₆O).



The ketone (b.p. 95–96° (0.4 mm), n_D^{25} 1.4857, $[\alpha]_D^{26}$ -10.4° (CHCl₃); found: C, 80.88; H, 10.80) was obtained in 34–38% yield from I and usually was contaminated with a small amount (ca. 3%) of a closely similar ketonic impurity (probably isomeric) as determined by vapor chromatography. The presence of a ketone function was shown by conversion to a semicarbazone (m.p. 175.5–178.5°; found: C, 68.71; H, 10.33) and unsaturation was demonstrated by the formation of a dihydroketone (semicarbazone, m.p. 156.5–158.5°; found: C, 68.56; H, 10.91) by hydrogenation with palladium-charcoal in methanol. The infrared spectrum of the unsaturated ketone (in CCl₄) lacked hydroxyl absorption and manifested bands at 1722 cm.⁻¹ (C=O), 1637 cm.⁻¹ (C=C), 1008 and 917 cm.⁻¹ (-CH=CH₂), the last three bands

(1) This investigation was supported by a fellowship (AF-6570) from the National Institute of Arthritis and Metabolic Diseases, Public Health Service.

(2) E. J. Corey and R. R. Sauers, *THIS JOURNAL*, **79**, 3925 (1957).

being absent in the spectrum of the dihydro derivative. The proton magnetic resonance spectrum (in CDCl_3 and relative to external CH_2Cl_2 as reference)³ indicated the presence of three olefinic hydrogens (-20 to $+30$ cycles), one methyl attached to carbonyl ($+131$ cycles; cf. acetone in CDCl_3 at $+133$ cycles) and three other methyl groups ($+174$ and $+179$ cycles). In accord with physical evidence for the structural feature R-CO-CH_3 , reaction of the unsaturated ketone with sodium hypobromite afforded a nor acid (liquid) which was characterized as the crystalline benzyl isothiuronium salt, m.p. $143-145^\circ$; found: C, 67.46; H, 8.80. These facts are uniquely accommodated by formula IV for the cleavage product.

Electrolytic oxidation of the acetate of I (III) affords the onocerane coupling product in good yield, but none of the ketone IV, consistent with the view that formation of IV requires hydrogen atom discharge from V.

Electrolytic oxidation of the C_8 epimer of I (II) also produces the cleavage product IV, but in addition considerable amounts of two similar ketonic substances (determined by vapor chromatography), possibly formed from V by migration of hydrogen and methyl and subsequent elimination.

We are currently investigating the scope of this reaction.

(3) The spectrum was obtained at 40 mc. with a Varian Model V-4300B high-resolution spectrometer fitted with a field-sensing stabilizer. A concentric tube cell was used.

DEPARTMENT OF CHEMISTRY AND
CHEMICAL ENGINEERING
UNIVERSITY OF ILLINOIS
URBANA, ILLINOIS

E. J. COREY
RONALD R. SAUERS
SHERLOCK SWANN, JR.

RECEIVED SEPTEMBER 3, 1957

THE BEHAVIOR OF $[\text{Fe}(\text{bipy})_3]^{+2}$ TYPE COMPOUNDS IN STRONG HClO_4

Sir:

It has been pointed out^{1,2,3} that the mechanisms proposed for the acid hydrolysis⁴ of $[\text{Fe}(\text{bipy})_3]^{+2}$ do not completely describe the experimental kinetic behavior. As a portion of a study to evaluate the effects of changes in the chelating agent on the rate of acid dissociation of iron(II)-methine type compounds, we have obtained evidence for the existence of protonated species in concentrated acid solutions of $[\text{Fe}(\text{PPI})_3]^{+2}$ (I), $[\text{Fe}(\text{bipy})_3]^{+2}$ (II), and $[\text{Fe}(\text{phen})_3]^{+2}$ (III). The formation of these species is accompanied by changes in spectra and magnetic susceptibility and is reversible upon dilution. The ability to form relatively stable protonated species may clarify the mechanism of the acid dissociation.

The visible spectrum of (I) perchlorate in water shows the maximum at $563 \text{ m}\mu$, $\epsilon = 8,790$. It is diamagnetic both in solution ($X_M = 530 \times 10^{-6}$)

(1) P. Krumholz, *J. Phys. Chem.*, **60**, 87 (1956).

(2) F. Basolo, J. C. Hayes and H. M. Neumann, *THIS JOURNAL*, **70**, 3807 (1954).

(3) J. H. Baxendale and P. George, *Trans. Faraday Soc.*, **46**, 736 (1950).

(4) $\text{bipy} = 2,2'$ -bipyridine, $\text{phen} = 1,10$ -phenanthroline, $\text{PPI} = 2$ -pyridinal- n -propylimine.

(slightly positive due to dissociation) and in the solid state ($X_M = -21.5 \times 10^{-6}$). (I) perchlorate dissolved in 8–12 M HClO_4 slowly changes to (ϵ_{max} at $540 \text{ m}\mu = 40.5$), with an effective moment of 5.0 B.M. Dilution with 1 M acid results in the rapid regeneration of (I) in yields as high as 95%. Since the ligand hydrolyzes in strong acid, Fe(II) does not react rapidly with the ligand when $\text{H}^+ > 0.2 M$, and the original complex can be regenerated, it is improbable that compound B is $[\text{Fe}(\text{PPI})_2]^{+2}$ or $[\text{Fe}(\text{PPI})]^{+2}$. Neither can a change in oxidation state be considered, for the reaction will take place in the presence of $\text{As}(\text{OH})_4^-$ and Sn^{+2} . We interpret these observations on the basis of the formation of a protonated species in which the ligands are bound by $4s4p^34d^2$ hybridization.

The action of concentrated HClO_4 on (II) results in a slow reaction. Initial (ϵ_{max} at $522 \text{ m}\mu = 8,700$; $\mu_{\text{eff}} = 0$), final (ϵ_{max} at $620 \text{ m}\mu = 15$; $\mu_{\text{eff}} = 5.2$). Although considerable dissociation to Fe(II) takes place, the solution will partially revert to (II) on dilution with 1 M acid. In the light of the evidence for the existence of protonated species in the 2,2',2''-terpyridine-iron(II) system⁵ and since rapid disproportionation of $[\text{Fe}(\text{bipy})]^{+2}$ to Fe(II) and (II) is highly unlikely in 1 M acid, it appears that these complexes associate with strong acids.

(III) chloride on addition to strong acid changes from red (ϵ_{max} at $510 \text{ m}\mu = 11,500$) to blue (ϵ_{max} at $605 \text{ m}\mu = 175$). A change in μ_{eff} from 0 to 4.9 accompanies the color change. Regeneration by dilution with 1 M acid results in 45% of the original (III). Treatment of d - $[\text{Fe}(\text{phen})_3]^{+2}$ with concd. H_2SO_4 does not result in complete racemization for after regeneration a portion of the optical activity remains.

In the Fe(III)-methine systems, definite absorption shifts are observed but no changes in magnetic susceptibility occur. Lowering the acid concentration regenerates the starting material. The stability toward dissociation of the +2 and +3 complexes is enhanced in concentrated acids.

In both the +2 and +3 states, concentrated solutions of NaClO_4 do not cause these changes, whereas association with H^+ or acids also takes place in H_2SO_4 and to a lesser extent in HClO_4 -HAc and concd. $\text{HCl-CH}_3\text{OH}$ mixtures. The spectra of the protonated species in HClO_4 and H_2SO_4 are identical in the visible region.

Strong association of the highly charged protonated complex with negative ions is indicated from kinetic measurements. Isolation has not been accomplished. Thus the constitution is not known but the kinetics of formation of the protonated complexes indicate that at least two H^+ are added and the major changes in spectra and magnetic moment take place in the final step.

The knowledge that the complexes have an affinity for concentrated acids supports the theory of the existence of lower protonated species in dilute acid and allows a quantitative explanation of the H^+ dependence of their dissociation without the introduction of "half-bonded" structures.⁶

(5) R. B. Martin and J. A. Lissfelt, *THIS JOURNAL*, **78**, 938 (1956).

(6) E. A. Healy and R. Kent Murmann, to be published.