pared by Markby, Sternberg and Wender,[7] who generously supplied us with crystals. The monoclinic crystals have lattice constants a = 8.18 Å., b = 13.37 Å., c = 11.02 Å., and β = 91°44′. The probable space group is $P2_1/n$. For four molecules per unit cell the calculated density is 1.43 g./cc. in agreement with the experimental density 1.46 g./cc. determined by the flotation method. Weissenberg intensity data involving 890 independent reflections were obtained photographically with Mo$K\alpha$ radiation. A three-dimensional structural analysis of the data including least squares refinement yielded refined positional and thermal parameters. The final discrepancy factor for individual isotropic thermal parameters is 8.1%; for anisotropic thermal parameters, 5.1%.

The molecular structure can be described as a sandwich in which the cobalt lies between a cyclopentadienyl ring and a tetramethylcyclopentadienone ring. The most interesting feature is that all the C—C bonds in the tetramethylcyclopentadienone ring are essentially equal, thus indicating complete delocalization of the four π-electrons. The stabilization of the complex then is accomplished in part by an electron transfer from the cobalt to give aromatic character in which the cobalt in effect becomes bonded to two cyclopentadienyl rings. Strong π-bonding between the rings and the cobalt, resulting in the use of all the low energy bonding orbitals of the metal, increases stability. Hence, this aromaticity gives rise to a mesoionic structure proposed by others.[7,13] A qualitative M.O. treatment of this type compound has been done.[14]

Of considerable interest is the fact that the cyclopentadienone ring is not planar; the carbonyl group is tipped out of the plane of the other atoms away from the cobalt such that the resulting angle of tilt is 9°. It is difficult to rationalize this effect as being electronic in origin, especially in the crystalline state where intermolecular forces must be considered. As expected, the cyclopentadienyl ring is planar although distorted.

The perpendicular distance from the cobalt to the cyclopentadienyl ring is 1.67 Å.; to the substituted ring 1.63 Å. Hence, the planes, if parallel, are 3.3 Å. apart. Actually, the calculated angle between the planes is approximately 3°, so they are almost parallel.

Another feature of the molecule is that the five carbon atoms of the two rings are eclipsed with respect to one another, that is, four of the corresponding C. . .C distances are 3.3 Å. apart.

Of prime interest is the comparison of these structural results with those for biscyclopentadienyl iron, better known as ferrocene.[15] The average C—C distance in the cyclopentadienyl ring in ferrocene is 1.40 Å.; in the cobalt compound 1.43 Å. The Fe—C distance in ferrocene of 2.05 Å. is comparable with a Co—C distance of 2.07 Å. The distance between the rings in ferrocene is also 3.3 Å. However, the rings in ferrocene are staggered rather than eclipsed.

This structural determination represents the first direct X-ray diffraction evidence for the existence of a sandwich complex involving a cyclopentadienone ring and clearly substantiates chemical evidence given independently by other workers[4-9] for these type compounds.

We wish to acknowledge the use of the facilities of the Numerical Analysis Laboratory at the University of Wisconsin. Also, financial assistance from the Petroleum Research Fund (No. 471A) is gratefully acknowledged.

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[13] E. Weiss and W. Hübel, *J. Inorg. Nucl. Chem.*, **11**, 42 (1959).

[14] D. A. Brown, *ibid.*, **10**, 39, 49 (1959); **13**, 212 (1960).

[15] J. D. Dunitz, L. E. Orgel and A. Rich, *Acta Cryst.*, **9**, 373 (1956).

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RECEIVED NOVEMBER 29, 1960

HOMOGENEOUS CATALYTIC HYDROGENATION OF OLEFINIC COMPOUNDS

Sir:

Although a variety of metal ions and complexes are now known[1] which activate molecular hydrogen homogeneously in solution and catalyze the reduction of inorganic substrates such as $Cr_2O_7^{2-}$ and Fe^{3+}, these have not, in general, proved effective catalysts for the hydrogenation of olefinic compounds. We now wish to report the successful hydrogenation, under homogeneous conditions, of several olefinic compounds including maleic, fumaric and acrylic acids, using chlororuthenate(II) complexes as catalysts.

Most of the experiments were made in aqueous 3 M HCl solution using maleic acid as substrate. Ru^{II} was generated by reduction of $(NH_4)_2RuCl_6$ with $TiCl_3$. With maleic acid in excess over Ru^{II}, hydrogenation to succinic acid proceeded at conveniently measurable rates over the temperature range 70 to 90°, according to the rate law, $k[H_2]\cdot[Ru^{II}]_{Total}$ with $\Delta H^* = 19$ kcal./mole and $\Delta S^* = -2$ e.u. The reaction apparently involves the formation of a Ru^{II}-olefin complex which reacts with hydrogen, *i.e.*

$$Ru^{II} + \text{Olefin} \longrightarrow Ru^{II}\cdot\text{Olefin (Fast)} \qquad (1)$$

$$Ru^{II}\cdot\text{Olefin} + H_2 \xrightarrow{k} Ru^{II} + \text{Saturated Product} \qquad (2)$$

In the case of maleic acid, the formation of a 1:1 complex with Ru^{II}, with a stability constant of 5×10^3 (3 M HCl, 20°), was confirmed spectrophotometrically.

Measurements of the uptake of ethylene and propylene by Ru^{II} solutions, and of the accompanying spectral changes, confirm that these olefins also form stable 1:1 complexes with Ru^{II}, but attempts to hydrogenate these under homogeneous conditions have not, thus far, proved successful.

These appear to be the first examples of Ru^{II} monoölefin complexes, although a diolefin (norbornadiene) complex, $C_7H_8RuCl_2$, believed to have a polymeric halogen-bridged structure, has been reported recently.[2]

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[1] J. Halpern, *J. Phys. Chem.*, **63**, 398 (1959); *Advances in Catalysis*, **11**, 301 (1959).

[2] E. W. Abel, M. E. Bennett and G. Wilkinson, *J. Chem. Soc.*, 3178 (1959).

Failure in earlier experiments to achieve catalytic hydrogenation of olefinic compounds with other metal ions and complexes (*e.g.*, Cu^{II}, Ag^{I} and Hg^{II}) which activate hydrogen homogeneously in solution[1] is attributable to two factors, (a) failure of the catalyst to activate the olefinic substrate as well as the hydrogen molecule and (b) the tendencies of these catalysts to undergo reduction themselves in preference to hydrogenation of the olefin. In the present system, complex formation between Ru^{II} and the olefinic compound apparently activates the latter, while stabilizing Ru^{II} itself against reduction (or disproportionation), and thus contributes to fulfillment of the requirements associated with both these factors.

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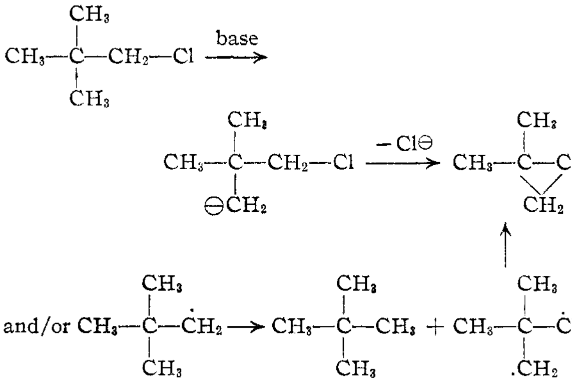
RECEIVED DECEMBER 22, 1960

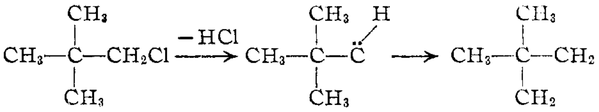
CARBENE INTERMEDIATE IN THE WURTZ REACTION. α-ELIMINATION OF HYDROGEN CHLORIDE FROM NEOPENTYL CHLORIDE

Sir:

The conversions of neopentyl chloride by (a) sodium metal[1] to 1,1-dimethylcyclopropane and neopentane, and (b) sodium *n*-propyl[2] to 1,1-dimethylcyclopropane were explained in the early 1940's by Whitmore and co-workers by assuming a carbanion intermediate which undergoes cyclic self-alkylation, or a diradical intermediate in the case of sodium reactions.



The recent observations[3] that bases convert alkyl halides to carbenes and that carbenes cyclize readily to cyclopropanes[4] by insertion at C_3 suggested an alternative mechanism for the conversions of neopentyl chloride to dimethylcyclopropane. If neopentyl chloride undergoes α-elimination of H and Cl to produce *t*-butylcarbene, this intermediate might be expected to cyclize to 1,1-dimethylcyclopropane.



The carbene mechanistic scheme is readily distinguished from the earlier proposals through a study of 1,1-dideuterioneopentyl chloride, $(CH_3)_3CCD_2Cl$, since the older mechanisms predict a dideuterio- and the carbene mechanism a monodeuterio-dimethylcyclopropane.

1,1-Dideuterioneopentyl alcohol was prepared by lithium aluminum deuteride reduction of trimethylacetic acid (72%, based on $LiAlD_4$). The alcohol was converted to the neopentoxytriethylsilane and then to neopentyl chloride (37%) with thionyl chloride by the method of Sommer, *et al.*[5] Proton magnetic resonance spectra (40 Mc.) of the neat alcohol and chloride showed no protium on the α-carbons, using the undeuterated alcohol and chloride to determine the δ's of the methylene groups.

The original observations of Whitmore, *et al.*, were confirmed, neopentyl chloride and sodium yielding neopentane (70%) and 1,1-dimethylcyclopropane (26%) (separated by gas chromatography and identified by gas phase infrared spectra of the pure substance). Under similar conditions 1,1-dideuterioneopentyl chloride is converted to neopentane (63%) and 1,1-dimethylcyclopropane (35%). Since neither infrared nor proton resonance spectroscopies yielded readily interpretable results, mass spectral cracking patterns were employed for isotopic analysis.[6]

Neopentane yields no parent peak, but instead yields a mass 57 peak ($C_4H_9^+$) by methyl cleavage. The labeled neopentane yielded peaks at 57, 58, 59, 60 and 61, with relative intensities 48.2, 7.7, 63.9, 100 and 4.3. By correcting for natural abundance C_{13} and assuming there is no isotope effect in methyl and hydrogen cleavages, the calculated composition is 58.6% tri-, 36.8% di-, 1.9% mono-deuterioneopentanes, and 2.8% undeuterated neopentane.

Unlabeled 1,1-dimethylcyclopropane yields peaks of mass 71, 70, 69 and 68, with relative intensities 5.9:100:7.3:0. The labeled 1,1-dimethylcyclopropane yields peaks of mass 72, 71, 70 and 69, with relative intensities 6.3:100:6.8:1.6. By correcting for natural abundance C_{13} and assuming no isotope effect in the cracking pattern, this mixture is calculated to be 0.3% $C_5H_{10}D_2$, 97.8% $C_5H_{11}D$ and 1.8% C_5H_{12}.

The carbene mechanism with intermediate $(CH_3)_3C\text{-}\ddot{C}\text{-}D$, is strongly indicated by the conversion of 1,1-dideuterioneopentyl chloride to monodeuterio-1,1-dimethylcyclopropane.

The 38% yield of $(CH_3)_3CCD_3$ is 58.6% of the total yield of neopentane. It is reasonable to suppose that the 23% conversion to $(CH_3)_3CCD_2H$

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(1) F. C. Whitmore, A. H. Popkin, H. I. Bernstein and J. P. Wilkins, *J. Am. Chem. Soc.*, **63**, 124 (1941).

(2) F. C. Whitmore and H. D. Zook, *ibid.*, **64**, 1783 (1942).

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(4) L. Friedman and H. Shechter, *ibid.*, **81**, 5512 (1959).

(5) L. H. Sommer, H. D. Blankman and P. S. Miller, *ibid.*, **76**, 803 (1954).

(6) We wish to thank Professor F. W. Lampe and Dr. Thomas Aczel (Humble Oil and Refining Company) for obtaining the cracking patterns of the reaction products.