

solutions) was found to proceed readily over the temperature range 28 to 50°, and the earlier kinetic measurements on this system by Just and Kauko⁴ have been confirmed and extended. The complete rate law was found to be $-d[CO]/dt = k[CO][MnO_4^-]$ with $\Delta H^* = 13$ kcal./mole and $\Delta S^* = -17$ e.u., both substantially constant over the pH range 1 to 13.

A remarkable feature of the latter reaction is its very marked sensitivity to catalysis by Ag^+ and Hg^{2+} (but not Cu^{2+} , Fe^{3+} , Cd^{2+} or Tl^{3+}). The rate law, indicated by preliminary measurements, for the catalytic path in dilute perchloric acid solution is, in each case, $k[CO][MnO_4^-][M]$ where $M = Ag^+$ or Hg^{2+} . For Ag^+ , $k(0^\circ) = 1.10 \times 10^5 M^{-2}sec^{-1}$, $\Delta H^* = 1.2$ kcal./mole and $\Delta S^* = -31$ e.u.; for Hg^{2+} , $k(0^\circ) = 1.06 \times 10^3 M^{-2}sec^{-1}$, $\Delta H^* = 6.4$ kcal./mole and $\Delta S^* = -21$ e.u. It is suggested that the remarkably high reactivities exhibited by CO in these catalytic reactions are related to favorable oxidation paths involving intermediates such as $[-Hg-CO-OMnO_3]$, analogous to that postulated in the oxidation of CO by Hg^{2+} . It also seems likely that there exists a connection between the Ag^+ -catalyzed oxidation of CO by MnO_4^- in solution and the very efficient oxidation of CO by solid $AgMnO_4$.⁵

Support of this work by the Alfred P. Sloan Foundation and the National Research Council of Canada is gratefully acknowledged.

(4) G. Just and Y. Kauko, *Z. physik. Chem.*, **82**, 71 (1913).

(5) M. Katz, *Advances in Catalysis*, **5**, 177 (1953).

(6) Alfred P. Sloan Research Fellow.

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A TRIHYDRIDO COMPLEX OF IRIIDIUM(III)

Sir:

The hydrido complexes $[IrH_nCl_{3-n}(PPh_3)_3]$ ($n = 1, 2$) have been reported recently.¹ We now wish to describe the preparation and properties of the third member of this series, $[IrH_3(PPh_3)_3]$ ($n = 3$) (I). This compound is the first reported example of a transition metal trihydride stabilized by tertiary phosphine ligands.

The yellow complex $[IrHCl_2(PPh_3)_3]$ ¹ readily dissolves in a tetrahydrofuran solution of lithium aluminum hydride to give a colorless solution, which, after hydrolysis with water or ethanol and removal of solvent at 12 mm., yields an off-white solid. Extraction with benzene and crystallization from 50% *n*-hexane-cyclohexane mixture affords trihydrido-*tris*-(triphenylphosphine)-*iridium*(III) as needles (35% yield).

Anal. Calcd. for $C_{54}H_{48}IrP_3$: C, 66.0; H, 4.9; Ir, 19.6; P, 9.5. Found: C, 66.3; H, 4.7; Ir, 19.0; P, 9.5.

The compound is diamagnetic in the solid state, monomeric in benzene solution and has a dipole moment of 4.95 D. Other properties are given in the table.

The deuterido complex corresponding to (I) (similarly prepared from $[IrHCl_2(PPh_3)_3]$ and Li-

(1) L. Vaska, *J. Am. Chem. Soc.*, **83**, 756 (1961).

TABLE I

Compound	M.p. (dec. in vacuum)	Color	ν_{IrH} (cm. ⁻¹)
(I) $[IrH_3(PPh_3)_3]$	227–229°	Colorless	2100, 1745 ^b
(II) $[IrH_2Cl(PPh_3)_3]$	218–220	Colorless	2210, 2130 ^c
(III) $[IrHCl_2(PPh_3)_3]^a$	261–263	Pale yellow	2230 ^c

^a Crystallizes with a molecule of benzene. ^b Chloroform solution. ^c Halocarbon mull.

AlD_4) shows absorption due to ν_{IrD} at 1535 and 1255 cm.⁻¹. The isotopic shift factors are in the range 1.37–1.40 (calculated 1.41).

Two isomeric forms of $[IrH_3(PPh_3)_3]$ are possible theoretically, but the presently available data do not allow us to distinguish between them with certainty.

(I) reacts with hydrogen chloride in ether, evolving hydrogen, and affording (II) and (III) with one and two equivalents of acid, respectively; (III) does not react with acid under these conditions. (II) and (III) probably are isomeric with Vaska's compounds¹ and (III) is similar in type to the recently reported hydrido complexes of rhodium and iridium.²

The author wishes to thank Dr. L. Vaska for the measurement of magnetic susceptibility, for supplying the first samples of the starting material and for useful discussion.

(2) J. Chatt and B. Shaw, *Chem. & Ind. (London)*, 931 (1960); J. Lewis, R. Nyholm and G. Reddy, *ibid.*, 1386 (1960).

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UNSATURATED MACROCYCLIC COMPOUNDS. XX.¹ SYNTHESIS OF THREE COMPLETELY CONJUGATED TWENTY-MEMBERED RING CYCLIC SYSTEMS

Sir:

We wish to report the synthesis of the completely conjugated twenty-membered ring cyclic systems 1,3,5,7,11,13,15,17-cycloeicosaoctaene-9,19-diyne (II or a stereoisomer), 1,3,5,7,9,11,13,15,17-cycloeicosanonaen-19-yne (VI or a stereoisomer) and 1,3,5,7,9,11,13,15,17,19-cycloeicosadecane (III or a stereoisomer). These compounds, the first examples of monocyclic conjugated 20 π -electron systems, were expected to be non-aromatic since they do not comply with Hückel's rule for aromaticity [presence of $(4n + 2)$ π -electrons].

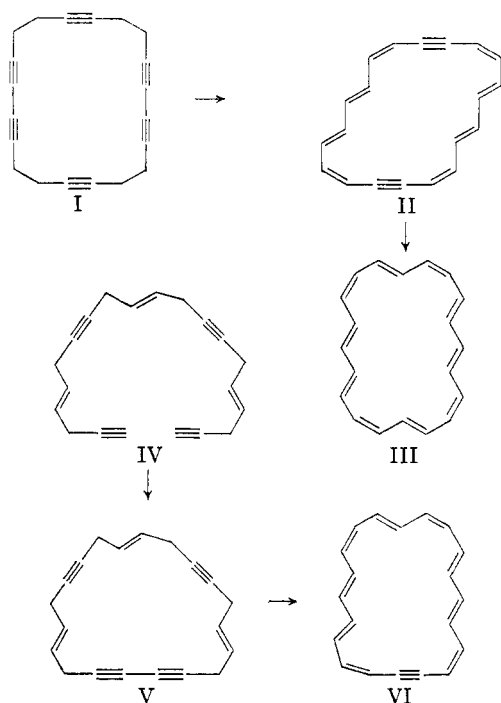
1,5,9-Decatriyne² on oxidation with cupric acetate in pyridine³ at 55° for 4 hr. yielded (besides other products)² 6% of the colorless cyclic dimer, 1,3,7,11,13,17-cycloeicosahexayne (I) [m.p. 230–231° dec.⁴; $\lambda_{\max}^{\text{isoctane}}$ 226, 238 and 255 m μ ; found: C, 93.91; H, 6.24; converted by full hydrogenation to cycloeicosane, m.p. and mixed m.p. 60–61°]. Rearrangement of I with potassium *t*-butoxide in *t*-butyl alcohol-benzene at 90° for 15 minutes yielded ca. 30% of an isomer (found: C, 93.03; H, 5.95) as dark brown-violet

(1) Part XIX, F. Sondheimer, R. Wolovsky and D. A. Ben-Efraim, *J. Am. Chem. Soc.*, in press.

(2) F. Sondheimer, R. Wolovsky and Y. Gaoni, *ibid.*, **82**, 754 (1960).

(3) *Inter al.*, see G. Eglington and A. R. Galbraith, *J. Chem. Soc.*, 889 (1959); F. Sondheimer, Y. Amiel and R. Wolovsky, *J. Am. Chem. Soc.*, **81**, 4600 (1959).

(4) Sample placed on block just below this temperature.



plates from pentane (red-brown in solution), m.p. 176–177° dec.⁴; $\lambda_{\text{max}}^{\text{isooctane}}$ 319 and 336 m μ (ϵ 109,000 and 74,000); acetylene band at 4.64 μ in the infrared (KBr). Full hydrogenation again led smoothly to cycloeicosane, m.p. and mixed m.p. 59–60°. The isomerization product is clearly a fully conjugated cycloeicosaoctaene-diyne and a symmetrical 1,11-diyne structure (II or a stereoisomer) appears most probable. The substance was reasonably stable and could be kept without appreciable change in light and air at room temperature for 24 hr in the solid state or for 12 days in dilute benzene solution.

Partial hydrogenation of II in benzene over a "Lindlar" palladium catalyst and then careful chromatography on alumina yielded first a yellow oily substance and then unchanged starting material. The yellow product appears to be cycloeicosadecaene (III or a stereoisomer) in view of the ultraviolet spectrum [$\lambda_{\text{max}}^{\text{isooctane}}$ 267, 284, 297, 375 and 396 m μ (ϵ 0.81, 0.83, 0.81, 0.20 and 0.19)],⁵ the infrared spectrum (absence of acetylene band in the 4.5–4.7 μ region) and full hydrogenation to cycloeicosane, m.p. 55–58°. Further structural evidence is provided by the fact that potassium *t*-butoxide rearrangement of *trans-trans*-1,11-cycloeicosadiene-5,7,15,17-tetrayne (I, replace single acetylenes by *trans*-double bonds), a reaction which also was expected to yield III or a stereoisomer, had led to crude yellow oily chromatography fractions with similar ultraviolet properties [e.g. $\lambda_{\text{max}}^{\text{pentane}}$ 268–272, 283, 297, 312, 373 and 394 m μ (ϵ 1.13, 1.61, 0.87, 0.69, 0.26 and 0.24)].¹

The nonaene-yne VI was prepared: *trans*-1,4-dibromo-2-butene on reaction with an excess of ethynylmagnesium bromide in tetrahydrofuran

(5) That all the ultraviolet maxima belong to the same chromophore was shown by the fact that all the chromatography fractions containing this substance showed essentially identical spectra and remained unchanged on re-chromatography.

in the presence of cuprous chloride furnished besides other products⁶ ca. 3% of all-*trans*-4,10,16-eicosatriene-1,7,13,19-tetrayne (IV) (m.p. 99–100°; no high-intensity absorption in the ultraviolet; found: C, 91.89; H, 7.69; converted by full hydrogenation to *n*-eicosane, m.p. and mixed m.p. 36–37°). Oxidation with cupric acetate in pyridine³ at 70° for 5 hr. yielded 18% of the colorless cyclic monomer, all-*trans*-1,7,13-cycloeicosatriene-4,10,16,18-tetrayne (V) [m.p. 116–117°; $\lambda_{\text{max}}^{\text{ether}}$ 229, 238 and 254 m μ (ϵ 480, 470 and 240); found: C, 92.60; H, 6.75], which on full hydrogenation gave cycloeicosane, m.p. and mixed m.p. 61–62°.

Compound V was rearranged with potassium *t*-butoxide in *t*-butyl alcohol-benzene at ca. 55° for 90 seconds. The least polar fractions obtained after chromatography on alumina gave ca. 20% of a compound which appears to be cycloeicosanonaenyne (VI or a stereoisomer). It was obtained as a yellow oil [$\lambda_{\text{max}}^{\text{ether}}$ 260, 270, 281 (infl.) and 340 m μ (ϵ 48,000, 47,000, 41,000 and 15,700)⁵; acetylene band at 4.53 μ in the infrared (chloroform)], which on full hydrogenation once more gave cycloeicosane (m.p. 56–58°). In addition a substance was isolated in ca. 2% yield from the most polar chromatography fractions which is most probably another isomer of VI. This isomer formed dark red crystals [red-brown in solution; $\lambda_{\text{max}}^{\text{ether}}$ 281 and 322 m μ (ϵ 0.45 and 0.54)] but it was obtained in too small quantity for further study. Both the isomers of VI as well as the decaene III were unstable and soon decomposed on standing either neat or in solution.

(6) See F. Sondheimer and Y. Gaoni, *J. Am. Chem. Soc.*, **82**, 5765, (1960).

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SECONDARY DEUTERIUM EFFECT IN METHYL RADICALS ADDITION REACTION. STRUCTURE OF THE TRANSITION STATE¹

Sir:

Addition of methyl radicals to olefinic, acetylenic or aromatic compounds leads to formation of new C–C bonds. The reactive center in each class of these compounds involves a carbon atom, although a different configuration characterizes each group. For example, in olefins the center (C*) is in a C=C* < $\frac{1}{2}$ moiety, whereas in aromatic hydrocarbons the structure is $\frac{1}{2}$ > C*–H. In previous communications from this laboratory² it was suggested that in radical addition reactions the initial structure of a reactive center is preserved in the transition state. The best argument in favor of this suggestion is found in the excellent linear relation between logs of the relevant rate constants per reactive center and the corresponding localization energies, since the latter were calculated on the assumption that the nuclear framework of the

(1) This work was supported by the National Science Foundation.

(2) (a) M. Szwarc and J. H. Binks, "Theoretical Organic Chemistry," Kekule Symposium, Butterworth Publications, London, 1959, p. 262; (b) J. H. Binks and M. Szwarc, *J. Chem. Phys.*, **30**, 1494 (1959).