17β-diol (m.p. 211–212°; $[\alpha]^{25}D$ +10.2°. Found for $C_{18}H_{30}O_2$: 3, 77.90; H, 11.05). Bromination of dione II in acetic acid furnished in high yields, 4β-bromo-5β,10β-estrane-3,17-dione, (m.p. 186–188°. Found for $C_{18}H_{25}BrO_2$: C, 60.90; H, 7.19) and dehydrobromination with refluxing pyridine gave Δ^4-norandrostene-3,17-dione (m.p. 159–161°, λ_{max} 239 mμ, log ε 4.20) identical with an authentic sample[3] in all respects.

Experiments were carried out employing Marker's procedures[4] for the preparation of estranediol (PtO_2 reduction of estrone), estranedione and estrene-3,17-dione of unassigned configurations. These were shown to be identical, respectively, with I, II and Δ^4-norandrostene-3,17-dione.

Hydrogenation of 19-nortestosterone acetate under similar conditions (RuO_2) followed by CrO_3–pyridine oxidation and hydrolysis yielded 5β,10β-estran-17β-ol-3-one (III) (m.p. 106–108°; $[\alpha]^{25}D$ +29.7° (dioxane). Found for $C_{18}H_{28}O_2$: C, 77.85; H, 10.31). When 17α-ethinyl-19-nortestosterone was reduced and then oxidized there was obtained in preponderant amount, 17α-ethyl-5β,10β-estran-17β-ol-3-one (IV) (m.p. 155–157°; $[\alpha]^{28}D$ +31.1°. Found for $C_{20}H_{32}O_2$: C, 78.51; H, 10.53) and in minor amount, 17α-ethyl-19-norandrostan-17β-ol-3-one[5] (m.p. 203–205°; $[\alpha]^{30}D$ +39.4°).

We confirmed the *trans* configuration for 17α-ethyl-19-norandrostan-17β-ol-3-one by its rotatory dispersion curve.[5] The A/B normal configuration for 5β,10β-estran-17β-ol-3-one and the 17α-ethyl analog is established by the rotatory dispersion curves which are identical to that of etiocholan-17β-ol-3-one.[6] Further the course of the bromination–dehydrobromination reactions support the normal assignment.

[3] We are indebted to Professor A. L. Wilds, University of Wisconsin, for providing this sample for our comparison.

[4] R. Marker and E. Rohrmann, THIS JOURNAL, **62**, 73 (1940).

[5] A. Bowers, H. J. Ringold and R. I. Dorfman, *ibid.*, **79**, 4556 (1957).

[6] Kindly performed by M. Marsh and J. Carson of these laboratories.

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RECEIVED JANUARY 3, 1958

A QUINONE IRON TRICARBONYL COMPLEX AND ITS SIGNIFICANCE IN ORGANIC SYNTHESIS

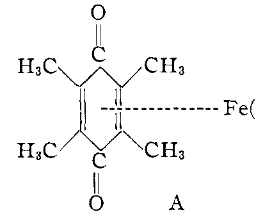
Sir:

Recently Longuet-Higgins and Orgel[1] predicted the existence of transition-metal complexes of cyclobutadiene on the basis of molecular orbital theory. Similar reasoning applied to the quinone molecule[2] led us to predict the existence of transition-metal complexes containing quinone as a ligand. We now have found that such complexes can be prepared and thus confirmed the validity of the basic theory advanced by Longuet-Higgins and Orgel.

When a mixture of dimethylacetylene and $Fe(CO)_5$ is placed in a flask and exposed to sunlight, large orange crystals are formed which decompose at about 50° and whose elementary composition corresponds to $Fe(CO)_5(CH_3C{\equiv}CCH_3)_2$ (I).

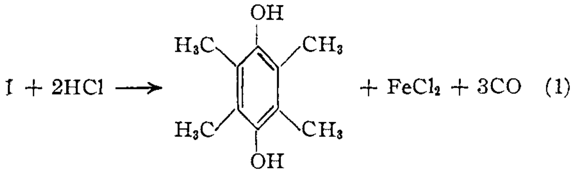
Calcd. for $C_{13}H_{12}O_5Fe$: C, 51.35, H, 3.97; Fe, 18.37. Found: C, 51.21; H, 4.04; Fe, 18.42.

This compound could either be an addition complex, formed by the addition of two molecules of dimethylacetylene to $Fe(CO)_5$, or the alkyne molecules may have interacted with some of the carbonyl groups to produce a new ligand. The infrared spectrum of I shows two bands at 4.84 and 4.97 μ attributable to terminal carbonyl groups and a doublet at 6.10 and 6.18 μ attributable to ketonic carbonyl. A structure compatible with the elementary composition and infrared spectrum of I is shown in A.



A

Strong support for structure A was obtained by acid treatment of I. Durohydroquinone[3] and carbon monoxide were obtained quantitatively according to



$I + 2HCl \longrightarrow$ $+ FeCl_2 + 3CO$ (1)

In addition, duroquinone[3] is quantitatively recovered when I is allowed to stand in air. Complexes analogous to I were prepared from 1-pentyne and 3-hexyne. Exposure of I to radioactive carbon monoxide for two weeks and decomposition of the product according to equation 1 showed that only the terminal carbonyl groups had exchanged. No activity was found in the quinone moiety.

Compounds capable to forming π-bonds with transition metals include olefins,[4] acetylenes,[5,6] cyclopentadienyl anion[7] and benzene.[8] In contrast to the mode of formation of these complexes, the quinone carbon skeleton is not preformed but is synthesized during complex formation.

Clarkson, Jones, Wailes and Whiting[9] have shown

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[1] H. C. Longuet-Higgins and L. E. Orgel, *J. Chem. Soc.*, 1969 (1956).

[2] In quinone the four molecular carbon π-orbitals, $\psi_1 = {}^1/_2(\phi_1 + \phi_2 + \phi_3 + \phi_4)$, $\psi_2 = {}^1/_2(\phi_1 + \phi_2 - \phi_3 - \phi_4)$, $\psi_3 = {}^1/_2(\phi_2 + \phi_3 - \phi_4 - \phi_1)$, $\psi_4 = {}^1/_2(\phi_1 - \phi_2 + \phi_3 - \phi_4)$, have the same symmetry as the corresponding orbitals in cyclobutadiene.[1] The ψ_2 and ψ_3 orbitals in quinone differ from the corresponding cyclobutadiene orbitals in that the latter are degenerate while the former are not.

[3] We are indebted to the Shell Development Co., Emeryville, California, for the infrared spectra of authentic samples of durohydroquinone and duroquinone and for a sample of duroquinone.

[4] J. Chatt and L. A. Duncanson, *J. Chem. Soc.*, 2939 (1953).

[5] J. Chatt, G. A. Rowe and A. A. Williams, *Proc. Chem. Soc.*, 208 (1957).

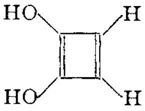
[6] H. Greenfield, H. W. Sternberg, R. A. Friedel, J. H. Wotiz, R. Markby and I. Wender, THIS JOURNAL, **78**, 120 (1956).

[7] L. Pauson, *Quart. Rev.*, **9**, 391 (1955).

[8] E. O. Fischer and W. Hafner, *Z. Naturforschung*, **10b**, 665 (1955).

[9] R. Clarkson, E. R. H. Jones, P. C. Wailes and M. C. Whiting, THIS JOURNAL, **78**, 6206 (1956).

that the complex $Fe_2C_{10}H_4O_8$, formed[10,11] by the interaction of acetylene with an alkaline solution of iron carbonyl anion, contains a four-carbon chain. The experimental evidence presented[9] is equally compatible with the presence of a cyclobutadiene ring such as



analogous to that proposed for $(CH{\equiv}CH)_2Fe(CO)_3$[1]

The principle of carbon skeleton synthesis during complex formation offers a new route to the formation of organic compounds which may have practical value in synthetic organic chemistry. Indeed, we succeeded in synthesizing durohydroquinone without isolation of an intermediate complex by merely adding methanolic HCl to the mixture of dimethylacetylene and $Fe(CO)_5$ during irradiation.

A complex similar to I may conceivably be an intermediate in Reppe's synthesis of hydroquinone from iron pentacarbonyl and acetylene at elevated pressure and temperature.[10]

(10) W. Reppe and H. Vetter, *Ann. Chem. Justus Liebig*, **582**, 133 (1953).

(11) H. W. Sternberg, R. A. Friedel, R. Markby and I. Wender, THIS JOURNAL, **78**, 3621 (1956).

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RECEIVED JANUARY 24, 1958

A CRYSTALLINE PENTAPOLYPHOSPHATE

Sir:

In the sodium[1] and potassium[2] phosphate systems, the largest chain oligophosphate which appears in the phase diagram is the tripolyphosphate. Because of this, there was considerable discussion in the scientific literature of the 40's that higher members of the homologous series of chain phosphates, such as the tetra- and pentapolyphosphates, do not exist. This notion has, of course, been disproved by modern tools such as ion exchange and paper chromatography.[3] Nevertheless, it is of considerable interest to point out here that pentapolyphosphate appears as a crystalline entity in a phase diagram.

In 1955, it was shown[4] that a crystalline salt of the composition $3PbO\cdot 2P_2O_5$ appeared in the lead phosphate phase diagram. Paper chromatographic studies[5] in this Laboratory demonstrated that this compound and a similar barium compound were truly tetrapolyphosphates. We have now found that the crystalline calcium phosphate called trömelite which appears in the calcium phosphate phase diagram[6] is a pentapolyphosphate—the anion of which consists of a chain of five phosphorus atoms alternating with oxygen atoms. This has been demonstrated by paper chromatography[3] of solutions made by dissolving the trömelite in various solutions containing ethylenediaminetetraacetate. These results will be reported in detail, along with data on the molecular constitution of the other crystalline calcium phosphates, in a forthcoming paper to be submitted to This Journal.

(1) E. P. Partridge, V. Hicks and G. V. Smith, THIS JOURNAL, **63**, 454 (1941); G. W. Morey and E. Ingerson, *Am. J. Sci.*, **242**, 1 (1944).

(2) G. W. Morey, THIS JOURNAL, **76**, 4724 (1954); G. W. Morey, F. R. Boyd, J. R. England and W. C. Chen, *ibid.*, **77**, 5003 (1955).

(3) *E.g.*, E. Karl-Kroupa, *Anal. Chem.*, **28**, 1091 (1956).

(4) R. K. Osterheld and R. P. Langguth, *J. Phys. Chem.*, **59**, 76 (1955).

(5) R. P. Langguth, R. K. Osterheld and E. Karl-Kroupa, *ibid.*, **60**, 1335 (1956).

(6) W. L. Hill, G. F. Faust and D. S. Reynolds, *Am. J. Sci.*, **242**, 457 (1944).

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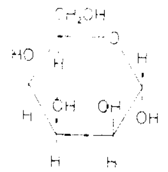
RECEIVED JANUARY 8, 1958

ISOLATION OF D-TALOSE FROM A NATURAL SOURCE

Sir:

Although D-talose (I) has been well-known for many years, it has not been isolated previously from natural sources. This communication reports the isolation of D-talose from the antibiotic, hygromycin B.[1] The antibiotic was hydrolyzed with 0.5 *N* sulfuric acid, and the sulfate was removed as barium sulfate. The resulting solution was passed over IR-120, and the effluent was concentrated to dryness under reduced pressure. The residue was triturated twice with methanol. The methanolic solution thus obtained yielded crystalline D-talose. The crude talose was purified by crystallization of the impurities from water, concentration of the aqueous, trituration of the residue with methanol and again crystallizing from the methanolic extract. The crystals thus formed had the following properties: m.p. 128–132°; $[\alpha]^{26}D$ +16.9° at equilibrium (*c* 1, H_2O). *Anal.* Calcd. for $C_6H_{12}O_6$: C, 39.99; H, 6.72; mol. wt., 180. Found: 39.96; H, 6.92; mol. wt. (crystallographic), 178. Melting points reported for α-D-talose are 133–134°,[2] 130–135°,[3] and 127–129°.[4] Reported rotations are, after mutarotation, +20.8°,[2] +19.7°,[3] and +20.6°.[4] Comparison of the product isolated from hygromycin B with synthetic α-D-talose[5] by means of X-ray diffraction patterns and paper chromatography indicated that the two were identical. The methylphenylhydrazone of the natural D-talose was prepared according to the procedure of Levene and Tipson.[3] This derivative melted at 153–154° (lit.[3] 154°) and upon admixture with an authentic sample showed no depression in melting point. The X-ray diffraction pattern of the derivative from natural material was identical with that from synthetic material.



More D-talose was obtained by concentration of the filtrate after removal of the first crop of crystalline material and trituration of the residue with methanol. This material was identified by melting

(1) R. L. Mann and W. W. Bromer, THIS JOURNAL, **80**, May (1958).

(2) W. W. Pigman and H. S. Isbell, *J. Research Natl. Bur. Standards*, **19**, 189 (1937).

(3) P. A. Levene and R. S. Tipson, *J. Biol. Chem.*, **93**, 631 (1931).

(4) W. Bosshard, *Helv. Chim. Acta*, **18**, 482 (1935).

(5) Supplied by General Biochemicals, Inc.