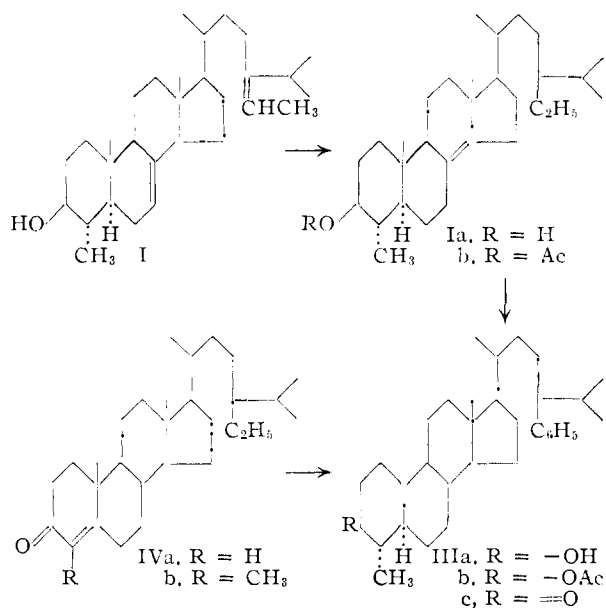


Hydrogenation of citrostadienol over platinum in acetic acid yielded iso-citrostenol (IIa) [$C_{30}H_{52}O$ (all new substances gave correct analyses); m.p. 152–153°, $[\alpha]_D^{23}$ +23°]; acetate (IIb) ($C_{32}H_{54}O_2$; m.p. 129–130°; $[\alpha]_D^{41}$ +41°). Hydrogenation of citrostadienol or of iso-citrostenol over platinum in acetic acid and hydrochloric acid gave citrostanol (IIIa) ($C_{30}H_{54}O$; m.p. 186–187°, $[\alpha]_D^{28}$ +28°); acetate (IIIb) ($C_{32}H_{56}O_2$; m.p. 144–145°, $[\alpha]_D^{39}$ +39°). Oxidation of IIIa with chromium trioxide led to citrostanone (IIIc) ($C_{30}H_{52}O$; m.p. 152–153°, $[\alpha]_D^{19}$ +19°).

Δ^4 -Stigmasten-3-one (IVa) on direct methylation with methyl iodide and potassium *t*-butoxide in *t*-butyl alcohol² gave 4-methyl- Δ^4 -stigmasten-3-one (IVb) ($C_{30}H_{50}O$; m.p. 130–131°, $[\alpha]_D^{99}$ +99°, λ_{max} 251 m μ , ϵ 15,500) which on reduction with lithium in liquid ammonia or on catalytic hydrogenation over palladium and subsequent acid treatment gave 4 α -methylstigmastan-3-one (IIIc)³ ($C_{30}H_{52}O$; m.p. 153–154°, $[\alpha]_D^{19}$ +19°). Further reduction with lithium aluminum hydride furnished 4 α -methylstigmastan-3 β -ol (IIIa) ($C_{30}H_{54}O$; m.p. 187–188°, $[\alpha]_D^{28}$ +28°); acetate (IIIb) ($C_{32}H_{56}O_2$; m.p. 143–144°, $[\alpha]_D^{38}$ +38°). The synthetic substances IIIa, IIIb and IIIc were found to be identical (mixture m.p., infrared comparison) with citrostanol, citrostanol acetate and citrostanone, respectively.



Citrostadienol on ozonolysis or successive treatment with osmium tetroxide and periodic acid yielded acetaldehyde (2,4-dinitrophenylhydrazone) and one double bond is therefore at $\Delta^{24(28)}$. The double bond in iso-citrostenol (IIa) is at $\Delta^{8(14)}$ in view of its spectrum (λ_{max} 210 m μ , ϵ 10,500)⁴ and the above hydrogenation results. The corresponding double bond in citrostadienol (λ_{max} 209 m μ , ϵ

5,500)⁴ must be at Δ^7 or Δ^8 . Reaction of I with excess osmium tetroxide and acetylation in pyridine (20°) gave a pentol triacetate ($3_{36}H_{60}O_8$; m.p. 221–222°) rather than a pentol diacetate (or a triacetoxy-anhydro compound).⁵ Cleavage of the unacetylated hydroxylation product with lead tetraacetate and acetylation gave a substance (m.p. 151–153°) which was a diketo-aldehyde (ν_{max} 2793 cm^{-1}). The second double bond in I is therefore at Δ^7 .

The occurrence of a 4-monomethylated sterol in nature is of considerable biogenetic interest, since it represents an intermediate type between the sterols and the tetracyclic triterpenes.^{6,7}

(5) Cf. H. Wieland and W. Benend, *Ber.*, **75**, 1708 (1942); L. F. Fieser and M. Fieser, "Natural Products Related to Phenanthrene," Reinhold Publ. Corp., New York, N. Y., 3rd Edition, 1949, p. 291.

(6) Cf. K. Bloch, *et al.*, *J. Biol. Chem.*, **218**, 319 (1956); **226**, 941 (1957); *Federation Proc.*, **15**, 323 (1956); *THIS JOURNAL*, **79**, 684 (1957).

(7) See also J. S. G. Cox, F. E. King and T. J. King, *Proc. Chem. Soc.*, 290 (1957).

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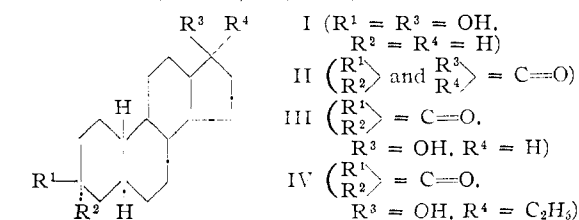
RECEIVED DECEMBER 16, 1957

PREPARATION OF 5 β ,10 β -ESTRANE-3,17-DIONE AND RELATED DERIVATIVES AND PROOF OF THEIR CONFIGURATION

Sir:

We wish to describe the synthesis of 5 β ,10 β -estrane-3,17-dione (II) and two derivatives (III and IV), and establish the configuration as belonging to the A/B normal series. Furthermore, this compound II was shown to be identical with estranedione B, of unknown configuration, obtained by oxidation of an estranediol B which was isolated from non-pregnant human urine.¹ This is of considerable biological importance in that these estranones and their corresponding alcohols may represent products of estrogen and 19-norsteroid metabolism.

Reduction at 1500 p.s.i. of 19-nortestosterone with ruthenium dioxide in ethanol followed by oxidation with N-bromoacetamide produced good yields of 5 β ,10 β -estrane-3,17-dione (II) (m.p. 179–181°; $[\alpha]_D^{25}$ +111.6° (1% in $CHCl_3$). Found for $C_{18}H_{26}O_2$: C, 78.72; H, 9.70).²



Sodium borohydride reduction of this dione II afforded 5 β ,10 β -estrane-3 β ,17 β -diol (I) (m.p. 202–204°; $[\alpha]_D^{25}$ +7.2°). Found for $C_{18}H_{30}O_2$: C, 77.50; H, 11.20) while sodium-propanol reduction of dione II yielded the epimer, 5 β ,10 β -estrane-3 α -

(1) R. E. Marker, E. Rohrmann, E. L. Wittle and E. J. Lawson, *THIS JOURNAL*, **60**, 1512 (1938).

(2) All melting points are uncorrected. We gratefully acknowledge valuable assistance by Messrs. G. M. Maciak, W. L. Brown, H. L. Hunter, elemental analysis; Miss A. VanCamp, X-ray data. All rotations are done in methanol unless otherwise specified.

(2) Cf. F. Sondheimer and Y. Mazur, *THIS JOURNAL*, **79**, 2906 (1957); N. W. Atwater, *ibid.*, **79**, 5315 (1957).

(3) The stereochemistry at C-4 and C-5 is based on evidence obtained in the cholesterol series [G. D. Meakins and O. R. Rodig, *J. Chem. Soc.*, 4679 (1956); F. Sondheimer and Y. Mazur, to be published].

(4) Cf. P. Bladon, H. B. Henbest and G. W. Wood, *J. Chem. Soc.*, 2737 (1952).

17 β -diol (m.p. 211–212°; $[\alpha]^{25}_D +10.2^\circ$. Found for C₁₈H₃₀O₂: C, 77.90; H, 11.05). Bromination of dione II in acetic acid furnished in high yields, 4 β -bromo-5 β ,10 β -estrane-3,17-dione, (m.p. 186–188°. Found for C₁₈H₂₆BrO₂: 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 m μ , log ϵ 4.20) identical with an authentic sample³ in all respects.

Experiments were carried out employing Marker's procedures⁴ for the preparation of estradiol (PtO₂ 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 (RuO₂) followed by CrO₃-pyridine oxidation and hydrolysis yielded 5 β ,10 β -estrane-17 β -ol-3-one (III) (m.p. 106–108°; $[\alpha]^{25}_D +29.7^\circ$ (dioxane). Found for C₁₈H₂₈O₂: C, 77.85; H, 10.31). When 17 α -ethynyl-19-nortestosterone was reduced and then oxidized there was obtained in preponderant amount, 17 α -ethyl-5 β ,10 β -estrane-17 β -ol-3-one (IV) (m.p. 155–157°; $[\alpha]^{25}_D +31.1^\circ$. Found for C₂₀H₃₂O₂: C, 78.51; H, 10.53) and in minor amount, 17 α -ethyl-19-norandrostane-17 β -ol-3-one⁵ (m.p. 203–205°; $[\alpha]^{30}_D +39.4^\circ$).

We confirmed the *trans* configuration for 17 α -ethyl-19-norandrostane-17 β -ol-3-one by its rotatory dispersion curve.⁵ The A/B normal configuration for 5 β ,10 β -estrane-17 β -ol-3-one and the 17 α -ethyl analog is established by the rotatory dispersion curves which are identical to that of etiocholan-17 β -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 Orgel¹ predicted the existence of transition-metal complexes of cyclobutadiene on the basis of molecular orbital theory. Similar reasoning applied to the quinone molecule² 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

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

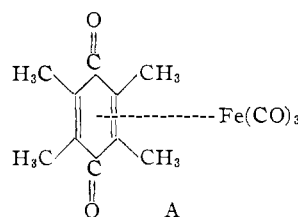
(2) In quinone the four molecular carbon π -orbitals, $\psi_1 = 1/2(\phi_1 + \phi_2 + \phi_3 + \phi_4)$, $\psi_2 = 1/2(\phi_1 + \phi_2 - \phi_3 - \phi_4)$, $\psi_3 = 1/2(\phi_2 + \phi_3 - \phi_1 - \phi_4)$, $\psi_4 = 1/2(\phi_1 - \phi_2 + \phi_3 - \phi_4)$, have the same symmetry as the corresponding orbitals in cyclobutadiene.¹ The ψ_2 and ψ_4 orbitals in quinone differ from the corresponding cyclobutadiene orbitals in that the latter are degenerate while the former are not.

the basic theory advanced by Longuet-Higgins and Orgel.

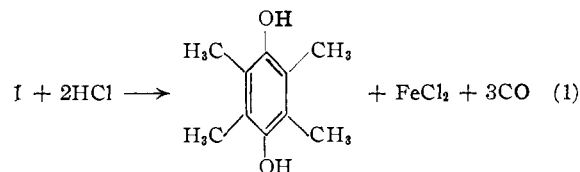
When a mixture of dimethylacetylene and Fe(CO)₅ is placed in a flask and exposed to sunlight, large orange crystals are formed which decompose at about 50° and whose elementary composition corresponds to Fe(CO)₅(CH₃C≡CCH₃)₂ (I).

Calcd. for C₁₃H₁₂O₅Fe: 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.



Strong support for structure A was obtained by acid treatment of I. Durohydroquinone³ and carbon monoxide were obtained quantitatively according to



In addition, duroquinone³ 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 of forming π -bonds with transition metals include olefins,⁴ acetylenes,^{5,6} cyclopentadienyl anion⁷ 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 Whiting⁹ have shown

(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).