

In the reaction of maleatopentamminocobaltic ion with  $\text{Cr}^{++}$ , fumaric acid is again produced during the electron transfer. The ratio fumaric/maleic acid increases linearly from zero with  $\text{H}^+$  concentration, but at 0.5 *M*  $\text{HClO}_4$ , only 32% fumaric acid is formed.

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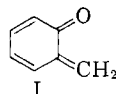
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RECEIVED JULY 20, 1959

# *o*-QUINONONE METHIDE<sup>1</sup>

Sir:

A multitude of reactions of substituted *o*-hydroxybenzyl alcohols give products which have been rationalized in terms of an *o*-quinone methide intermediate (I).<sup>2</sup> These could have been formed by other reaction paths, however, and the evidence

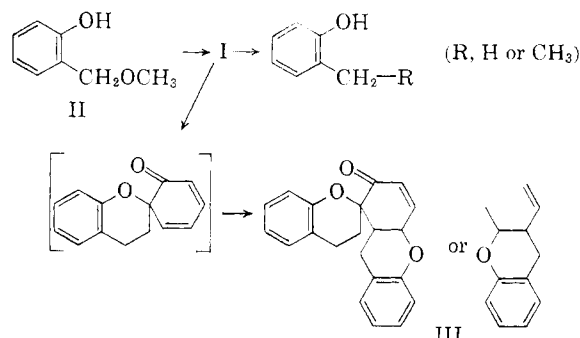


for the actual existence of I, even as a transient species,<sup>3</sup> is therefore lacking.

We wish to report the preparation of I in an impure state by the pyrolysis of *o*-methoxymethylphenol (II). Passage of II in the gaseous state through an open (unpacked) quartz tube in a state of high dilution (nitrogen) at a total pressure of 1–5 mm. and a temperature of 500–650° afforded a light yellow pyrolysate. This material, trapped at liquid nitrogen temperature, remained solid up to about –50° where it became liquid and appeared to be quite stable. As the temperature was allowed to rise to 0° colorless solid began to form and the mixture became a “slush” at 25°. The solid was shown from chemical and spectral data to be a trimer of I having structure III (m.p. 191–192°) and was obtained in yields of 15–20%. Treatment of the liquid pyrolysate at –50° with cold ethereal  $\text{LiAlH}_4$  gave *o*-cresol in about the same yield as that obtained of trimer in a “warming” experiment (isolated as the phenylurethane, m.p. and m.m.p. 139–140°). Similarly, treatment with cold ethereal  $\text{CH}_3\text{MgI}$  afforded *o*-ethylphenol (phenylurethane, m.p. and m.m.p. 140°) in about the same yield. The starting ether was shown not to react with these reagents under the conditions used. A heptane solution of pyrolysate (*ca.*  $10^{-5}$  *M*), allowed to warm while being studied in a spectrophotometer, showed profound spectral changes in the ultraviolet during the first five minutes and was still changing after 24 hr. at room temperature. Absorption by other components in the mixture precluded specific spectral assignments although it is clear that III had started to form before the first reading was made and its concentration increased steadily with time.

Trimer III may be obtained directly in yields as high as 70% by increasing the concentration of pyrolysis substrate. In these experiments, the

trimer appears to be formed in the gaseous state and solidifies on the walls of the tube immediately below the heated zone.



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RECEIVED SEPTEMBER 3, 1959

# STERIODS. CXXXV.<sup>1</sup> 10 $\beta$ -FLUORO STEROIDS; A NOVEL REACTION OF PERCHLORYL FLUORIDE.

Sir:

Treatment of estradiol (I) in dimethylformamide with perchloryl fluoride ( $\text{ClO}_3\text{F}$ )<sup>2</sup> for twenty hours at room temperature afforded a compound (60–70%), m.p. 152–154°,  $[\alpha]_D - 27^\circ$ ,<sup>3</sup>  $\gamma_{\text{max}}^{\text{EtOH}}$  240  $\mu$ ,  $\log \epsilon$  4.06 infrared  $\nu_{\text{max}}^{\text{KBr}}$  at 2.9, 6.0, 6.12 and 6.21  $\mu$ , which we formulate as 10 $\beta$ -fluoro- $\Delta^1$ -dehydro-19-nortestosterone (II) on the basis of the spectral characteristics and analysis (found for  $\text{C}_{18}\text{H}_{23}\text{O}_2\text{F}$ : C, 74.20; H, 7.60; F, 6.20) and the reactions. Reduction of II with sodium borohydride in methanol or with Raney nickel in refluxing methanol gave back estradiol (I). Catalytic hydrogenation of II in pyridine, dioxane or ethanol solution over 10% palladium-barium sulfate catalyst afforded, in addition to some estradiol, a saturated ketone (III), m.p. 181–182.5°,  $[\alpha]_D + 14^\circ$ , infrared  $\nu_{\text{max}}^{\text{KBr}}$  at 2.8 and 5.86  $\mu$  (found for  $\text{C}_{18}\text{H}_{27}\text{O}_2\text{F}$ : C, 73.78; H, 9.16; F, 6.17). The rotatory dispersion curve of II was very similar to that of 1,4-cholestadiene-3-one<sup>4</sup> from which the 10-fluorine atom is presumed to be in the  $\beta$  configuration, while the rotatory dispersion curve of the saturated ketone (III) was of the type characteristic for rings A/B *cis*-fused steroids<sup>5</sup> and the compound is therefore formulated as 10 $\beta$ -fluoro-19-nor-5 $\beta$ -androstane-17 $\beta$ -ol-3-one.

The above reaction with perchloryl fluoride has been applied to a large number of other steroidal phenols with analogous results. For example 3-hydroxy - 17 $\beta$  - acetyl - 1,3,5(10) - estratriene (“aromatic progesterone”)<sup>6a,b,c</sup> (IV) yielded 10 $\beta$ -fluoro- $\Delta^1$ -dehydro-19-norprogesterone (V), m.p. 108–109.5°,  $[\alpha]_D + 62^\circ$ ,  $\gamma_{\text{max}}^{\text{EtOH}}$  241  $\mu$ ,  $\log \epsilon$

(1) Paper CXXXIV, L. Knox, J. Zderic, J. Pérez Ruelas, C. Djerassi and H. J. Ringold, *THIS JOURNAL*, **81**, in press (1959).

(2) Pennsylvania Salt Manufacturing Co., Philadelphia 2, Pa.

(3) Melting points are uncorrected. Rotations were determined in chloroform.

(4) C. Djerassi, R. Riniker and B. Riniker, *THIS JOURNAL*, **78**, 6362 (1956).

(5) C. Djerassi and W. Closson, *ibid.*, **78**, 3761 (1956).

(6) (a) L. Velluz and G. Muller, *Bull. soc. chim. France*, 166 (1950); (b) C. Djerassi, G. Rosenkranz, J. Iriarte, J. Romo and J. Berlin, *THIS JOURNAL*, **73**, 1523 (1951); (c) J. S. Mills, H. J. Ringold and C. Djerassi, *ibid.*, **80**, 6118 (1958).

(1) The authors are indebted to the Robert A. Welch Foundation for the financial support of this study.

(2) Cf. N. J. L. Megson, “Phenolic Resin Chemistry,” Academic Press, Inc., New York, N. Y., 1958.

(3) P. D. Gardner, H. Sarrafizadeh R. and L. Rand, *THIS JOURNAL*, **81**, 3364 (1959).

4.04 infrared  $\gamma_{\max}^{\text{KBr}}$  at 5.89, 6.00, 6.13 and 6.2  $\mu$  (found for  $\text{C}_{20}\text{H}_{25}\text{O}_2\text{F}$ : C, 76.06; H, 8.17; F, 5.54). Details of these and other experiments will shortly be published in full.

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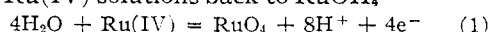
RECEIVED AUGUST 31, 1959

# THE INDUCED OXIDATION OF BOUND WATER BY RUTHENIUM(IV)<sup>1</sup>

Sir:

In studying the aqueous chemistry of ruthenium(IV) we have observed an interesting phenomenon which is believed to be the induced oxidation of bound water. These results were obtained on solutions of Ru(IV) prepared by the reduction of aqueous  $\text{RuO}_4$  either with  $\text{H}_2\text{O}_2$  or ferrous ion. Unless special precautions are taken, the resulting Ru(IV) is present as a hydrolyzed polymer.<sup>2</sup> This polymer is built up by the addition of  $\text{RuO}_2 \cdot x\text{H}_2\text{O}$  or  $\text{Ru}(\text{OH})_4 \cdot x\text{H}_2\text{O}$  units to monomeric Ru(IV), which has been characterized in separate experiments simply as the ruthenyl ion,  $\text{RuO}^{++}$ .

The unexpected occurs when one attempts to re-oxidize Ru(IV) solutions back to  $\text{RuO}_4$



Except for ruthenyl, which requires exactly four equivalents as indicated by equation (1), the polymeric solutions show a continuous increase in the number of equivalents with increasing polymeric weight (as shown by the ultracentrifuge). Thus some solutions requiring 8.0 equivalents per mole of ruthenium have been prepared. The spectra and molar extinction coefficients also change regularly, although the magnetic susceptibility remains constant.

We now believe that the excess number of equivalents of oxidizing agent over that required by equation (1) comes from the simultaneous oxidation of bound water in the polymer.

Analyses are determined by addition of an excess of standardized acidic ceric or dichromate to the ruthenium solutions, pumping off the volatile  $\text{RuO}_4$  and back-titrating<sup>3</sup> with standard ferrous sulfate. The oxygen released has also been determined manometrically and in every case examined has been equal to the required amount in excess of an oxidation equivalence of 4. Ceric and dichromate alone both have the potential necessary to oxidize water, but under the conditions of these experiments the rate is infinitesimally slow. Total ruthenium was determined by spectrophotometric measurement of the  $\text{RuO}_4$  formed on oxidation of the Ru(IV) solutions by periodate in a closed system.<sup>4</sup>

The question arises as to whether the high equivalence numbers,  $n$ , arise merely from the catalytic action of some ruthenium species on the oxidation

of the solvent water. That this possibility is unlikely follows from these considerations: (1) ruthenyl solutions show no such effect; (2)  $n$  is the same when either ceric or dichromate is used as the oxidizing agent; (3)  $n$  is independent of both the concentrations of the ruthenium and oxidizing agent over very large ranges; (4)  $n$  is independent of the reaction time; (5)  $n$  increases smoothly with molecular weight, and (6) solutions of  $\text{RuCl}_3$  can also be oxidized to  $\text{RuO}_4$ , presumably not going through well defined polymeric Ru(IV) species, and require only the expected 5 equivalents per mole of ruthenium. The simplest explanation for the preferential oxidation of bound water is the weakening of the O-H bond in the ruthenium polymeric structure. There appears to be no *a priori* reason why this phenomenon should not be quite general and evidence already has been obtained in our laboratory<sup>5</sup> that suspended  $\text{ReO}_2 \cdot x\text{H}_2\text{O}$  being oxidized to  $\text{ReO}_4^-$  shows a similar behavior.

(5) J. P. King, private communication.

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RECEIVED JULY 3, 1959

# THE TOTAL SYNTHESIS OF A NATURALLY OCCURRING PENTACYCLIC TRITERPENE SYSTEM

Sir:

We wish to report the total synthesis of the triterpene  $\alpha$ -onocerin (I).<sup>1</sup> Since this has been cyclized<sup>1</sup> to  $\alpha$ -onocerin and the latter has been converted<sup>2</sup> to hopenone-I (II), the first total synthesis of a naturally occurring pentacyclic triterpene system has thus been completed.

The tricyclic ketone (III)<sup>3</sup> was methylated to the 4,4-dimethyl  $\Delta^5$  compound, reduced catalytically with Pd-C in acetic acid to the *trans*-dihydroketone (IV), m.p. 55-57° (found: C, 79.57; H, 8.89). Birch reduction of the anisole ring, followed by HCl-MeOH hydrolysis and rearrangement, gave the tricyclic hydroxy enone (V) m.p. 148-149° (found: C, 77.60; H, 9.91). The acetate m.p. 111-112° (found: C, 74.79; H, 9.35) was ozonized in ethyl acetate at -70° to produce (91%) the ketopropionic acid (VI) m.p. 167-168° (found: C, 66.39; H, 8.47). The methyl ester, m.p. 84-86° (found: C, 67.36; H, 8.88) was ketalized under vigorous conditions<sup>4</sup> and the resulting ketal was transformed (56%) to the diphenylethylene (VII), m.p. 128-130°,  $\lambda_{\max}^{\text{MeOH}}$  249 m $\mu$  (4.33), 255 m $\mu$  (4.36) (found: C, 81.28; H, 8.14) by the successive steps of Grignard reaction with phenylmagnesium bromide, refluxing with 80% acetic acid for six hours and treatment with acetic anhydride-pyridine at room temperature. The diphenylethylene (VII) was oxidized (70%) with ruthenium tetroxide-sodium periodate in

(1) This research was supported by E. I. du Pont de Nemours and Co. and the U. S. Atomic Energy Commission under contracts AT(07-2)-1, AX-2271.

(2) Ru(IV) polymers also have been observed by others: *cf.*, H. H. Cady, Ph.D. Thesis, University of California at Berkeley, 1957.

(3) The direct titration of Ru(IV) with ceric or dichromate is too slow.

(4) H. H. Cady and R. E. Connick, *THIS JOURNAL*, **80**, 2646 (1958).

(1) D. H. R. Barton and K. H. Overton, *J. Chem. Soc.*, 2639 (1955).

(2) K. Schaffner, L. Caglioti, D. Arigoni and O. Jeger, *Helv. Chim. Acta*, **41**, 152 (1958).

(3) J. T. Rundquist, Ph.D. thesis, Harvard, 1951; *cf.* F. H. Howell and D. A. H. Taylor, *J. Chem. Soc.*, 1248 (1958).

(4) H. Hirschmann and J. W. Corcoran, *THIS JOURNAL*, **78**, 2325 (1956).