

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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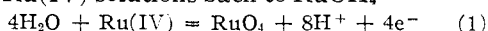
RECEIVED AUGUST 31, 1959

### 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

(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).

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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### 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

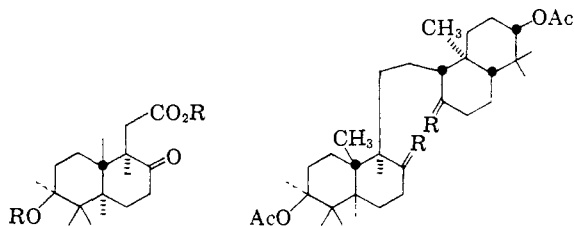
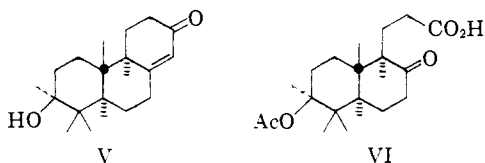
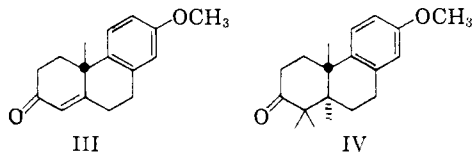
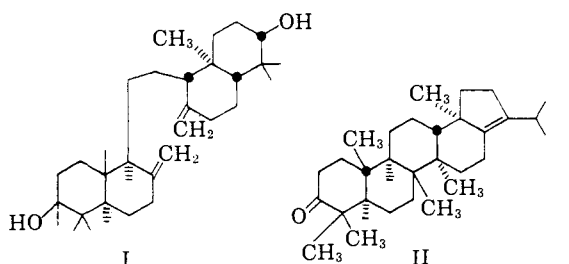
(1) D. H. R. Barton and K. H. Overton, *J. Chem. Soc.*, 2639 (1955).

(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).

acetone-water<sup>5</sup> for fifteen hours at room temperature to the *dl*-acetoxyketoacid (VIII) m.p. 238–240° (found: C, 65.50; H, 8.19), hydrolyzed to the *dl*-hydroxy acid (IX) m.p. 186–187° (found: C, 67.09; H, 8.97). Resolution was effected at this point by transformation of IX into the *dl*-methyl ester-half phthalate (X) m.p. 209–210° (found: C, 66.80; H, 7.15) by treatment with diazomethane and then phthalic anhydride in pyridine. Strychnine produced an acetone insoluble salt, m.p. 225–227°, cleaved by ethyl acetate–10% hydrochloric acid to the half phthalate (+X) m.p. 185–187°  $[\alpha]_{\text{CHCl}_3}^D + 23.5^\circ$  which was hydrolyzed to the hydroxyketoacid (+IX) m.p. 174–176°,  $[\alpha]_{\text{CHCl}_3}^D + 59.4^\circ$  (found: C, 67.05; H, 8.95). The acetone soluble strychnine salt similarly gave the half phthalate (–X) m.p. 188–190°,  $[\alpha]_{\text{CHCl}_3}^D - 23.5^\circ$ , hydrolyzed to the hydroxyketoacid (–IX) m.p. 171–173°,  $[\alpha]_{\text{CHCl}_3}^D - 57.8^\circ$  (found: C, 67.22; H, 9.15).



VIII, R = Ac, R' = H

IX, R, R' = H

X, R = HO<sub>2</sub>C–C<sub>6</sub>H<sub>4</sub>–C(=O)–, R' = CH<sub>3</sub>

XI, R = O

XII, R = CHCO<sub>2</sub>C<sub>2</sub>H<sub>5</sub>

The acid (–IX) on Kolbe electrolysis (platinum electrodes, methanol, trace of methoxide at 50°), followed by acetylation gave (29%) the diacetoxy dione (XI), m.p. 165–166°,  $[\alpha]_{\text{CHCl}_3}^D - 33.9^\circ$  (found: C, 72.31; H, 9.48), identical in all respects with the known substance<sup>1</sup> from the ozonolysis of  $\alpha$ -onocerin diacetate (I). Reaction of the dione

(5) R. Pappo and A. Becker, *Bull. Res. Council Israel*, **5A**, 300 (1958); F. Sondheimer and R. Mechoulam, private communication.

with ethoxyacetylenemagnesium bromide, followed by treatment with 10% methanolic-sulfuric acid at room temperature produced (35%), the di- $\alpha,\beta$ -unsaturated ester (XII) m.p. 154–155°,  $\lambda_{\text{max}}^{\text{EtOH}}$  224 m $\mu$ , log  $\epsilon$  4.60 (found: C, 71.85; H, 9.23). Hydrolysis with 10% methanolic potassium hydroxide, and then refluxing with copper chromite in quinoline for one hour and reacylation led (30%) to  $\alpha$ -onocerin diacetate, m.p. 220–221°,  $[\alpha]_{\text{CHCl}_3}^D + 29.8^\circ$  (found: C, 77.70; H, 10.39). This was completely identical with the diacetate of natural  $\alpha$ -onocerin (infrared, mixed melting point).

We wish to thank Mr. Melvin Deutsch for his preparation of considerable amounts of the tricyclic ketone III used in this work and Professor F. Sondheimer for his constructive suggestions during the last stages of this synthesis.

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#### PROTONATION OF FERROCENE BY STRONG ACIDS<sup>1</sup> Sir:

Although the course of Friedel-Crafts acylation reactions involving ferrocene is in general analogous to that encountered with benzenoid aromatics, certain aspects of these transformations are exceptional. Thus, when equimolar quantities of ferrocene, acyl halide and aluminum chloride are employed, monoacylferrocenes are formed to the virtual exclusion of 1,1'-diacylferrocenes. These results require that the rate constant for the first acylation step ( $k_1$ ) be significantly greater than that for the second step ( $k_2$ ). When, however, acylation is carried out with an excess of aluminum chloride, the major products are instead the 1,1'-diacylferrocenes. Broadhead, Osgerby and Pauson<sup>2</sup> have attributed these latter results to an inhomogeneity of the reaction medium. We have been unable to detect, by filtration, any significant inhomogeneity in these solutions. Neither are the products interconverted under the reaction conditions.

We suggest that these results are best accounted for in terms of the *effective* removal of ferrocene from the reaction through formation of a relatively stable, non-acylable complex salt with aluminum chloride and hydrogen chloride. These observations, derived from the results of several carefully controlled acetylations (Table I), support this conclusion.

The apparent ratio of rate constants ( $k_2/k_1$ )<sup>3</sup> increases as reaction proceeds to completion and hydrogen chloride is generated (compare expts. 1 and 2). Prior saturation of the reaction solution with hydrogen chloride results in a marked

(1) This investigation was supported by a research grant (RG-4772) from the National Institutes of Health, Public Health Service.

(2) G. D. Broadhead, J. M. Osgerby and P. L. Pauson, *J. Chem. Soc.*, 650 (1958).

(3) Calculated from the expression derived by W. G. McMillan, *This Journal*, **79**, 4838 (1957), for second order competitive consecutive processes.