4.04 infrared $\gamma_{max}^{KBr}$ at 5.89, 6.00, 6.13 and 6.2 μ (found for $C_{20}H_{25}O_2F$: C, 76.06; H, 8.17; F, 5.54). Details of these and other experiments will shortly be published in full.

RESEARCH LABORATORIES
SYNTEX, S. A.
APDO. POSTAL 2679
MEXICO, D. F.
J. S. MILLS

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## THE INDUCED OXIDATION OF BOUND WATER BY RUTHENIUM(IV)[1]

*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 $RuO_4$ either with $H_2O_2$ or ferrous ion. Unless special precautions are taken, the resulting Ru(IV) is present as a hydrolyzed polymer.[2] This polymer is built up by the addition of $RuO_2\cdot xH_2O$ or $Ru(OH)_4\cdot xH_2O$ units to monomeric Ru (IV), which has been characterized in separate experiments simply as the ruthenyl ion, $RuO^{++}$.

The unexpected occurs when one attempts to reoxidize Ru(IV) solutions back to $RuOH_4$

$$4H_2O + Ru(IV) = RuO_4 + 8H^+ + 4e^- \qquad (1)$$

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 $RuO_4$ and back-titrating[3] 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 $RuO_4$ formed on oxidation of the Ru(IV) solutions by periodate in a closed system.[4]

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 $RuCl_3$ can also be oxidized to $RuO_4$, 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 phenomen should not be quite general and evidence already has been obtained in our laboratory[5] that suspended $ReO_2\cdot xH_2O$ being oxidized to $ReO_4^-$ shows a similar behavior.

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[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: *c.f.*, 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).

[5] J. P. King, private communication.

DEPARTMENT OF CHEMISTRY
PURDUE UNIVERSITY
LAFAYETTE, INDIANA
F. P. GORTSEMA
J. W. COBBLE

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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 α-onocerin (I).[1] Since this has been cyclized[1] to α-onocerin and the latter has been converted[2] to hopenone-I (II), the first total synthesis of a naturally occurring pentacyclic triterpene system has thus been completed.

The tricyclic ketone (III)[3] 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[4] and the resulting ketal was transformed (56%) to the diphenylethylene (VII), m.p. 128–130°, $\lambda_{max}^{MeOH}$ 249 mμ (4.33), 255 mμ (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

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[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).