In the reaction of maleatopentamminocobaltic ion with Cr^{++}, fumaric acid is again produced during the electron transfer. The ratio fumaric/maleic acid increases linearly from zero with H^+ concentration, but at 0.5 *M* $HClO_4$, only 32% fumaric acid is formed.

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RECEIVED JULY 20, 1959

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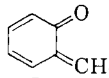
o-QUINONONE METHIDE[1]

Sir:

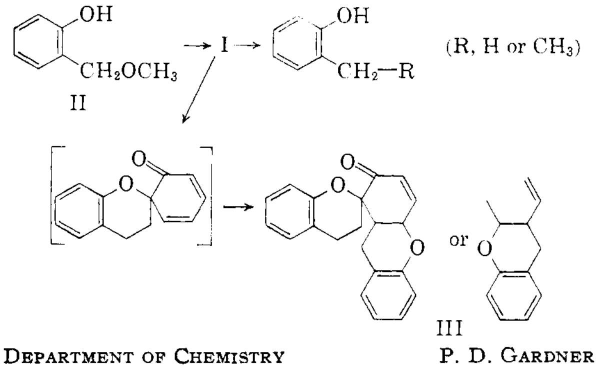
A multitude of reactions of substituted *o*-hydroxybenzyl alcohols give products which have been rationalized in terms of an *o*-quinone methide intermediate (I).[2] These could have been formed by other reaction paths, however, and the evidence for the actual existence of I, even as a transient species,[3] is therefore lacking.



I

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 $LiAlH_4$ 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 CH_3MgI afforded *o*-ethylphenol (phenylurethan, 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

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(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).

STEROIDS. CXXXV.[1] 10β-FLUORO STEROIDS; A NOVEL REACTION OF PERCHLORYL FLUORIDE.

Sir:

Treatment of estradiol (I) in dimethylformamide with perchloryl fluoride (ClO_3F)[2] for twenty hours at room temperature afforded a compound (60–70%), m.p. 152–154°, $[\alpha]_D$ − 27°,[3] γ_{max}^{EtOH} 240 mμ, log ε 4.06 infrared ν_{max}^{KBr} at 2.9, 6.0, 6.12 and 6.21 μ, which we formulate as 10β-fluoro-Δ^1-dehydro-19-nortestosterone (II) on the basis of the spectral characteristics and analysis (found for $C_{18}H_{23}O_2F$: 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°, infrared ν_{max}^{KBr} at 2.8 and 5.86 μ (found for $C_{18}H_{27}O_2F$: 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[4] from which the 10-fluorine atom is presumed to be in the β configuration, while the rotatory dispersion curve of the saturated ketone (III) was of the type characteristic for rings A/B *cis*-fused steroids[5] and the compound is therefore formulated as 10β-fluoro-19-nor-5β-androstan-17β-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-17β-acetyl-1,3,5(10)-estratriene ("aromatic progesterone")[6a,b,c] (IV) yielded 10β-fluoro-Δ^1-dehydro-19-norprogesterone (V), m.p. 108–109.5°, $[\alpha]_D$ + 62°, γ_{max}^{EtOH} 241 mμ, log ε

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(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).