Oxymercuration-Jones Oxidation of β- and γ-Hydroxyolefinic Acids

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A treatment of 12-hydroxyoctadec-*cis*-9-enoic acid (I) and 9-hydroxyoctadec-*cis*-12-enoic acid (II) in the presence of a catalytic amount of mercuric acetate reacts with Jones reagent to afford 9,12-dioxooctadecanoic acid in high yield, involving two different mechanistic routes.

Oxymercuration-demercuration reactions of β- and γ-hydroxyolefinic acids have been investigated thoroughly by Gunstone and co-workers (1). Recent reports (2,3) on oxymercuration and simultaneous treatment of Jones reagent to terminal olefins gave methyl ketones. This selective ketonization has created new interest in the synthesis of fatty oxo derivatives. In light of the above reports, β- and γ- hydroxyolefinic acids have been exploited by us for the synthesis of 1,4-dioxo acids which are potential synthetic intermediates. Recently reports (4,5) have appeared for the synthesis of 1,4-dioxo acid from γ-hydroxyolefinic acid by reaction with $AgCrO_4$-I_2 complex followed by m-CPBA oxidation and also from the β- and γ-hydroxyacetylenic acids by a two step process involving oxymercuration-demercuration and oxidation by Jones reagent. Here we have evolved a direct but selective and one-step method for the conversion of both β- and γ-hydroxyolefinic (ricinoleic and isoricinoleic) acids into 1,4-dioxo acids.

MATERIALS AND METHODS

All the methods were the same as reported in our earlier communications (5,6).

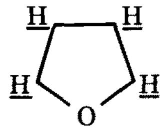
EXPERIMENTAL

Oxymercuration-Jones oxidation of I and II. In separate experiments, to a solution of acetone (80 ml), water (2 ml) and mercuric acetate (4 g), I and II (6 g) each were added and then kept at bath temperature (50–60 C) for four hr. Oxymercurated products I_a and II_a (2.9 g) each were taken from the reaction mixture and to the remaining portion Jones reagent (60 ml, 0.6M) was added over four hr while the bath temperature was maintained at 30–35 C. The dark green brown solution was stirred for another two hr. Then the contents were taken out in ice cold water, extracted with ether and dried over sodium sulphate. Evaporation of ether gave a semi-solid (III) in both cases which on crystalization from petrol-acetone gave white crystals of III. It melted at 94–95 C.

Analysis: Found, C, 69.13; H, 10.33 for $C_{18}H_{32}O_4$; calcd, C, 69.19; H, 10.32%; IR (KBr, cm^{-1}): 1700 (COOH), 1692 (C=O). NMR ($CDCl_3$, δ): 2.67 s ($OC\text{-}CH_2\text{-}CH_2\text{-}CO$); 2.3 m ($-C_8$, $-C_{13}$ and C_2 methylene protons). Mass: M+ m/e 312; 227, 171, 169, 113.

Demercuration of I_a. The oxymercurated adduct (I_a) was treated with $NaBH_4$ (0.5M, 20 ml), NaOH (3M, 30 ml) and was acidified with HCl at 0 C to complete the demercuration. Products were extracted with ether and dried over sodium sulphate. Evaporation of solvent gave I_b as solid; it melted at 112–117 C (lit. 109–118 (7)). IR (KBr, cm^{-1}): 3340 (OH), 1700 (COOH). NMR (CCl_4, δ): 3.7 m (2 × *O*H,D_2O exchangeable), 3.2 m (C*H*-OH). Compound I_b on treatment with Jones reagent gave III. Demercuration of I_a (1.2 g) in acetone (30 ml) with H_2SO_4 (10 N, 10 ml) gave a liquid product I_c, which on TLC plate showed a R_f similar to that of I.

Demercuration of II_a. Oxymercurated adduct (II_a 1.5 g) was treated with $NaBH_4$/NaOH followed by HCl for demercuration, as described above. This product, extracted with ether, dried and, with evaporation of the solvent, gave a liquid product (II_b) in quantitative yield. IR (neat, cm^{-1}): 1700 (COOH), 1160, 1020 (C-O). NMR (CCl_4, δ): 4.3 and 3.9



Demercuration of II_a (1.2 g) in acetone (30 ml) with H_2SO_4 (10 N, 10 ml) gave a white solid (II_c) which melted at 112–117 C, and spectral data were found similar to that of I_b.

Discussion. Oxymercuration-Jones oxidation reactions of β- and γ-hydroxy olefinic acids are outlined in Scheme 1. The route of formation of this unusual dioxo acid is also given in Scheme 1. The IR band at 1692 for isolated oxo functions along with a shoulder at 1700 cm^{-1} for COOH, characteristic NMR signal for four protons of the two methylene groups sandwiched between the two oxo functions at δ 2.67 and mass spectrum (Scheme 2) confirms the formation of 1,4-dioxo acid from the β- and γ-hydroxyolefinic acids. Formation of this acid is believed to occur in two steps from β- and γ-hydroxyolefinic acids. In the case of β-hydroxyacid, the incoming hydroxy group during oxymercuration is attached preferentially to the unsaturated carbon farther from the substituent (1). Here no hydroxyl participation is possible because of the *cis* geometry of the double bond. Jones reagent, when added to the mercurated product (I_a), will act both as reducing agent (demercuration) and oxidizing agent (oxidation of hydroxyl group) to give the desired 1,4-dioxo acid III.

In the case of γ-hydroxyolefinic acid the formation of III occurs via the intermediacy of cyclic ether (II_b). Here, too, Jones reagent performs a dual role when it reacts with mercurated cyclic ether (II_a) to afford the 1,4-dioxo acid.

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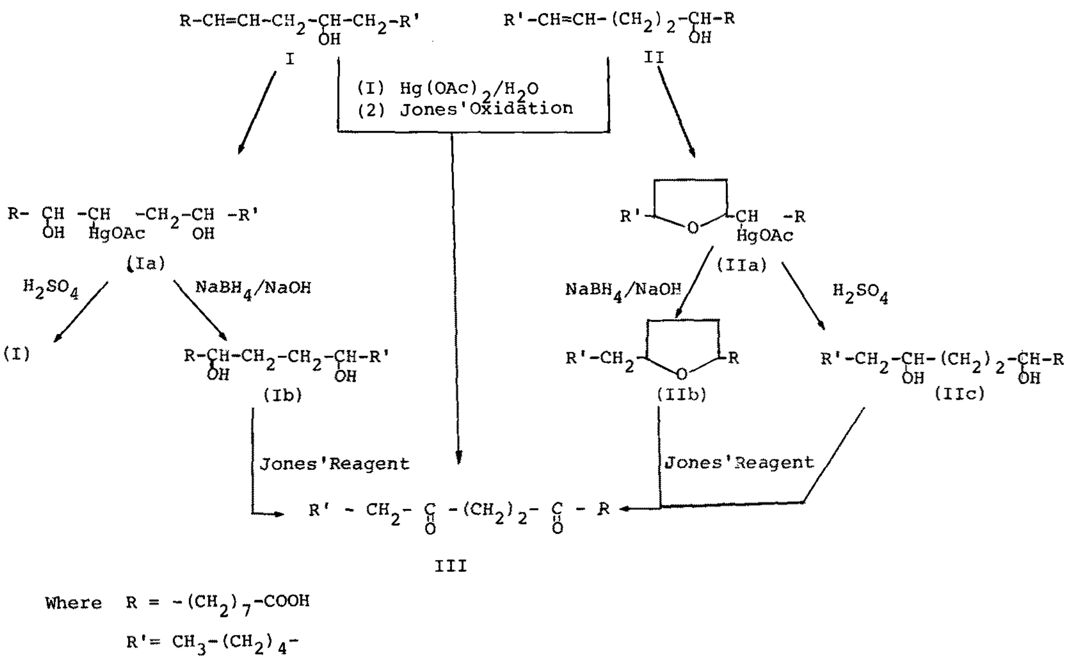
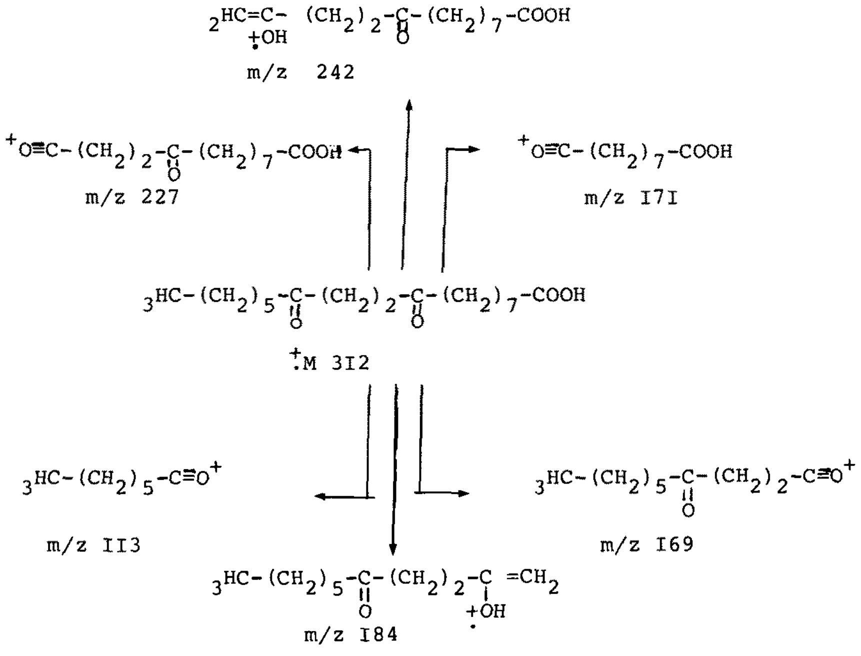


SCHEME 1.



SCHEME 2.

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