

Novel Synthesis of a 1,4-Dioxo Derivative by the Reaction of a γ -Hydroxyolefinic Acid with the Silver Chromate-Iodine Complex followed by *m*-Chloroperbenzoic Acid Oxidation

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Reaction of the complex of silver chromate and iodine with a γ -hydroxyolefinic acid (isoricinoleic) yielded 13-iodo-9,12-epoxyoctadecanoic acid, which on treatment with *m*-chloroperbenzoic acid gave a quantitative yield of 9,12-dioxo-octadecanoic acid.

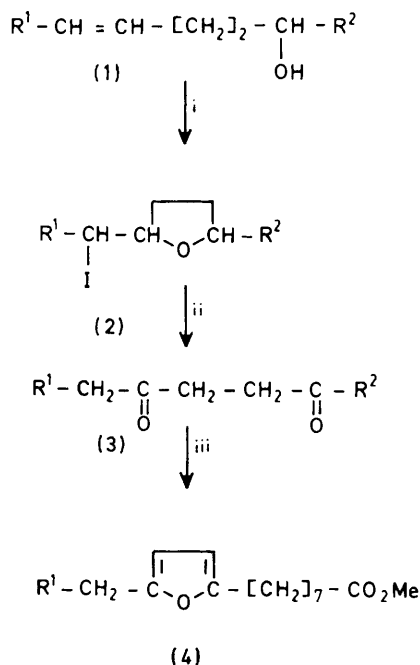
Fatty acids containing the furan system have been isolated from natural sources^{1,2} and a number of methods for partial synthesis of certain furan ester isomers have been reported from linoleic and ricinoleic acids,³ through several isomeric intermediates. Increasing interest in this chemistry and biochemistry prompted the need for a synthesis of selective intermediates leading to a side product-free regioselective furanoid acid. We chose a mild selective and quantitative route utilizing naturally occurring isoricinoleic acid, as yet to be exploited in the synthesis of furanoid acids (Scheme 1).

Isoricinoleic acid (**1**) (isolated from *Wrightia tinctoria* seed oil) reacted with the silver chromate-iodine-pyridine complex according to the procedure described by Cardillo and Shimizu⁴ and gave 13-iodo-9,12-epoxyoctadecanoic acid (**2**) (ca. 96% yield) as an oil. The formation of the 1,4-epoxide in high

yield is ascribable to neighbouring group participation and iodonium ion stability, in a reaction where intramolecular nucleophilic attack competes successfully with intermolecular reaction. The methyl ester of (**2**) showed ¹H n.m.r. signals at δ 3.7 (CH) and 8.2 (CH₂), [*m/z* 311 (*M*-I, 28%), 281 (*M*-MeOCO[CH₂]₇, 40%), and 227 (*M*-R¹CHI, 63%)].

Oxidation of (**2**) with *m*-chloroperbenzoic acid (ArCO₃H) gave 9,12-dioxo-octadecanoic acid (**3**) [m.p. 95–95.5 °C; ca. 85% yield; i.r. 1692 cm⁻¹ (C=O); ¹H n.m.r. δ 2.3 (R¹CH₂CO-[CH₂]₂COR²) and 2.66 (R¹CH₂CO[CH₂]₂COR²); *m/z* 312 (*M*⁺, 3%), 242 (via McLafferty rearrangement, 13%), 227 (*M*-R¹CH₂, 3%), 184 (McLafferty, 24%), 171 (*M*-R²CO, 23%), 169 (*M*-R², 29%), and 113 (*M*-R¹CH₂CO, 44%)].

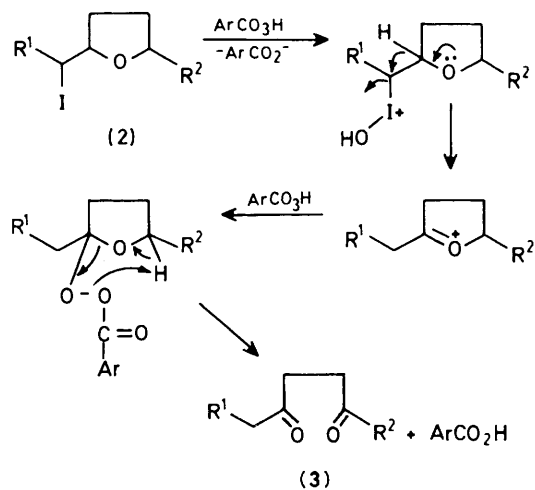
The mechanism suggested for the formation of dioxo acid (**3**) is shown in Scheme 2. The first step involves the oxidation



Scheme 1. $\text{R}^1 = \text{Me}[\text{CH}_2]_4$; $\text{R}^2 = [\text{CH}_2]_7, \text{CO}_2\text{H}$. Reagents: i, $\text{Ag}_2\text{CrO}_4\text{-I}_2\text{-pyridine}$; ii, $m\text{-ClC}_6\text{H}_4\text{CO}_3\text{H}$; iii, $\text{BCl}_3\text{-MeOH}$.

of compound (2) at iodine by ArCO_3H followed by a 1,2-rearrangement yielding an oxonium ion. The oxonium ion then reacts with more peracid giving a peroxide that could ultimately collapse to the observed product. The acid catalysed nature of the reaction has been ascertained by performing the reaction in the presence of various buffers.

Pure methyl 9,12-epoxyoctadeca-9,11-dienoate (4)⁵ in 95% yield was prepared by refluxing (3) with 10% boron trichloride-methanol for 30 min {i.r. 1580, 1640, and 1015 cm^{-1} (furan ring); ^1H n.m.r. δ 5.8 (=CH-); m/z 308 (M^+ , 43%), 237 ($M - \text{R}^1\text{CH}_2$, 30%), and 165 ($M - \text{MeOCO}[\text{CH}_2]_6$, 82%)}



Scheme 2

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