

OXIDATIVE CLEAVAGE OF DITERPENIC GLYCOLS

WITH JONES REAGENT

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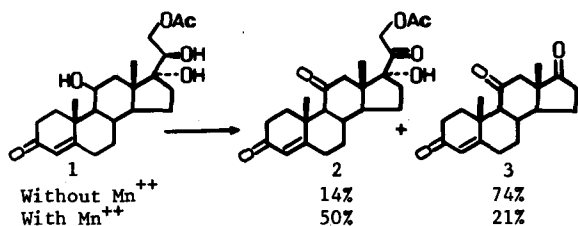
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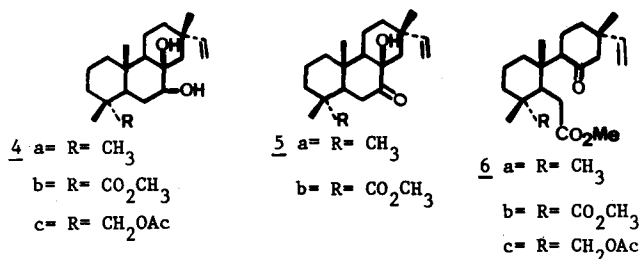
**Abstract:** The use of Jones reagent for the oxidation of diterpenic glycols is discussed.

The oxidative cleavage of glycols has received considerable attention not only for analytical applications but also for preparative purposes. The diols may be directly oxidized, but they can also be generated in situ from olefinic compounds thus extending further the scope of the reaction.

For the cleavage of diols, the common reagents employed are periodic acid and its salts<sup>1</sup> and lead tetraacetate<sup>2</sup>, both of which give good to excellent results. Chromium derivatives albeit giving some good results<sup>3</sup>, show an erratic behaviour as can be seen in the oxidation of cortisol 21-acetate (1) to androst-4-en-3,11,17-trione (3)<sup>4</sup>.



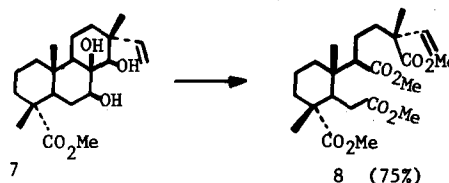
In the course of a research program, aiming at the synthesis of gibberelin analogs<sup>5</sup>, we came across the conversion of substrates 4 and 5 into ketoesters 6. For this purpose, we found that Jones oxidation followed by diazomethane esterification, proved to be a particularly useful procedure, affording good to excellent yields (Table 1).



SUBSTRATE	PRODUCT	YIELD
4a	6a	97%
4b	6b	95%
4c	6c	95%
5a	6a	90%
5b	6b	75%

Table 1

The reaction is rapid and reasonably clean, being run as a titration procedure and can be applied systematically to this class of compounds. The products are isolated by the usual extraction (CHCl<sub>3</sub>) work-up and purified by chromatographic filtration. More complex molecules can be oxidized with good results, as can be seen by the conversion of 7 into 8.



Although considering the more common periodate derivatives suitable for the oxidative cleavage, we feel that the lower cost and the excellent results obtained with the Jones reagent justifies its use for compounds which do not require the more selective properties of periodate salts.

**Typical experimental procedure:** The diol (1 mmole) is dissolved in 10 ml of acetone. To this solution, 0.6 ml of Jones reagent is added dropwise with stirring, to the point of a persistent brown colour. The excess of Jones reagent is consumed by reaction with 5 drops of *i*-PrOH and, after solvent removal in vacuum, the residue is extracted with CHCl<sub>3</sub>, washed with H<sub>2</sub>O, dried under Na<sub>2</sub>SO<sub>4</sub> and evaporated. The remaining oil is treated with CH<sub>2</sub>N<sub>2</sub> and filtered through silica gel to afford the ketoester as a colourless oil which can be further purified by crystallization.

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