

## Note

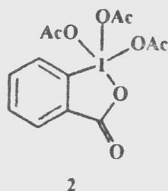
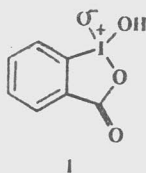
### Oxidation of the secondary alcohol present in some common sugar derivatives with Dess-Martin periodinane

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Oxidation of the secondary alcohol present in some common sugar derivatives **3**, **5**, **7**, **9** to the corresponding ketones can be performed conveniently with Dess-Martin periodinane **2**, prepared from hydroxyiodinane oxide **1**.

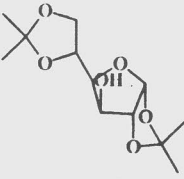
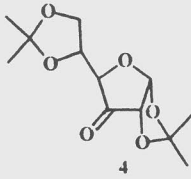
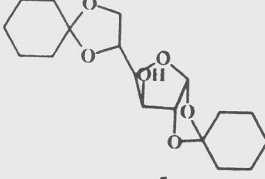
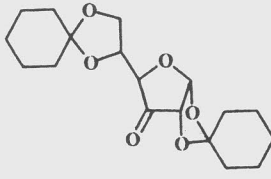
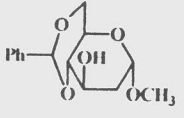
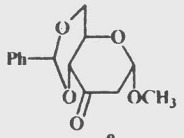
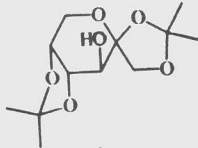
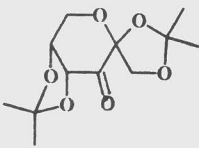
The Dess-Martin periodinane<sup>1</sup>, 1,1,1-tris(acetyloxy)-1,1-dihydro-1,2-benziodoxol-3-(1*H*)-one **2** has become a reagent of choice for the oxidation of primary alcohols to aldehydes and secondary alcohols to ketones<sup>2</sup>. This reagent offers several advantages over conventional reagents such as mild reaction conditions, near neutral *pH* in the reaction medium, need to use only stoichiometric amount of the reagent and avoiding toxic chemicals based on chromium etc. However, the main disadvantage is that its shelf life is rather limited<sup>3</sup>. Due to the moisture sensitivity of the reagent, it has to be stored under argon in amber-glass bottles, in freezer and even then only freshly made reagent was reported to effect higher yields<sup>3</sup>. On the other hand, the precursor for the Dess-Martin periodinane **2**, the hydroxyiodinane oxide, 1-hydroxy-1,2-benziodoxol-3-(1*H*)-one 1-oxide **1** is a stable solid with long shelf life at room temperature<sup>4</sup>. We report herein that it is convenient to generate Dess-Martin periodinane **2** *in situ* and employ it for the oxidation of secondary alcohol present in some common sugar derivatives to the corresponding ketones in good yield.



Acetylation of hydroxyiodinane oxide **1**, carried out under a blanket of dry nitrogen, following the procedure described by Ireland<sup>5</sup> resulted in Dess-Martin periodinane **2** in the reaction vessel (see Experimental). The supernatant light brownish-red liquid was withdrawn with a syringe and the resulting solid periodinane was washed with freshly dried ether three times *via* an operation some what similar to washing off mineral oil from sodium hydride mineral oil suspension with dry hydrocarbon solvents. In our hands, this procedure hardly removed any reagent (less than 5%). The periodinane **2** resulting from ether washings was a white crystalline solid, dissolved readily in dry dichloromethane or in dry 1,2-dichloroethane at rt. or in dry carbon tetrachloride at 65°C (oil-bath).

Following the above described procedure, we have prepared the Dess-Martin periodinane **2** and employed it for the oxidation of the secondary alcohol present in some common sugar derivatives and the results are gathered in the Table I. Oxidation of glucose diacetone, 1,2:5,6-di-*O*-isopropylidene  $\alpha$ -D-glucofuranose **3** to the corresponding ketone **4** was conducted conveniently in dichloromethane at rt for 5h or in 1,2-dichloroethane at 65°C for 2h. The ketone **4** was prepared previously by oxidation of the alcohol **3** with an expensive reagent ruthenium dioxide<sup>6</sup> or with pyridinium dichromate under stringent conditions<sup>7</sup>. It was observed that the oxidation of glucose dicyclohexylidene derivative, 1,2:5,6-di-*O*-cyclohexylidene- $\alpha$ -D-glucopyranose **5** was sluggish and resulted in unreactable mixture when the reaction was conducted at rt in dichloromethane. However, the reaction was neat and desired ketone **6** was obtained in good yield when it was conducted in carbon tetrachloride at 65°C for 4.5h or in 1,2-dichloroethane reflux for 4h. Previously this oxidation was effected with ruthenium dioxide<sup>8</sup>. Oxidation of the deoxyulose benzylidene derivative to methyl 4,6-*O*-benzylidene-2-deoxy- $\alpha$ -D-erythro-hexopyranosid-3-ulose **8**<sup>9</sup> took place readily in dichloromethane within 30 min at rt. Previously this oxidation was performed with pyridinium dichromate<sup>10</sup>. In the

Table I- Oxidation of secondary alcohol present in some common sugar derivatives with Dess-Martin periodinane.

Substrate	Product	Reaction conditions	Yield <sup>a</sup>
		CH <sub>2</sub> Cl <sub>2</sub> , 5h, rt C <sub>2</sub> H <sub>4</sub> Cl <sub>2</sub> <sup>b</sup> , 2h, 65°C	72 83
		CCl <sub>4</sub> , 4.5h, 65°C C <sub>2</sub> H <sub>4</sub> Cl <sub>2</sub> , 4h reflux	73 74
		CH <sub>2</sub> Cl <sub>2</sub> , 5h, rt	90
		C <sub>2</sub> H <sub>4</sub> Cl <sub>2</sub> , 4h reflux	60

a. Yields are of the isolated and purified products; b. C<sub>2</sub>H<sub>4</sub>Cl<sub>2</sub> refers to 1,2-dichloroethane.

same manner oxidation of fructose diacetonide derivative **9**<sup>11</sup> to the corresponding ketone **10** took place readily in dichloromethane within 1h at rt. Previously this oxidation was performed with either ruthenium tetroxide<sup>12</sup> or dimethyl sulfoxide/acetic anhydride<sup>13</sup>.

In conclusion, we say that Dess-Martin periodinane can be prepared conveniently and used for further oxidation reaction in a one-pot procedure. This reagent can be used for the oxidation of the secondary alcohol present in some common sugar derivatives to the corresponding ketones.

## Experimental Section

**General procedure for the oxidation of an alcohol functional group with Dess-Martin periodinane 2.** To hydroxyiodinane oxide **1** (0.56g, 2.0mmol), TsOH.OH<sub>2</sub><sup>14</sup> (5mg), and a magnetic stirring bar, under a blanket of dry nitrogen, in a 25mL flame dried

two-necked flask, acetic anhydride (2mL) was added with a syringe. The flask was immersed in an oil-bath maintained at 80°C. The reaction mixture was stirred at this temperature for 20min. and then cooled in crushed-ice bath when a white solid periodinane separated from the reaction. After allowing the solid to settle down the supernatant reddish-brown liquid was withdrawn with a syringe. Left over solid was washed with dry ether (3 x 5mL) in the following sequence of operations: (i) adding dry ether with a syringe, (ii) stirring for 1 min, (iii) allowing the solid to settle down and (iv) withdrawing supernatant liquid with a syringe. This washing left behind white crystalline periodinane **2** (0.83g, 98%), mp. 134°C dec. (lit. m.p. 134°C<sup>5</sup>). To this periodinane dissolved in dichloromethane (10 mL), glucose diacetonide **3** (0.498g, 1.9mmol) in dichloromethane (5mL) was added and stirring continued at rt. The oxidation was complete in 5 h (TLC). The dichloromethane solution

was washed with ice-cold 1N NaOH (2 x 10mL), water (10mL), brine (5mL), dried (MgSO<sub>4</sub>) and evaporated to furnish the ketone **4** as a colourless syrup (0.39g, 78%,  $[\alpha]_{\text{CHCl}_3}^{\text{D}} = +106^\circ$ . lit.<sup>15</sup>  $[\alpha]_{\text{CHCl}_3}^{\text{D}} = +107^\circ$ ) which was identical with the authentic sample (TLC, co-TLC, IR and <sup>1</sup>H NMR). Alternatively, work-up of the reaction mixture can be carried out by passing the reaction mixture through a short plug of basic alumina (1cm x 5cm) and solvent removed to get the ketone. Oxidation of other sugar derivatives **5,7,9** having a secondary alcohol resulted in the corresponding ketones **6,8,10**, which showed expected chromatographic behavior and spectral data.

### Acknowledgement

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(b) Dess D B & Martin J C, *J Org Chem*, 48, **1983**, 4156.
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