J. Org. Chem. **1993**, *58*, 2899 **2899**

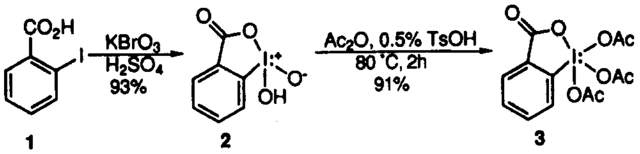
An Improved Procedure for the Preparation of the Dess–Martin Periodinane

Robert E. Ireland* and Longbin Liu

Department of Chemistry, University of Virginia,
Charlottesville, Virginia 22901

Received December 15, 1992

The Dess–Martin periodinane,[1] 1,1,1-triacetoxy-1,1-dihydro-1,2-benziodoxol-3(1*H*)-one (**3**), has become the reagent of choice for the oxidation of primary and secondary alcohols to aldehydes and ketones, respectively.[2] The mild reaction conditions (at room temperature and either slightly acidic or virtually neutral pH) are especially suitable for substrates containing sensitive functional groups. Since this reagent is no longer commercially available,[3] it is routinely prepared in many research laboratories following the literature procedure.[1] We have found, however, that it is often difficult to obtain reproducible results under these conditions (vide infra). We now offer a modified procedure that is highly reproducible and renders pure Dess–Martin periodinane in excellent yield



1 2 3

In the original Dess–Martin procedure,[1] 2-iodobenzoic acid (**1**) was oxidized by $KBrO_3$ to the hydroxyiodinane oxide **2** which was then treated with a mixture of acetic anhydride and acidic acid at 100 °C for ca. 40 min. In a revised procedure,[1b] the acetylation was conducted at 85 °C. The mixture was then concentrated at 40 °C, and the product was isolated by filtration followed by washing with ether. In our hands, we found the acetylation of the hydroxyiodinane oxide **2** often proceeded slowly and resulted in mixtures of incompletely acetylated products. The yields of isolated periodinane **3** were moderate and varied widely.[4] In quite a few cases, exclusive formation of a monoacetylated product[5,6] was observed under the Dess–Martin conditions. Further evidence for the sporadic behavior of the Dess–Martin acetylation can be found in the literature. Thus, Evans et al.[7] obtained periodinane **3** by heating a mixture of the hydroxyiodinane oxide **2** in $HOAc/Ac_2O$ at 80 °C "only until dissolution was complete (ca. 10 min)". Ayling and co-workers[8] found that "continuous passage of dry inert gas through the reaction head space" facilitates the acetylation. Dess and Martin pointed out that the rate of acetylation depended on the particle sizes of the hydroxyiodinane oxide **2** and suggested that it be monitored for product formation by ^1H NMR.

By using only a catalytic amount of TsOH in place of HOAc, we were able to effect the acetylation of the hydroxyiodinane oxide **2** in 91% yield in less than 2 h. The modified reaction has been performed several times on a 100-g scale. *The product formed was always the desired Dess–Martin periodinane **3**, and the isolated yield always exceeded 90%.* An added bonus of this modification is that the product precipitates completely, thus eliminating the need to evaporate the excess solvents. This improved procedure should prove to be a convenient method for the preparation of Dess–Martin periodinane.

Experimental Section

CAUTION! The Dess–Marin precursor oxide **2** was reported to be explosive under excessive heating (>200 °C) or impact.[9]

1,1,1-Triacetoxy-1,1-dihydro-1,2-benziodoxol-3(1*H*)-one (3). 1-Hydroxy-1,2-benziodoxol-3(1*H*)-one (**2**) (100 g)[10] was added to a 1-L round-bottomed flask containing Ac_2O (400 mL), $TsOH{\cdot}H_2O$ (0.5 g), and a magnetic stirring bar. The flask was equipped with a drying tube and was immersed in an oil bath at ca. 80 °C. The mixture was stirred for 2 h and then cooled in an ice–water bath. The cold mixture was filtered through a fritted glass funnel followed by rinsing with anhydrous ether (5 × 50 mL). The resulting white, crystalline solid **3** (138 g, 91%[11]) was quickly transferred to an argon flushed amber-glass bottle and stored in a freezer: mp 134 °C (lit.[1b] mp 133–134 °C); ^1H NMR, ^{13}C NMR and IR all agree with those reported by Dess and Martin.[1b]

Acknowledgment. We thank Robert S. Meissner and James L. Gleason for helpful discussions. Support for this work through a grant (GM41983) from the National Institutes of Health is gratefully acknowledged.

---

[1] (a) Dess, D. B.; Martin, J. C. *J. Org. Chem.* **1983**, *48*, 4156. (b) Dess, D. B.; Martin, J. C. *J. Am. Chem. Soc.* **1991**, *113*, 7277.

[2] See, *inter alia*, the 74 publications cited by Dess and Martin[1b] where this reagent was employed in syntheses.

[3] Aldrich once offered the Dess–Martin periodinane.

[4] The workup was modified in our laboratory as follows: the reaction mixture was cooled in an ice bath, and the resulting precipitate was filtered and washed with ether. Further workup of the resulting mother liquid often resulted in mixtures of products.

[5] This material gives the following ^1H NMR ($CDCl_3$, 300 MHz) data: δ 8.25 (dd, J = 1.2, 7.5 Hz, 1 H), 8.00 (d, J = 8.1 Hz, 1 H), 7.92 (dt, J = 1.5, 7.4 Hz, 1 H), 7.71 (dt, J = 0.9, 7.8 Hz, 1 H), 2.26 (s, 3 H).

[6] Formation of considerable amount of monoacetate has been observed by others and informed to Dess and Martin. See ref 1b.

[7] Evans, D. A.; Kaldor, S. W.; Jones, T. K.; Clardy, J.; Stout, T. J. *J. Am. Chem. Soc.* **1990**, *112*, 7001.

[8] Bailey, S. W.; Chandrasekaran, R. Y.; Ayling, J. E. *J. Org. Chem.* **1992**, *57*, 4470.

[9] Plumb, J. B.; Harper, D. J. *Chem. Eng. News* **1990**, July 16, 3.

[10] This material was prepared according to the Dess–Martin procedure, but was further rinsed with 3 × 50 mL of anhydrous ether following the ethanol washings.

[11] An overall 91% yield of **3** starting from **1** was obtained in one experiment.

0022-3263/93/1958-2899$04.00/0