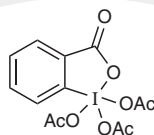


Dess–Martin Periodinane



Alternative names: 1,1,1-triacetoxy-1,1-dihydro-1,2-benziodoxol-3(1H)-one; DMP; 1,1,1-triacetoxy-1 λ^5 ,2-benziodoxol-3(1H)-one

CAS number: 87413-09-0

FW: 424.14

MF: C₁₃H₁₃IO₈

Key Science of Synthesis Articles

Zhdankin, V. V., *SOS*, (2007) **31a**, 169. (Section 31.4.1.1.2.1) (synthesis)

Podlech, J., *SOS*, (2007) **25**, 38. (Section 25.1.2.2.3) (applications)

Usage

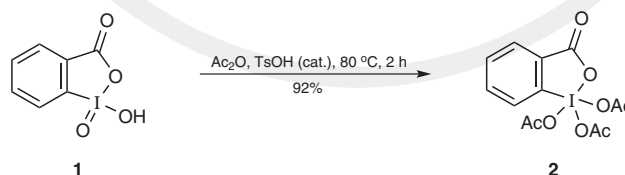
One of the most useful oxidizing agents for the oxidation of primary and secondary alcohols to aldehydes and ketones, respectively, is the Dess–Martin periodinane.^[1,2] This reagent selectively oxidizes alcohols in the presence of nonhydroxylic functional groups such as alkenes, sulfides, enols, ethers, furans, and secondary amides. The mild reaction conditions (room temperature and the absence of acidic or basic additives), high chemoselectivity, and preparative convenience make this reagent especially suitable for the oxidation of substrates containing sensitive functional groups. It is stable indefinitely when protected from atmospheric moisture and requires a simple workup procedure.

The susceptibility of the Dess–Martin periodinane to moisture on prolonged storage, restricts the practical applications of this reagent.

Availability

Dess–Martin periodinane is commercially available, but can be easily prepared from **1-hydroxy-1,2-benziodoxol-3(1H)-one 1-oxide** (2-iodylbenzoic acid, IBX). Iodylarenes can be converted into acetates or trifluoroacetates by treatment with the appropriate carboxylic acid anhydride.^[2-4] This method is particularly useful for the preparation of 1,1,1-triacetoxy-1,1-dihydro-1,2-benziodoxol-3(1H)-one (**2**), an important reagent commonly known as Dess–Martin periodinane. This reagent is sensitive to moisture and should be handled and stored in a dry atmosphere.

Scheme 1 Preparation of Aryliodine(V) Carboxylates from Iodylarenes^[2-4]

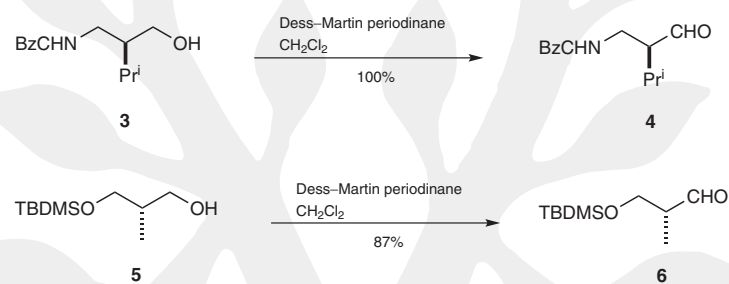


for references see p 6

1,1,1-Triacetoxy-1,1-dihydro-1,2-benziodoxol-3-(1H)-one (Dess–Martin Periodinane, 2):^[4]

CAUTION: 1-Hydroxy-1,2-benziodoxol-3(1H)-one 1-oxide (2-iodylbenzoic acid) is explosive under impact or heating above 200 °C.

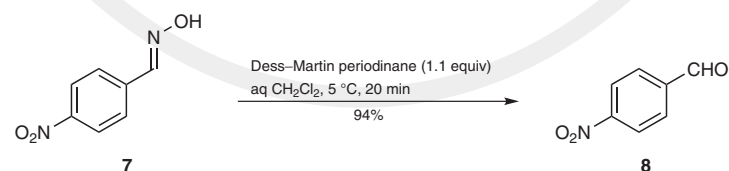
1-Hydroxy-1,2-benziodoxol-3(1H)-one 1-oxide (**1**; 100 g, 0.36 mol) was added to a 1-L round-bottomed flask containing Ac₂O (400 mL), TsOH•H₂O (0.5 g), and a magnetic stirrer bar. The flask was equipped with a drying tube and was immersed in an oil bath at ca. 80 °C. The mixture was stirred for 2 h, and then cooled in an ice–water bath. The cold mixture was filtered through a fritted glass funnel and the material obtained was rinsed with anhyd Et₂O (5 × 50 mL). The resulting colorless, crystalline product was quickly transferred to an argon-flushed amber-glass bottle and stored in a freezer; yield: 138 g (92%); mp 134 °C.

Sample Transformations**Scheme 2** Oxidations Using Dess–Martin Periodinane^[5,6]**(S)-2-[(Benzyloxycarbonyl)amino]-3-methylbutanal (4); Typical Procedure:^[5]**

The (*S*)-isomer of the alcohol **3** (1.00 mmol) in anhyd CH₂Cl₂ (2 mL) was added to a stirred soln of Dess–Martin periodinane (530 mg, 1.25 mmol) in CH₂Cl₂ (5 mL) at 0 °C, and then the mixture was allowed to warm to rt. The addition of more of the oxidant may be necessary (monitoring by TLC). When the reaction was complete, excess oxidant was destroyed by the addition of 1 M NaOH. After 5 min of vigorous stirring, the mixture was diluted with Et₂O (10 mL), the organic layer was separated, and the aqueous layer was extracted with Et₂O (2 ×). The combined extracts were washed with brine, dried (MgSO₄), and concentrated; yield: quant.

(S)-3-(*tert*-Butyldimethylsiloxy)-2-methylpropanal (6); Typical Procedure:^[6]

Dess–Martin periodinane (198 g, 466 mmol) was suspended in CH₂Cl₂ (100 mL) and the (*S*)-isomer of the alcohol **5** (50.0 g, 245 mmol) was added at 0 °C. The mixture was stirred for 1 h, and then filtered through a pad of Na₂SO₄, prior to removal of the solvent; yield: 43.1 g (87%).

Scheme 5 Arenecarbaldehydes by Cleavage of Arenecarbaldehyde Oximes^[7]

4-Nitrobenzaldehyde (8); Typical Procedure:^[7]

Dess–Martin periodinane (0.93 g, 2.2 mmol) was added at 5 °C to a stirred soln of 4-nitrobenzaldehyde oxime (7; 0.33 g, 2 mmol) in CH₂Cl₂ (20 mL), which prior to use was saturated with H₂O. After 20 min, TLC indicated complete disappearance of the substrate. The mixture was diluted by the addition of cold aq 5% NaOH (30 mL), followed by H₂O (40 mL). The organic layer was separated, washed with H₂O (40 mL), and dried (Na₂SO₄). Upon removal of the solvent under reduced pressure, the crude product was purified by column chromatography (silica gel); yield: 0.28 g (94%); mp 106 °C.

Applications Found in Science of Synthesis**Hetarenes by Oxidative Cyclization**

1,2,4-Triazoles by oxidation and cyclization of amidrazones

– Section 13.14.1.4.2.2 [Vol. **13** (2004), p 617]

Tetrahydropyridines by oxidative cyclization of ω-hydroxycarbamates

– Section 33.4.19.1.1.4.3 [Vol. **33** (2007), p 637]

Benzopyrans by oxidative cyclization of (hydroxymethyl)benzo-1,4-quinones

▲ – Section 37.4.3.3.1 [Vol. **37** (2008), p 570]

Carboxylic Acids by Oxidation of Primary Alcohols (CH₂OH → CO₂H)

Carboxylic acids by oxidation of alcohols

– Section 20.2.1.5.2.2 [Vol. **20a** (2006), p 196]

Aldehydes by Oxidation of Primary Alcohols (CH₂OH → CHO)

Aldehydes by oxidation of primary alcohols

▲ – Section 25.1.2.2.3 [Vol. **25** (2007), p 38]*

– Section 36.1.9.1 [Vol. **36** (2008), p 423]

– Section 36.11 [Vol. **36** (2008), p 1031]

– Section 43.4.1.4.4 [Vol. **43** (2008), p 249]

– Section 45.30.1.1.6.1 [Vol. **45b** (2010), p 1370]

▲ – Section 46.6.3.3 [Vol. **46** (2010), p 275]

▲ – Section 47.1.1.1.3.2.1 [Vol. **47a** (2010), p 34]

2-Haloaldehydes by oxidation of 2-halohydrins

– Section 25.4.1 [Vol. **25** (2007), p 463]

Ynals by oxidation of propargyl alcohols

▲ – Section 25.5.1.3.2 [Vol. **25** (2007), p 512]

▲ – Section 47.1.3.1.1.1.7 [Vol. **47b** (2010), p 619]

Arenecarbaldehydes by oxidation of arylmethanols

▲ – Section 25.6.2.2.4 [Vol. **25** (2007), p 539]

Aldehydes by oxidation of unsaturated allylic alcohols

– Section 25.7.1.1 [Vol. **25** (2007), p 711]

3-Hydroxyaldehydes by hydroboration/oxidation of allylic or propargylic alcohols

– Section 25.9.5.1.3 [Vol. **25** (2007), p 786]

Glycosidylaldehydes by oxidation of glycosidyl alcohols

– Section 37.7.3.1.3.8.2 [Vol. **37** (2008), p 822]

Allenyl aldehydes by oxidation of allenyl alcohols

– Section 44.2.5.4.1 [Vol. **44** (2008), p 320]

for references see p 6

Aldehydes or Ketones by Oxidative Deprotection of Acetals [C(XR)₂R → C(O)R]Aldehydes by oxidation of *S,S*-acetals

– Section 25.1.7.2.4.2 [Vol. 25 (2007), p 180]

Aldehydes or Ketones by Oxidative Cleavage of R₂C=X Compounds (X = N, P, S, etc.)**(R₂C=X → R₂C=O)**

Arenecarbaldehydes by cleavage of arenecarbaldehyde oximes

▲ – Section 25.6.4.4 [Vol. 25 (2007), p 580]

1,2-Diketones by hydrolysis of α -oximes

– Section 26.4.1.1.2.3 [Vol. 26 (2005), p 670]

Aldehydes or Ketones by Oxidation of Methylene Groups in RCH₃ or RCH₂R compounds**(R = carbon group) [CH₂R → C(O)R]** α,β -Dioxo amides from β -oxo amides

– Section 21.5.2.1.1.1 [Vol. 21 (2005), p 487]

Ketones by Oxidation of Secondary Alcohols (R₂CHOH → R₂C=O) α -Oxo acids by oxidation of α -amino or α -hydroxy acids

– Section 20.2.5.1.2.1 [Vol. 20a (2006), p 361]

 α -Oxo esters by oxidation of α -hydroxy esters

– Section 20.5.8.1.4.1 [Vol. 20b (2007), p 1098]

Ketones by oxidation of α -fluoro alcohols

▲ – Section 26.1.1.2.5.6 [Vol. 26 (2005), p 68]

Menthone by oxidation of menthol

▲ – Section 26.1.1.2.5.6 [Vol. 26 (2005), p 68]

 α,α -Difluoro ketones by oxidation of α,α -difluoro secondary alcohols

▲ – Section 26.5.1.1.2 [Vol. 26 (2005), p 746]

 α,α -Dialkoxy ketones by oxidation of α,α -dialkoxy secondary alcohols

▲ – Section 26.5.7.1.3.1 [Vol. 26 (2005), p 787]

Ketones by oxidation of α -hydroxy *N,O*-acetals

– Section 26.5.10.1.2 [Vol. 26 (2005), p 818]

 α,α -Disulfanyl ketones by oxidation of α -hydroxy-1,3-dithianes

– Section 26.5.11.1.3 [Vol. 26 (2005), p 833]

Propargyl ketones by oxidation of propargyl alcohols

– Section 26.7.1.1.2 [Vol. 26 (2005), p 975]

Ketones by oxidation of benzylic alcohols

– Section 26.8.1.1.2.2 [Vol. 26 (2005), p 992]

Ketones by oxidation of allylic alcohols

– Section 26.9.1.1.2 [Vol. 26 (2005), p 1048]

Oxonitriles by oxidation of hydroxynitriles

– Section 26.10.1.1.1 [Vol. 26 (2005), p 1124]

3-Oxo 2,2'-difluoro carboxamides by oxidation of 3-hydroxy 2,2'-difluoro carboxamides

– Section 26.10.2.1.1.1 [Vol. 26 (2005), p 1143]

1,2-Diketones by oxidation of α -hydroxy ketones

– Section 26.4.1.1.3.3 [Vol. 26 (2005), p 676]

– Section 26.10.3.1.1.1 [Vol. 26 (2005), p 1186]

Hydroxy ketones by oxidation of protected diols

– Section 26.11.2.1.1.1 [Vol. **26** (2005), p 1230]

Azido ketones by oxidation of azido alcohols

– Section 26.11.3.1.1.1 [Vol. **26** (2005), p 1255]

Ketones by oxidation of secondary alcohols

– Section 29.9.1.1.1.1.3 [Vol. **29** (2007), p 619]

– Section 29.9.1.1.1.1.6 [Vol. **29** (2007), p 624]

– Section 29.9.1.1.1.4.1 [Vol. **29** (2007), p 634]

– Section 29.6.1.2.6.2 [Vol. **29** (2007), p 707]

– Section 36.1.9.18 [Vol. **36** (2008), p 451]

– Section 38.8.3.1.3 [Vol. **38** (2010), p 351]

– Section 44.2.4.1.3 [Vol. **44** (2008), p 290]

– Section 46.6.6 [Vol. **46** (2010), p 332]

– Section 47.1.1.4.3.4 [Vol. **47a** (2010), p 185]

Allenyl ketones by oxidation of alkynyl alcohols

– Section 36.1.9.1 [Vol. **36** (2008), p 423]

Selenetan-3-ones by oxidation of selenetan-3-ols

– Section 39.25.1.1.3.1 [Vol. **39** (2008), p 1038]

Allenyl ketones by oxidation of allenyl alcohols

– Section 44.2.5.4.1 [Vol. **44** (2008), p 320]

Ketones by Oxidation of R₂CHX Compounds (X = OR, N, S, Hal, B, etc.) (R₂CHX → R₂C=O)**α,β-Dioxo amides from β-hydroxy-α-(phenylsulfanyl) amides**

– Section 21.5.2.1.1.3 [Vol. **21** (2005), p 490]

Quinones (also Quinone Imines, Quinomethanes) by Oxidation of Arenes (incl. heterosubstituted arenes) or Partially Unsaturated Cyclic Hydrocarbon Skeletons**Benzoquinones by oxidation of benzenes**

– Section 28.1.3.1.1.4 [Vol. **28** (2006), p 58]

Nitrogen-substituted benzo-1,4-quinones by oxidation of anilides

– Section 28.1.4.1.3 [Vol. **28** (2006), p 75]

Benzoquinone imines by oxidation of *ortho*-substituted anilides

– Section 28.9.1.1.1.6 [Vol. **28** (2006), p 644]

Benzo-1,2-quinone imines by oxidation of protected carbamates (cascade reaction to give polycycles)

– Section 28.9.1.2.1.1 [Vol. **28** (2006), p 670]

R–N=O Compounds or R–NO[•] Compounds by Oxidation of R–N–OH Compounds (N–OH → N–O[•] or N=O)**Acyl nitroso compounds by oxidation of unsubstituted *N*-hydroxy amides**

– Section 21.13.2 [Vol. **21** (2005), p 834]

Acyl nitroso compounds by oxidation of *N*-hydroxy amides

– Section 21.13.11.1.3 [Vol. **21** (2005), p 874]

Other Oxidations***O,O*-Acetals by oxidation of *S,S*-acetals**

– Section 29.6.1.2.6.2 [Vol. **29** (2007), p 351]

for references see p 6

References

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