SYNLETT Spotlight 14

2-Iodoxybenzoic Acid (IBX) and Dess-Martin Periodinane (DMP)

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Recently, 2-iodoxybenzoic acid (IBX) \(^{1b}\) \([-1\text{-hydroxy-1,2-benziodoxol-3(1}H\text{-one}]^{-1}\) and Dess-Martin Periodinane (DMP) \(^{2b}\) \([-1,1,1\text{-triacetoxy-1,1-dihydro-1,2-benziodoxol-3(1}H\text{-one}]^{-1}\) [CAUTION!]\(^{1b}\) as oxidants have added glory to a long tradition of hypervalent iodine chemistry. DMP has attracted particular attention as the reagent of choice for oxidation of alcohols to the carbonyl compounds; \(^{1b}\) Mildness, wide functional group tolerance, high yields without over-oxidation, and easy work-up procedure makes them versatile. IBX also oxidizes vic-diols without cleaving the glycol C-C bond, \(^{1b,3a}\) allows oxidative deamination, \(^{3b}\) oxidative ring closure of amino alcohols to diols without cleaving the glycol C-C bond, \(^{1a,3a}\) allows oxidative deoximation, \(^{3b}\) oxidative ring closure of amino alcohols to aminals; \(^{3c}\) Popularity of DMP as a preferred chemoselective oxidant in the plan of total synthesis is reflected by its current use in antifungal polycyclopropane compounds, \(^{4b}\) immunosuppressant sanglifehrin A, \(^{4b}\) potent antitumor agents saponin OSW-1 \(^4b\) and macrolide tedanolide. \(^{4b}\)

Preparation: These reagents can be readily prepared from 2-iodoxybenzoic acid \(^{1b}\) and used. Incidentally, IBX is a precursor of DMP.

Abstracts

A) Use of IBX in DMSO as a selective oxidant opens up new avenue for the conversion of 1,4-bisprimary or 1,4-primary-secondary diol to \(\gamma\)-lactol. This implies that the oxidation of the primary hydroxyl group in 3 is considerably faster than the secondary hydroxyl function of either 3 or 4, which could not previously be accomplished in one step.\(^6\)

B) The oxidation of an acetylenic diol, such as 2-butyne-1,4-diol 5 to the unstable dial, trapped in situ with phosphorous ylide, provides a convenient homologation method to prepare diyne 6, which has potential use in the synthesis of polycyclopropane natural products.\(^4d\)

C) An expeditious oxidative deoximation using DMP proceeds selectively in the presence of alcohols, O-methyl oximes, tosylhydrazones, acid sensitive groups and moieties in very high yields, in short time and under mild reaction conditions.\(^7\)

D) Remarkable tolerance of wide varieties of sensitive functional group during oxidation of alcohol 9 to aldehyde 10 highlights use of DMP as the reagent of choice in synthesis of complex multifunctional 18-membered antitumor macrolide, tedanolide.\(^4d\)

References


(2) IBX/DMP is reported to be explosive under excessive heating and also under impact by Plumb, J. B.; Harper, D. J. Chem. Eng. News 1990, July 16, 3.


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