SYNLETT

Spotlight 14

This feature focuses on a reagent chosen by a postgraduate, highlighting the uses and preparation of the reagent in current research

Recently, 2-iodoxybenzoic acid (IBX) and Dess-Martin Periodinane (DMP) have attracted particular attention as the reagent of choice for oxidation of alcohols to the carbonyl compounds. 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, allowing oxidative deamination to amino alcohols to aminals and one pot selective 5'-oxidation/olefination of 2'-deoxynucleosides. Popularity of DMP as a preferred chemoselective oxidant in the plan of total synthesis is reflected by its current use in antifungal polycyclopropane compounds, immunosuppressant sanglifehrin A, potent antitumor agents saponin OSW-1 and macrolide tedanolide.

Preparation: These reagents can be readily prepared from 2-iodoxybenzoic acid and Dess-Martin Periodinane, respectively, as shown.

Abstracts

A) Use of IBX in DMSO as a selective oxidant opens up new avenue for the conversion of 1,4-bisaryl or 1,4-aromatic-secondary diol to γ-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.

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 dienyne 6, which has potential use in the synthesis of polycyclopropane natural products.

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.

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.

References

2. (a) 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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