SYNLETT Spotlight 6

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

Ceric(IV) Ammonium Nitrate

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Among lanthanide reagents, ceric(IV) ammonium nitrate (CAN), $\text{Ce}^{\text{IV}}(\text{NH}_4)_2(\text{NO}_3)_6$, is the most notable oxidant and has been utilized extensively for a broad variety of oxidative transformations in organic chemistry. Recent studies have revealed protocols for mild conditions, fast conversions and convenient working-up procedures, and, in addition to the electron transfer capability, Lewis acid properties extend the scope of transformations. The oxidation of various functional groups and especially unsaturat-

ed systems with CAN is well established and was reviewed some years ago.¹ In transition metal mediated radical additions of CH-acidic compounds to olefins, CAN turned out to be superior to $\text{Mn}(\text{OAc})_3$ in many respects, especially when mild and non-acidic conditions are required.^{2,5b} Furthermore, the reagent offers selective methods of introducing and removing various protecting groups *via* electron transfer or Lewis acid catalysis.

Abstracts

A) Besides other functionalities, selective oxidation of benzylic positions is applicable using CAN. In pyrrole **1**, the methyl group in 2-position is exclusively converted to aldehyde **2** in 95% yield in an easy and convenient way.³

B) Radical functionalization of double bonds with CAN like azidonitration opens up an easy access to synthetically useful compounds. Introduction of the phenylseleno group in various alkenes, e.g. allyl alcohol **3**, can be simply achieved by oxidation of diphenyl diselenide.⁴

C) CAN promotes radical additions of CH-acidic compounds to olefins at low temperatures. Dimedone **5** was used for the synthesis of dihydrofuran **7** from cyclohexene **6** in a one-pot reaction in excellent yield.^{5a} Mild CAN-mediated additions of malonates to glycals allowed the first application of this methodology in carbohydrate chemistry.^{5b}

D) Selective removal of several protecting groups like *t*-butoxycarbonyl, tetrahydropyranyl, trityl, 4-methoxyphenyl and dithioacetal proceeds smoothly with CAN. Amino acids can be boc-deprotected with catalytic amounts of CAN,^{6a} while removal of the *N*-(4-methoxyphenyl) protection in lactam **8** requires 3 equivalents of CAN due to electron transfer mechanism.^{6b}

References

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