

SYNLETT Spotlight 191

Tetra-*N*-propylammonium Perruthenate (TPAP)

Compiled by Kuladip Sarma



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

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Introduction

The crystalline, non-volatile and air-stable material tetra-*N*-propylammonium perruthenate (TPAP) is an important commercial catalytic oxidant, mostly used in natural products synthesis due to its ease of use, excellent performance and versatility.¹ In 1987, Ley and co-workers first introduced TPAP as a readily soluble, nonvolatile, air-stable oxidant for alcohols.^{1,2} It behaves as an overall three-electron oxidant for a wide range of multifunctional species. The full potential of TPAP was revealed when its catalytic behavior with *N*-methylmorpholine *N*-oxide (NMO) as terminal oxidant was uncovered.³ It is stable at room temperature and may be stored for long periods under low-temperature condition. The TPAP–O₂ oxidizing system meets several principles of Green Chemistry⁴ and raises the prospect for industrial oxidations because of (i) its applicability in oxidation of a wide range of alcohols, (ii) its potential as terminal oxidant with air, (iii) the simple sep-

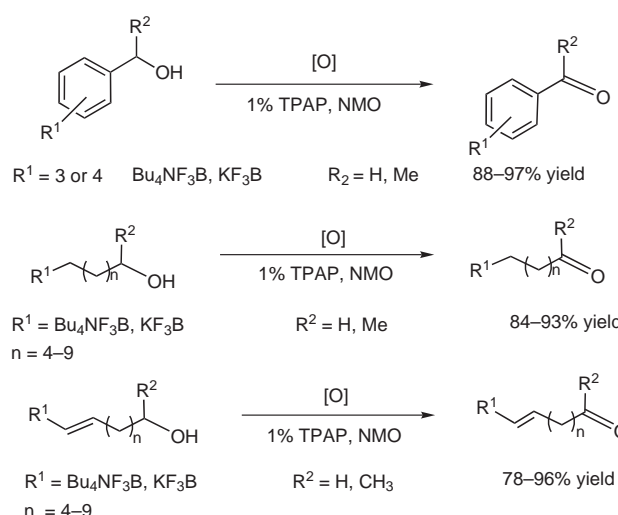
aration of the catalyst from the products, and (iv) its chemoselectivity and tolerance against many functional groups. The catalyst is inert towards double bonds, polyenes, enones, halides, cyclopropanes, epoxides, acetals, esters, amides, lactones, amines, peroxides, and catechols. Clean oxidation of alcohols occurs with TPAP in systems where competitive β -elimination poses a problem with other oxidants.⁵ In addition to that, oxidation with TPAP can be achieved without racemization of the adjacent stereogenic α -centers and without double-bond migration.⁴

Preparation

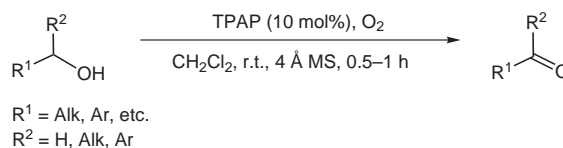
The preparation of TPAP is a one-pot synthesis in which RuCl₃·*n*H₂O is oxidized to [RuO₄][−] with excess sodium bromate (NaBrO₃) in aqueous sodium carbonate solution. Subsequent addition of (*n*-Pr₄N)OH gives TPAP as dark green crystals, which are further purified.⁶

Abstracts

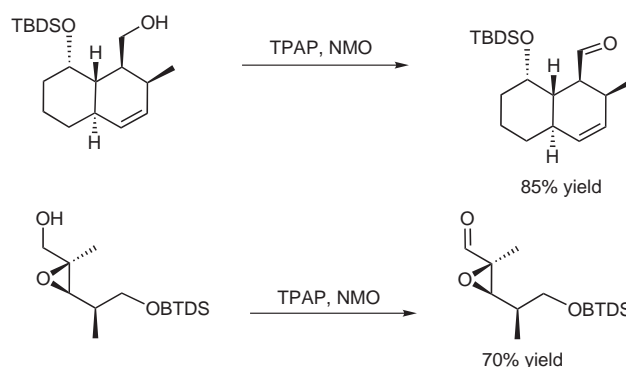
(A) Primary and secondary aliphatic and aromatic alcohols are efficiently oxidized to the corresponding carbonyl compounds in the presence of a tetrabutylammonium trifluoroborate group or potassium organotrifluoroborate. Alkyl, alkenyl, and aryl trifluoroborates were tolerated in this process, without cleavage of the carbon–boron bond.⁷



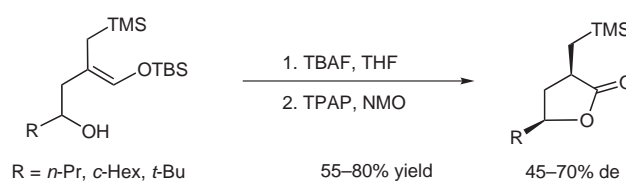
(B) TPAP is capable of oxidizing primary and secondary alcohols to the corresponding aldehydes and ketones under very mild aerobic conditions in 80–90% yield.⁸



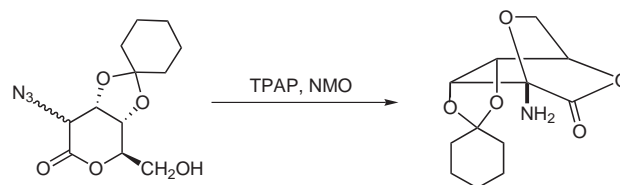
(C) In the oxidation of the primary hydroxyl functionality in decaline by the TPAP/NMO system, the double bond and the silyl-protected hydroxyl functionality present in the same molecule are not affected. Similarly, the open-chain alcohol is oxidized chemoselectively in the presence of an epoxide moiety.⁹



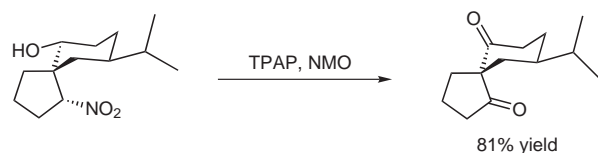
(D) TPAP with NMO in the presence of TBAF promotes the intramolecular Sakurai cyclization of an ene adduct to afford the corresponding lactone, the key intermediate in the synthesis of amphidinol.¹⁰



(E) TPAP/NMO shows an unanticipated transformation of an α -azido lactone to a bicyclic amine in the course of the synthesis of 5-epihydantocidin from D-ribose.¹¹



(F) Fukumoto and co-workers used the TPAP/NMO system in the Nef reaction to transform the NO_2 group and the secondary hydroxyl group to ketone functionalities in the synthesis of (\pm)-spirojatamol and (\pm)-erythrodiene.¹²



References

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