

Polymer supported perruthenate (PSP): a new oxidant for clean organic synthesis

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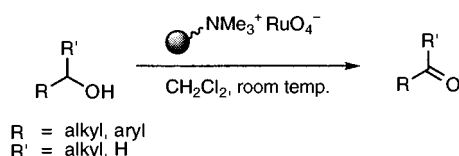
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A polymer supported perruthenate reagent has been prepared and used in the conversion of primary and secondary alcohols to aldehydes and ketones, respectively, affording pure products without the need for conventional work-up procedures.

There is a need to develop new methods for organic synthesis which afford products free from contaminating by-products or excess reagents, but do not require the need for time consuming work-up and purification methods. Numerous applications can be envisaged for these methods in catalytic processes, atom efficient reactions, clean technology and combinatorial chemistry.

Some years ago we developed the use of tetra-*n*-propylammonium perruthenate (TPAP) as a mild, catalytic, room temperature oxidant for organic synthesis.¹ This reagent has become a popular oxidant especially for the conversion of primary and secondary alcohols to aldehydes and ketones.² Here we report on the preparation and use of a polymer bound³ version of this reagent.

The polymer supported perruthenate (PSP) reagent was obtained by adding Amberlyst anion exchange resin (IR 27) containing quaternary ammonium groups,⁴ to an aqueous solution of powdered potassium perruthenate⁵ and exposing the mixture to ultrasound for 5 min until the solution became clear. The PSP reagent resin was then filtered, washed with water and dried. Approximately 20 mg (1 mmol) of potassium perruthenate was used per gram of Amberlyst resin, although optimal loadings on this particular support system have not been investigated. This PSP reagent was then used in a series of alcohol to carbonyl group oxidation reactions in dichloromethane as solvent,[†] sometimes in the presence of 4 Å molecular sieves to act as a dehydrating agent² when *N*-methylmorpholine *N*-oxide (NMO) or trimethylamine *N*-oxide (TMAO) were used as co-oxidants in the catalytic cycle, and sometimes without these additives when the reagent was used stoichiometrically (Scheme 1, Table 1).



Scheme 1

In the initial experiments the alcohol (0.5 mmol) was added to a mixture of the PSP reagent (20 mol%), molecular sieves (4 Å) and the co-oxidant ‡ (NMO or TMAO, 1.0–1.5 equiv.) in

dichloromethane (5 ml) at room temperature.§ Upon consumption of the starting material (indicated by TLC) the reaction was worked-up by filtration followed by evaporation *in vacuo*. The yields of the corresponding carbonyl compounds were then estimated by gas chromatography or NMR spectroscopy. Most of these reactions were complete after a period of 16 h in good to excellent yields and, where comparisons could be made with other polymer supported reagents,⁶ the PSP-reagent was usually superior. When the reactions were performed in the absence of the 4 Å molecular sieves (entries 5b, 5c, 10b, 10c) they proceeded more slowly (36–48 h), but with similarly high yields. Again the only products observed were the expected aldehydes or ketones and, in the cases where the reaction had not gone to completion, the starting material was the only by-product. To further diminish the amount of side-products, oxidations were performed with only one equivalent of the co-oxidant which meant that the amine by-products *N*-methylmorpholine or the highly volatile trimethylamine were removed on evaporation to give the carbonyl product uncontaminated by any other impurity (entries 2, 3, 7a, 7b). Also, when the alcohol was reacted with stoichiometric amounts of the PSP reagent (1.5 equiv., entries 5b, 6b, 10c), a high yield of the carbonyl compound was obtained after 36–48 h without the need for added co-oxidant or molecular sieves.⁷ The yield in these processes could be further increased by using a ten-fold excess of PSP-reagent (entries 5c, 6c). The use of stoichiometric PSP-reagent therefore constitutes a clean technology process for the preparation of carbonyl compounds from alcohols.

The filtered spent polymer reagent can be reused in combination with a co-oxidant. Oxidation of benzyl alcohol in combination with NMO thus afforded only a minor decrease in yields: >95% (first run), 88% (second run) and 72% (third run). Alternatively, the spent PSP-reagent can be reactivated by external treatment with NMO and exploited in further oxidation reactions. This recycling process is obviously crucial in our need to establish efficient new catalytic reagents for organic synthesis.

Further applications of the PSP system will be reported in due course.

Acknowledgements




































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† Acetonitrile can be used as solvent in place of dichloromethane.

‡ No difference in rate or yield was observed between NMO and TMAO.

§ Neither ultrasound nor boiling the reaction mixture in dichloromethane resulted in a significant change in reaction rate or yield.

Table 1 Oxidations of alcohols to carbonyl compounds using PSP-reagent in CH₂Cl₂ at room temperature

Entry	Alcohol	Product	t/h	Yield (%)	Co-oxidant	Molecular sieves (4 Å)
1a			16	50 ^b	NMO (1.5 equiv.)	yes
1b			48	64	TMAO (1.5 equiv.)	yes
2			18	60	TMAO (1.0 equiv.)	yes
3	C ₈ H ₁₇ -OH		16	54	NMO (1.0 equiv.)	yes
4			16	62	NMO (1.5 equiv.)	yes
5a			16	91	NMO (1.5 equiv.)	yes
5b			36	83	none ^d	no
5c			48	>95	none ^e	no
6a			16	>95	NMO (1.5 equiv.)	yes
6b			36	85	none ^d	no
6c			48	>95	none ^e	no
7a			14	>95	TMAO (1.0 equiv.)	yes
7b			16	>95	NMO (1.0 equiv.)	yes
8			26	77	NMO (1.5 equiv.)	yes
9^c			16	75	NMO (1.5 equiv.)	yes
10a			16	>95	NMO (1.5 equiv.)	yes
10b			36	>95	NMO (1.5 equiv.)	no
10c			48	85	none ^d	no

^a Yields were determined by NMR spectroscopy unless stated otherwise. ^b Yield determined by gas chromatography. ^c The product was obtained as a *cis-trans* mixture. ^d 1.5 equiv. of the PSP-reagent were used. ^e The PSP-reagent was used in 10-fold excess.

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