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Sodium Percarbonate as an Oxygen Source for MTO Catalyzed Epoxidations

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Since its introduction by the Herrmann group in 1991,[1] the singularly efficient epoxidation of olefins using methyltrioxorhenium (MTO) in the presence of hydrogen peroxide has elicited much interest. MTO is of particular benefit for the epoxidation of notoriously unreactive monosubstituted olefins.[2] One of the initial difficulties with the MTO−H_2O_2 reaction was decomposition of acid-sensitive epoxides exposed to the system's inherent acidity. This difficulty was addressed by the introduction of a substoichiometric amount of pyridine[3] into the reaction mixture, which served not only to stabilize acid-susceptible epoxides, but also to enhance the rate of epoxidation. Subsequently, it was reported that either pyrazole (pz)[4] or 3-cyanopyridine[2,5] was superior as an accelerant.

In the MTO epoxidation, aqueous hydrogen peroxide is typically added dropwise to a dichloromethane solution of the olefin, accelerant, and MTO.[3] Sources of the peroxide other than aqueous hydrogen peroxide, for example, urea−hydrogen peroxide adduct[6] or bis(trimethylsilyl)peroxide,[7] have been successfully applied to the MTO epoxidation. Sodium percarbonate (SPC), together with sodium perborate (SPB), represent two of the most powerful, yet underused, oxidants available.[8] SPC and SPB are particularly advantageous owing to their ease of handling and storage. Epoxidation of α,*β*-unsaturated ketones has been achieved using either SPC[9] or SPB.[10] In addition, there have been reports of epoxidation by SPB in the presence of acetic anhydride[11] or acetic acid,[12] or by SPC in the presence of trifluoroacetic anhydride.[13] SPC has been used in chromium-catalyzed oxidation in organic solvents, although this method requires a phase-transfer catalyst.[14]

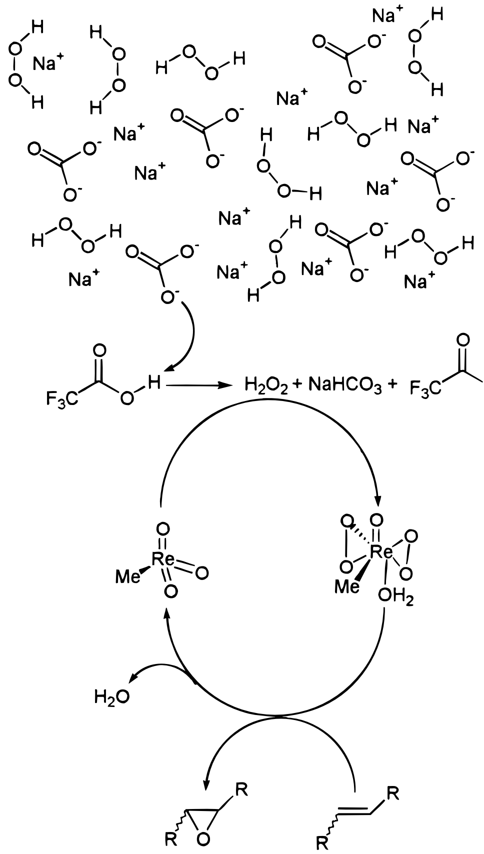
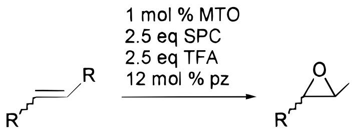


Figure 1. Mode of activation of MTO by SPC/TFA for epoxidation of olefins.

Scheme 1



A means to combine the tremendous epoxidizing power of MTO with the mildness of either SPB or SPC was sought. SPB is known to exist as a hydrate of the disodium salt of a 1,4-diboratetroxane having discrete peroxo−boron bonds.[15] An X-ray study of the crystal structure of SPC has revealed that H_2O_2 is found whole, encapsulated by hydrogen bonds in a Na_2CO_3 matrix.[16] SPC is known to decompose both in water[17] and in organic solvents[18] to release H_2O_2, albeit very slowly. It was hypothesized that the use of an acid should aid in the release of H_2O_2 from both SPB and SPC. Upon

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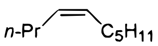
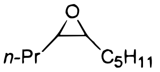
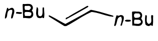
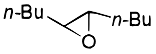
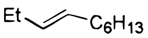
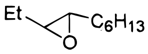
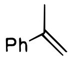
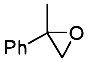
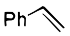
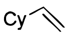
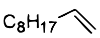
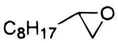
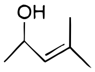
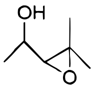
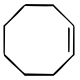
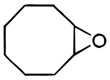
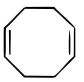
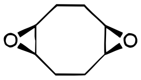
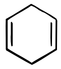
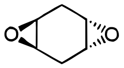
Table 1. Examples of SPC-MTO epoxidation of olefins

Entry	Starting Material	Product[a]	Time (h)	Yield (%)[d]
1			6[b]	96
2			6[b]	85
3			6[b]	78
4			3[b]	91
5			12[c]	96
6			15[c]	76
7			15[c]	94
8			6[b]	91
9			2[b]	94
10			16[b]	95
11			16[c]	92

[a] Products were identified by ^{1}H NMR and ^{13}C NMR spectroscopy. Reactions were performed on a 10 mmole scale. [b] THF as solvent. [c] CH_2Cl_2 as solvent. [d] Yields are isolated yields.

addition of either acetic or trifluoroacetic acid to a mixture of SPC, pyrazole, cyclooctene, and MTO in THF a vibrant yellow color—characteristic of the peroxo-activated MTO species—was noted. After being stirred for 2 h, the TFA/SPC reaction resulted in complete conversion of the olefin to the epoxide, while the yield for the AcOH reaction was markedly lower. No reaction was observed when SPB was used as the oxygen source, nor was the distinct yellow color observed. In the absence of MTO no epoxide was formed, consistent with the inability of SPC to form peracids directly from organic acids.[8a] Inorganic acids, namely 4 N HCl in 1,4-dioxane or concentrated H_2SO_4 were tried in the reaction; no epoxide formation was noted.

A combination of 2.5 equiv of SPC, 2.5 equiv of TFA, 1 equiv of olefin, 12 mol % pyrazole, and 1 mol % MTO in either THF or CH_2Cl_2 was found to effectively convert a wide range of olefins to epoxides. The overall process is depicted in Scheme 1. Results are sumarized in Table 1. Using less than 2.5 equiv of SPC/TFA resulted in lower yields. Further, it was noted that addition of the MTO in two portions, the second addition approximately halfway through the reaction, improved the yield of epoxide.

As a peroxide source SPC in concert with TFA has some advantages over aqueous hydrogen peroxide. The slow trans-phasic interaction between SPC and the acid ensures the slow release of H_2O_2. In contrast to the aqueous H_2O_2 reaction no external cooling is required. Monitoring the pH of the reaction mixture[19] revealed that while the pH was initially low, ca. 2.5, it rose to a constant value of 10.5 after 15 min.

A disadvantage of the present route is the requirement that TFA be used as the acid. As the acid neutralizes the SPC, it chips away at the carbonate sarcophagus in which the H_2O_2 is held (Figure 1). Thus, liberation of H_2O_2 is accompanied by formation of $NaHCO_3$ together with carbonic acid (CO_2 evolution is observed) and F_3COONa. The sodium salts produced in this way will be negligibly soluble in organic solvents. Epoxidation of α-methyl styrene was attempted using AcOH in place of TFA. While the characteristic yellow color of the activated rhenium species was indeed evident, at best 70% conversion of the olefin was observed. Of note is that the reaction with AcOH, either in CH_2Cl_2 or in THF, was much more difficult to stir, suggesting that the inorganic salts produced during the course of the reaction were

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(19) Accurate monitoring of pH for nonaqueous systems is known to be fraught with difficulties; see, for example: Gold, V.; Grist, S. *J. Chem. Soc., Perkin Trans. 2* **1972**, 89. In the present study, 200 μL aliquots were removed at 5 min intervals and diluted into 5 mL of H_2O and the pH measured.

interfering with the release of H_2O_2; a fairly common problem with solid phase reagents when the desired reaction with a component in solution produces a new solid phase which effectively covers the reactive surface, precluding further reaction. Fortuitously, this does not occur when $F_3COO^{-+}Na$ is the new salt produced at the surface.

Of note in Table 1 is the ready epoxide formation with monosubstituted olefins (entries 6 and 7). For terminal olefins the use of CH_2Cl_2 as solvent afforded better yields. Both cis and trans olefins are readily epoxidized.

A novel means to harness the oxidizing power of sodium percarbonate, a so-called "solid form" of H_2O_2 has been demonstrated.[16] The added safety and ease of handling using SPC, commonly employed as an additive in household washing detergent and toothpaste, in place of aqueous hydrogen peroxide, together with the slow release of the H_2O_2 due to the trans-phasic nature of its release from SPC render this a useful method.

Experimental Section

All compounds in Table 1 have been previously isolated and characterized.[3,20]

Typical Procedure. To a solution of *cis*-4-decene (1.8 mL, 10 mmol) in THF (7 mL) were added SPC (3.9 g, 25 mmol), pyrazole (82 mg, 1.2 mmol), and MTO (12.5 mg, 0.05 mmol). The mixture was stirred vigorously as TFA (1.9 mL, 25 mmol) was added dropwise over the course of 2 min. After addition of a few drops TFA, a vibrant yellow color was noted. After the mixture was stirred for an additional 3 h, a further aliquot of MTO (12.5 mg, 0.05 mmol) was added, and stirring was continued for 3 h. The mixture was introduced into a separatory funnel together with CH_2Cl_2 and water. The organic phase was removed, and the aqueous phase was further extracted with CH_2Cl_2. To the combined organic extracts was added a trace of MnO_2 to decompose any remaining peroxide. The solution was dried over $MgSO_4$ and filtered, and the solvent was removed under vacuum. Purification was achieved by Kugelrohr distillation to afford the product as a clear oil (1.49 g, 96%). For diolefins, twice the amounts of MTO, SPC, THF, and pyrazole were employed.

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