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A NEW CLASS OF EPOXIDATION REAGENTS

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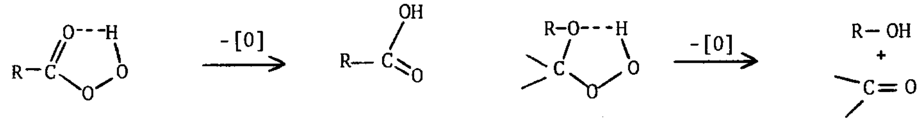
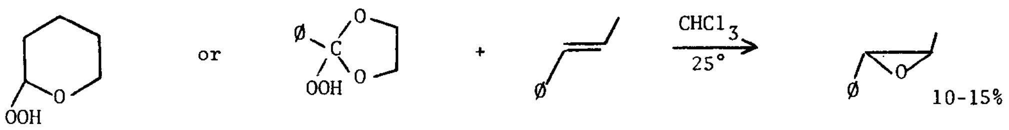
The structural similarities between peroxy acids **A** and α-hydroperoxy ethers **B** suggest that the latter may also be capable of oxygen transfer reactions as shown.



A **B**

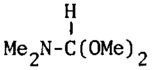


1 **2** **3** **4**

We find that either **1**[1] or **2**[2] indeed epoxidize the unexceptional olefin trans-β-methyl styrene, albeit in low yield. Similar results attended in situ generation of structures related to **B**. Thus the epoxide **4** was obtained in 10-40% yields when a solution of **3** in the orthoesters **5** - **8** or the ketal **9** was treated with 90% H_2O_2. The DMF acetal **10** suffered oxidation to **11** under these conditions.

$R\text{-}C(OEt)_3$
5 R = OEt
6 R = H
7 R = CH_3
8 R = ϕ

$Me_2C(OMe)_2$
9



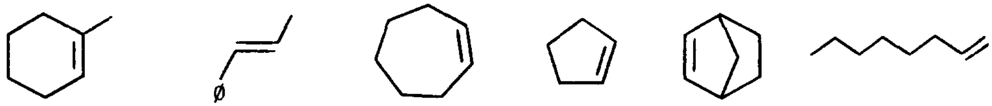
$Me_2N\text{-}\overset{H}{C}(OMe)_2$

10

$Me_2N\text{-}CO_2Me$
11

Since singlet molecular oxygen ($^1O_2$) is frequently a product of dehydrating agent - H_2O_2 combinations[3] we tested for its presence in these systems. When solutions of **5** - **9** and 9,10 diphenyl anthracene (DPA) in THF were treated with 90% H_2O_2, DPA 9,10 endoperoxide (a product characteristic of $^1O_2$)[4] was obtained only with **5**.

The most promising of these epoxidation reagents, ethyl orthoacetate **7**, was examined to optimize epoxide yields. The order of reagent combination had little effect on the yield of epoxide ($\sim$ 40%) but the presence of ethanol slows the epoxidation rate. Best results were obtained when the olefin (2 mmol) was dissolved in **7** (2 ml) and .5 ml 90% H_2O_2 was added. After 4 hrs. at 25° the reaction solution was diluted with CH_2Cl_2, washed with H_2O, dried and, if possible, concentrated. Then another portion of **7** and H_2O_2 are added. Yields of epoxide obtained by this method are shown below.



epoxide yield (gc/nmr) 99% 85% 68% 95% 81% 15%

In addition to the mild epoxidation conditions that these new systems provide, the possibility exists of generating optically active derivatives of **8** from appropriate carbonyl precursors. Our study of this approach to asymmetric epoxidation is underway.

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