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IRON(II) CATALYZED PERSULFATE OXIDATION OF ALKENES TO VICINAL DIACETATES

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Abstract: Mono- and disubstituted alkenes are converted to trans-vicinal diacetates by heating with an acetic acid solution of ammonium persulfate and a ferrous sulfate catalyst.

Persulfate, $S_2O_8^{2-}$, oxidation of aromatic compounds has been investigated by transition metal catalyzed[1], thermal[2], and radiolysis methods[3,4]. For the most part these studies have focused on the mechanistic aspects of this reaction and less so on synthetic applications. These studies have shown that single electron oxidation of the aromatic π-system to a radical cation by sulfate radical anion, $SO_4^{\cdot-}$, or a highly oxidized metal ion, is the first step toward ring hydroxylation or benzylic substitution via proton loss. The rate of aromatic oxidation has been found to correlate well with σ^+ values and gave a ρ value of -1.9[5]. If the ionization potential of the aromatic ring is indicative of which other π-systems should react, one would expect alkenes to be oxidized by metal ion/persulfate systems[6]. One example of persulfate oxidation of alkenes has been reported[7], along with another which proposed competitive oxidation of alkenes and alcohols[8].

We have investigated the oxidation of alkenes with several metal catalyzed persulfate systems and report here our results[9,10]. In connection with another project we needed to investigate the chemistry of monomeric manganese(III) species. One approach was to decompose persulfate with a manganese(II) salt which would result in sulfate radical anion and manganese(III) formation. Thus 1-octene was reacted with ammonium persulfate and 5 mole % manganese(II) acetate in refluxing acetic acid. The synthetic outcome in eq. 1 was encouraging, and further variations in the catalyst used and the amount of persulfate oxidant employed are summarized in Table 1.

The results in eq. 1 show a modest production of 1,2-diacetates with lesser amounts of the two possible monoacetates. A control reaction run without catalyst produced the same products,

$$C_8H_{17}CH{=}CH_2 + (NH_4)_2S_2O_8 \xrightarrow{HOAc} C_8H_{17}\underset{\displaystyle AcO\ OAc}{CHCH_2} + C_8H_{17}\underset{\displaystyle OAc}{CH_2CH_2} + C_8H_{17}\underset{\displaystyle OAc}{CHCH_3} \qquad \text{eq. 1}$$

$Mn(OAc)_2$ catalyst	43%	4%	8%
no catalyst	10%	6%	21%

however, the reaction mixture was much more complex and the diacetate was only a minor constituent. Varying the catalyst and amount of oxidant (Table 1) led to the use of excess oxidant (4.4 eq.) with 5 mole % ferrous sulfate catalyst to maximize the yield of 1,2-diacetate. While 5 mole % catalyst was sufficient for small scale reactions (1.5 mmole olefin), 25 mole % of this inexpensive catalyst proved beneficial for larger scale (40 mmole olefin) preparations. Treating the hot reaction mixture with acetic anhydride was also found to convert the small amounts of 1,2-hydroxyacetates which were formed to the corresponding diacetate.

Table 1

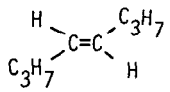
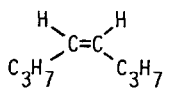
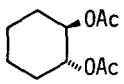
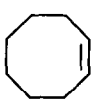
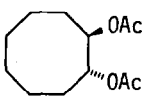
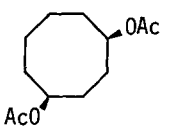
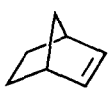
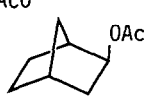
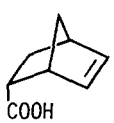
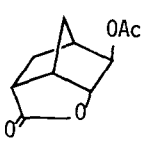
Entry	Catalyst	Eq. Cat.	Eq. $S_2O_8^{2-}$	Yield, %[a] Diacetate	Monoacetates
1	$Co(OAc)_2$	.05	2.2	17	14
2	AgOAc	.01	2.2	21	3
3	$CuSO_4$	.10	4.4	31	2
4	$Mn(OAc)_2$	.05	2.2	43	12
5	$FeSO_4$	.05	2.2	51	18
6	$FeSO_4$	.05	4.4	95	2
7	$FeSO_4$	.05	5.0	69	2
8	$FeSO_4$	.05	8.0	15	0
9	$FeSO_4$	.01	4.4	57	1
10	$FeSO_4$	1.0	6.0	61	2

[a]Yield was determined by GC with an internal standard and appropriate response factors. Each reaction used a 0.21 M solution of 1-decene in refluxing acetic acid with the catalyst and oxidant amounts listed.

Typical preparative results are shown in Table 2. Terminal alkenes react cleanly in refluxing acetic acid to give diacetates. Cyclohexene (entry 5) reacted in a stereospecific (> 99%) fashion to give the trans-1,2-diacetate. Trans-4-octene (entry 3) likewise was highly stereoselective (> 98%), however, cis-4-octene (entry 4) showed a mixture of d,ℓ : meso diacetates. This is because the original alkene geometry is not rigorously maintained during the reaction[11]. Cyclooctene (entry 6) displayed high trans-stereoselectivity in the 1,2-diacetate produced, however a transannular 1,4-adduct was also seen. Norbornene (entry 7) was the only example studied which gave a monoacetate, although this was shown not to be a result of simple acid catalyzed addition of acetic acid to the double bond. Entry 8 showed the acceptability of intramolecular carboxylic acid cyclization with this oxidation procedure.

Monosubstituted alkenes react best at reflux temperature whereas disubstituted alkenes react more efficiently at lower temperatures. The material balance is primarily made up of acidic material, which is the diacid corresponding to cleavage between the olefinic carbons, and very non-polar telomeric products. This new one-pot procedure compares well with other common and less common[12] preparations of vicinal diacetates and has the advantage of the inexpensive reagents required. Trisubstituted alkenes gave complex mixtures upon attempted oxidation. These latter results as well as a mechanistic explanation of this process will be forthcoming.

Table 2

Entry	Alkene	Diacetate	Temp[a]	Yield, %[b]
1	$C_6H_{13}CH{=}CH_2$	$C_6H_{13}CH(OAc)CH_2(OAc)$	116°	79
2	$C_8H_{17}CH{=}CH_2$	$C_8H_{17}CH(OAc)CH_2(OAc)$	116°	76
3		$C_3H_3CH(OAc)CH(OAc)C_3H_7$ (meso)	80°	76
4		$C_3H_7CH(OAc)CH(OAc)C_3H_7$ (meso : d,ℓ; 32 : 68)	90°	49
5			80°	79
6			50°	16
				12
7			70°	61
8			80°	32

[a]Temperature at which the oxidation was performed. [b]Yield is based on chromatographed, distilled or recrystallized products. Products were identified by NMR, IR, MS and GC comparison with authentic samples or literature data. [c]3-Cyclooctenyl acetate (9%) and 1,8-octanedioic acid (35%) were also isolated.

Typical procedure: The alkene (0.04 mole), ammonium persulfate (0.10 mole), and ferrous sulfate heptahydrate (0.01 mole) were heated in acetic acid (125 mL) for 2-4 hours. Acetic anhydride (2 mL) was added to the reaction and the mixture allowed to cool to room temperature. The reaction mixture was diluted with water (500 mL) and extracted with ether or petroleum ether (3x). The combined organic layers were extracted with water and saturated sodium bicarbonate solution, dried, and evaporated. Products were purified by recrystallization, distillation or chromatography.

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