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ALKENE OXIDATION BY AN IRON(II)/PERSULFATE/ACETIC ACID SYSTEM

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Abstract - Mono- and disubstituted alkenes were converted to trans-vicinal diacetates by heating with an iron(II)/persulfate/acetic acid system. The synthetic utility and limitations were identified. A mechanism for the transformation is proposed which involves an initial addition of sulfate radical anion to the alkene followed by solvolysis, addition, hydrolysis, and acetylation.

The persulfate ion, $S_2O_8^{2-}$, is an inexpensive and easily handled oxidant which is seeing continued[2] and growing usage.[3] It is an extremely powerful oxidant (E^o = 2.01 V, aq); however, the high activation energy barrier (approximately 30 kcal mol^{-1}) to uncatalyzed homolytic decomposition renders persulfate less useful at reasonable temperatures. Transition metal catalysts greatly facilitate the decomposition of aqueous persulfate solutions. This allows shorter reaction times, but also complicates the mechanistic possibilities because of the high valent metal species which is produced in addition to a reactive sulfate radical anion, eq. 1.

$$S_2O_8^{2-} + M^{n+} \longrightarrow M^{n+1} + SO_4^{\overline{\cdot}} + SO_4^{2-}$$

eq. 1

The catalyzed reaction of persulfate ion with unsaturated organic compounds has been studied by many laboratories. However, most of these efforts have focused on aromatic substrates[4] because of their relationship to the Elbs[5] reaction and reactions of Fenton's reagent, H_2O_2/Fe(II)[6]. Studies of persulfate reaction with alkenes have generally been limited to identifying the intermediate produced by reaction of the sulfate radical anion with an alkene.[7-9] The general process observed in these cases has been addition to form a β-sulfatoalkyl radical. Only one other synthetic example of persulfate oxidation of alkenes has been reported[10] besides our earlier communication of this work[11], and one report has proposed a competitive oxidation of alkenes and alcohols.[12] Polymerization of vinyl monomers can also be catalyzed by persulfate.[13]

We initiated our study of alkene oxidation by heating 1-decene to reflux in acetic acid with a transition metal salt and ammonium persulfate. Two monoacetates and the 1,2-diacetate were the major products formed. The results with several different transition metal salts are summarized in Table 1. All the conditions tested, along with a control reaction with no transition metal species, gave the same three products as the major components in the product mixture. The variation in performance of the additive roughly increased as the redox potential of the oxidized metal ion decreased. Thus the strong oxidants Co(III) and Ag(II) gave poor yields of diacetates, while a weak oxidant, Fe(III), was the best. Copper(II), a relatively mild oxidant, did not fare as well as anticipated on this scale. However, it is the most efficient of all these metal ions at oxidizing alkyl radicals, and so may be intercepting a radical intermediate at some stage and thereby preventing efficient formation of diacetates. It was interesting that when run with no additive the reaction still gave the same mix of products. In this case though, the monoacetates outweighed the diacetates.

1-Decene, in addition to the diacetate product, produced both primary and secondary monoacetates with the secondary predominating. Differing ratios of monoacetates were obtained with the various metal ion reactions (Fig. 1). It was shown independently that the present reaction conditions do produce the secondary monoacetate by acid catalyzed Markovnikov addition of acetic acid across the double bond. The primary monoacetate, on the other hand, was produced via a reaction manifold which required persulfate. The results in Fig. 1 indicated that a system containing 5 mole % Fe(II) gave the least amount of primary acetate.

Further testing of the ferrous sulfate addend was done by varying the amount of the addend as well as persulfate in a

Table 1. Various Transition Metal Catalysts Employed in Persulfate Oxidation of 1-Decene

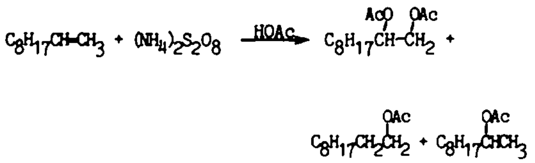
Entry	Catalyst	Mole Equiv. Catalyst	Mole Equiv. Persulfate	Yield, %[a] Diacetate	Yield, %[a] Monoacetates
1	$Co(OAc)_2$	0.05	1.1	17	14
2	AgOAc	0.01	1.1	21	3
3	$CuSO_4$	0.10	2.2	31	2
4	$Mn(OAc)_2$	0.05	1.1	43	12
5	$FeSO_4$	0.05	1.1	51	18
6	None	—	1.1	10	27

[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.

Table 2. Optimization of Diacetate Yield with Iron(II) Catalyst

Entry	Catalyst	Mole Equiv. Catalyst	Mole Equiv. Persulfate	Yield, %[a] Diacetate	Yield, %[a] Monoacetate
1	$FeSO_4$	0.05	1.1	51	18
2	$FeSO_4$	0.05	2.2	95	2
3	$FeSO_4$	0.05	2.5	69	2
4	$FeSO_4$	0.05	4.0	15	0
5	$FeSO_4$	0.01	2.2	57	1
6	$FeSO_4$	1.00	3.0	61	2

[a] See footnote a from Table 1.



$$C_8H_{17}CH{=}CH_3 + (NH_4)_2S_2O_8 \xrightarrow{HOAc} C_8H_{17}\overset{AcO}{CH}-\overset{OAc}{CH_2} + C_8H_{17}CH_2\overset{OAc}{CH_2} + C_8H_{17}\overset{OAc}{CH}CH_3$$

no catalyst	1	:	3.5
Cu(II) catalyst	1	:	1
Ag(I) catalyst	1	:	2
Mn(II) catalyst	1	:	2
Co(II) catalyst	1	:	3
Fe(II) catalyst, 1%	1	:	4
Fe(II) catalyst, 5%	1	:	>20

Fig. 1 **Monoacetate Formation Ratio**

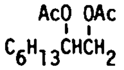
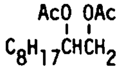
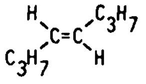
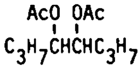
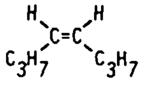
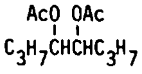
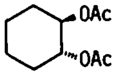
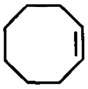
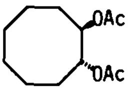
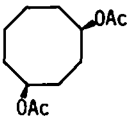
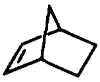
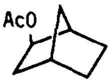
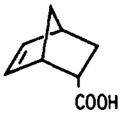
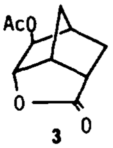
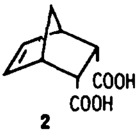
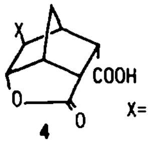
series of small scale (1-2 mmole) experiments (Table 2). Entries 1-4 show that the diacetate yield maximized at 2.2 mole equiv. of persulfate. The yield dropped when the Fe(II) was reduced from 5 mole % to 1 mole % (entries 2, 5), but stayed relatively unchanged when the amount was increased to 100 mole % (entries 3, 6). When the reaction was scaled up to 40 mmole of alkene, it proved useful to increase the amount of Fe(II) up to 25 mole %.

Small amounts of hydroxyacetates were found to be produced in the reaction. These could be converted to diacetates by treating the hot reaction mixture with acetic anhydride and allowing the mixture to cool before workup. This simplified the isolation of the 1,2-diacetate product, however, it should be noted that hydroxyacetates had been produced in the reaction.

The synthetic results using the optimized conditions above are listed in Table 3. Entries include mono- and disubstituted alkenes. Trisubstituted alkenes will be discussed below. The yields are modest to good, and compare favorably with other one-step preparations of 1,2-diacetates from alkenes. In particular most metal oxidant (e.g. $Pb(OAc)_4$,[14] $Tl(OAc)_3$,[15] $NaBiO_3$,[16] Re_2O_7,[17] Te(IV)[18] routes are fraught with side reactions and formation of a multitude of products.

The stereochemistry of 1,2-diacetate formation can be discerned from entries 3-6. *Trans*-4-octene, cyclohexene,

Table 3. Preparation of 1,2-Diacetates from Alkenes.

Entry	Alkene	Diacetate	Temp,°C[a]	Yield,%[b]
1	$C_6H_{13}CH{=}CH_2$	 $C_6H_{13}\overset{\mathrm{AcO}}{\overset{\vert}{C}}H\overset{\mathrm{OAc}}{\overset{\vert}{C}}H_2$	116	79
2	$C_8H_{17}CH{=}CH_2$	 $C_8H_{17}\overset{\mathrm{AcO}}{\overset{\vert}{C}}H\overset{\mathrm{OAc}}{\overset{\vert}{C}}H_2$	116	76
3		 $C_3H_7\overset{\mathrm{AcO}}{\overset{\vert}{C}}H\overset{\mathrm{OAc}}{\overset{\vert}{C}}HC_3H_7$ (meso)	80	76
4		 $C_3H_7\overset{\mathrm{AcO}}{\overset{\vert}{C}}H\overset{\mathrm{OAc}}{\overset{\vert}{C}}HC_3H_7$ (meso : d,l; 32 : 68)	90	49
5			80	79
6		  (4 : 3)	50	28[c]
7			70	84
8	 **1**	 **3**	116	43
9	 **2**	 X=OAc **4**	70	40[d]

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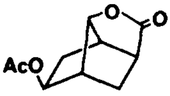
[a] Temperature at which the oxidation was performed. [b] Yield is based on chromatographed, distilled or recrystallized products. [c] 3-Cyclooctenyl acetate (9%) and 1,8-octanedioic acid (35%) were also isolated. [d] Also obtained were **4**, X=OH (15%); **4**, X=H (5%); **2** dimethyl ester (2%); and **2** anhydride (20%) after treatment with diazomethane.

and cyclooctene (entries 3, 5, and 6) gave 1,2-diacetates which had resulted from highly stereoselective (< 98%) anti-addition. *Cis*-4-octene (entry 4) gave predominantly (68:32) the d,l-diacetate which was also the result of anti-addition. The lower stereoselectivity in this case may be the result of either rotation about the sp^2 carbon atoms at some intermediate stage during the reaction or isomerization of the cis double bond prior to diacetoxylation. In a separate experiment *cis*-4-octene was in fact shown to be unstable to the reaction conditions through conversion to a *cis/trans* mixture (14/86) by a trace of sulfuric acid (< 1%)[19] in 90° C acetic acid (28 hrs).

Cyclooctene (entry 6) gave in addition to the *trans*-1,2-diacetate a product resulting from transannular 1,4-hydrogen transfer, the *cis*-1,4-diacetate. Transannular chemistry commonly occurs in an eight-membered ring that has a radical or carbonium ion intermediate.

Anti-addition of the two carboxylate moieties continues in the two norbornene acids, **1** and **2** (entries 8 and 9). In both cases a lactone acetate, **3** or **4**, was produced. The yields in these latter two cases were somewhat low, however no substantial amount of other neutral (after diazomethane esterification of any free carboxylic acids) products could be isolated. In particular, the product of rearrangement, **5**,[20] and the bis-lactone, **6**,[21] were not observed.

Norbornene itself (entry 7) did not give a diacetate as the major product, but instead the monoacetate. Trace amounts of what were presumed to be diacetates could be detected by gas chromatography but were not isolated. The monoacetate appears to be the result of acid catalyzed addition of acetic acid across the strained norbornene double bond, as this addition could be effected by potassium bisulfate in refluxing acetic acid in 84% yield.[22]



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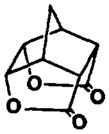

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The material balance was always poor when only the volatile, neutral products were isolated under the iron/persulfate reaction conditions. In an effort to identify all the possible minor byproducts, a reaction was run under deliberately nonoptimum conditions to magnify these effects. Thus when 1-decene was heated to reflux with ferrous sulfate (25 mole %) and ammonium persulfate (2.5 mole equiv.) under threefold dilution, the following neutral products were obtained: starting material and telomer (approx. 13%), 2-decyl acetate (2%), 1,2-decyl diacetate (56%), γ-dodecalactone (9%), and unidentified polyacetates (approx. 4%). In addition, the acidic material upon diazomethane esterification consisted of methyl nonoate (16%). The major byproducts can be accounted for in a number of ways. The γ-decalactone may be the result of acetic acid radical addition to 1-decene followed by oxidation of the type reported by Giordano *et al.*[23] in a related system which contained a large acetate ion concentration. The telomer would be a logical contaminant if a radical intermediate were involved in the mechanism (see Fig. 3), and the nonanoic acid is a result of oxidative cleavage of the double bond. This may well occur at the hydroxyacetate stage as diols are known to be readily cleaved by persulfate.[24] In any case, the major byproducts are easily removed by a bicarbonate extraction or simple distillation.

Trisubstituted alkenes were more easily oxidized and also more easily overoxidized. Use of an excess of persulfate generally led largely to overoxidation and uncharacterized mixtures. When a stoichiometric amount of oxidant was used the major products obtained were ketones. Several examples are shown in Fig. 2; however, in all cases the yields were not synthetically useful.

In considering a mechanism for this iron catalyzed persulfate diacetoxylation several facts had to be born in mind. a) The most efficient metal additive was the least likely to act as an oxidant itself. b) A high level of anti-addition was observed. c) *Endo*-norbornenedicarboxylic acid, 2, cyclized to an acetoxylactone and not a dilactone. d) No rearrangement of the norbornyl system was seen. A mechanism consistent with these facts is shown in Fig. 3.

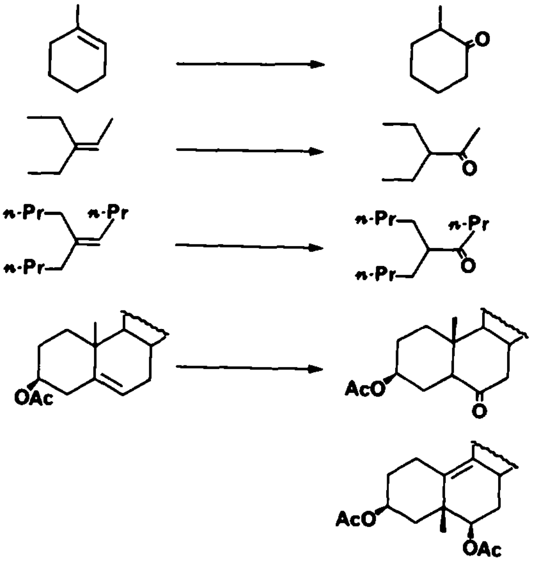
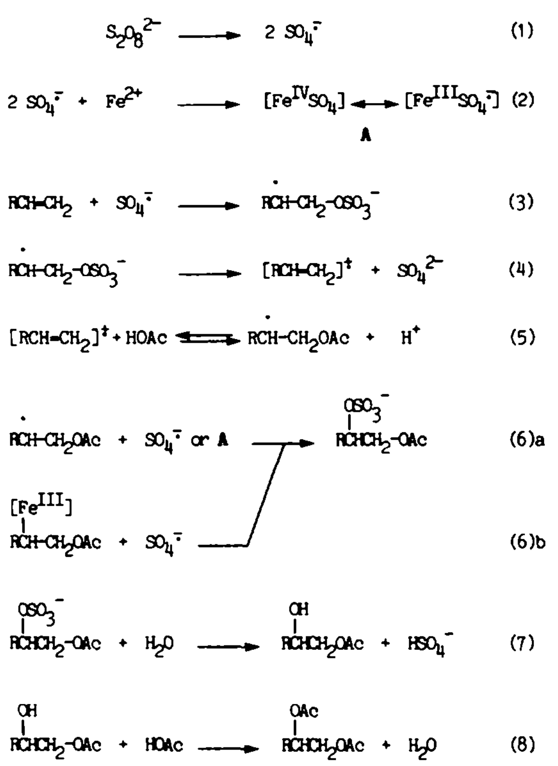


Figure 2.

The reaction is initiated by an uncatalyzed thermal decomposition of persulfate (step 1). Simple homolytic decomposition of persulfate is well known, but what we found to be surprising was that Fe(II) salts did not catalyze persulfate decomposition to any appreciable extent. Thus aqueous and nonaqueous systems of persulfate and metal ions can differ substantially in their chemistry. Persulfate decomposition was followed by iodometric titration of aliquots taken from refluxing acetic acid solutions which contained various additives. The rate of decomposition did not vary by more than a factor of four when the reaction was allowed to proceed with no catalyst, $FeSO_4$, $Fe(NH_4)(SO_4)_2$, $FeSO_4$ and olefin, or simply olefin. The slight variation in reaction rates appear to be related to the solubility of ammonium persulfate and the ionic strength of the solution, as addition of $(NH_4)_2SO_4$ led to a rate decrease very similar to that of $FeSO_4$ or $Fe(NH_4)(SO_4)_2$. Moreover it should be noted that ammonium persulfate and its decomposition product, $(NH_4)_2SO_4$, have very limited solubility in hot acetic acid. The conclusion drawn from these kinetic studies was that Fe(II) was not catalyzing the decomposition of persulfate, but must be improving the yield of diacetate by slightly altering the product determining step of the mechanism.

We have also found that the diacetoxylation may be run in the presence of 25 mole % Fe(III), introduced as $Fe(NH_4)(SO_4)_2$, and this resulted in an isolated diacetate yield of 68%. This tends to confirm the proposition that Fe in the +2 oxidation state is not specifically required, for there is no obvious mechanism for reduction of Fe(III)



$$S_2O_8^{2-} \longrightarrow 2\,SO_4^{\cdot -} \qquad (1)$$

$$2\,SO_4^{\cdot -} + Fe^{2+} \longrightarrow \underset{\mathbf{A}}{[Fe^{IV}SO_4] \longleftrightarrow [Fe^{III}SO_4^{\cdot -}]} \qquad (2)$$

$$RCH{=}CH_2 + SO_4^{\cdot -} \longrightarrow R\dot{C}H\text{-}CH_2\text{-}OSO_3^{-} \qquad (3)$$

$$R\dot{C}H\text{-}CH_2\text{-}OSO_3^{-} \longrightarrow [RCH{=}CH_2]^{+\cdot} + SO_4^{2-} \qquad (4)$$

$$[RCH{=}CH_2]^{+\cdot} + HOAc \rightleftharpoons R\dot{C}H\text{-}CH_2OAc + H^{+} \qquad (5)$$

$$R\dot{C}H\text{-}CH_2OAc + SO_4^{\cdot -} \text{ or } \mathbf{A} \longrightarrow R\overset{OSO_3^{-}}{CH}CH_2\text{-}OAc \qquad (6)a$$

$$\overset{[Fe^{III}]}{R\dot{C}H}\text{-}CH_2OAc + SO_4^{\cdot -} \longrightarrow R\overset{OSO_3^{-}}{CH}CH_2\text{-}OAc \qquad (6)b$$

$$R\overset{OSO_3^{-}}{CH}CH_2\text{-}OAc + H_2O \longrightarrow R\overset{OH}{CH}CH_2OAc + HSO_4^{-} \qquad (7)$$

$$R\overset{OH}{CH}CH_2\text{-}OAc + HOAc \longrightarrow R\overset{OAc}{CH}CH_2OAc + H_2O \qquad (8)$$

Fig. 3 Proposed Mechanism

to Fe(II). The Fe(II) additive, presumably is oxidized to Fe(III) by sulfate radical anion, and possibly to an Fe(IV) $\longleftrightarrow [Fe^{III}\text{-}OSO_3^{\cdot -}]$ species, **A**, as in step 2 of Fig. 3. In this way the Fe additive could produce or stabilize, at least transiently, a one electron oxidant which would take part in the product determining step 6a.

The third step of the proposed mechanism was substantiated by several literature values for the rate constant of $SO_4^{\cdot -}$ addition to carbon-carbon double bonds which were all within the range of $4 \times 10^8 - 5 \times 10^9\ M^{-1}\ s^{-1}$, 25° C).[7] Thus addition to the double bond was only slightly slower than diffusion controlled. ESR spectra of the intermediate radicals definitely established them to be β-sulfatoalkyl radicals.[8,9,25] The direct formation of olefin radical cations through single electron transfer oxidation by $SO_4^{\cdot -}$ has also been shown not to occur.[9] The reported rate constant for $SO_4^{\cdot -}$ reaction with acetic acid was four orders of magnitude lower than that of reaction with alkenes. Acetate oxidation was two orders of magnitude lower.[7] Thus oxidation of the acetic acid solvent should not compete effectively with alkene addition. In this regard, it was satisfying that under our reaction conditions no more than trace amounts of CO_2 evolution were ever observed by barium hydroxide trapping. When the reaction was conducted in the presence of excess potassium acetate, however, acetate oxidation and the concomitant CO_2 evolution were observed.[26,27] This kinetic and ESR data coupled with the low redox potential of Fe(III) makes $SO_4^{\cdot -}$ addition the most reasonable way to initiate reaction of the C=C.

The β-sulfatoalkyl radical produced in step 3 should suffer one primary fate. Elimination of a good leaving group from β-substituted radicals to produce olefin radical cations and the leaving group anion has been shown by Schulte-Frohlinde et al. to be a very facile process.[28] While they have not studied β-sulfato radicals specifically, β-sulfate ester radicals were shown to eliminate at rates faster than they could determine ($\geq 10^6\ s^{-1}$, 18° C). The corresponding β-phosphato radicals eliminate also as either the esters, the free acids or acid salts. The olefin radical cation which was produced in step 4 should then react preferentially with the more nucleophilic acetic acid solvent to produce a β-acetoxy radical, step 5. Reversal of this step is of course allowed by the logic of step 4, however it would be nonproductive.

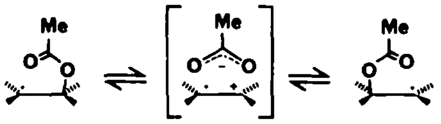
The β-acetoxyalkyl radical may combine with $SO_4^{\cdot -}$ or species **A** to produce the relatively stable β-acetoxysulfate of step 6a. The efficiency of this step would be enhanced by a high concentration of $SO_4^{\cdot -}$ or a stabilized form of $SO_4^{\cdot -}$. This is consistent with our results which demonstrated the greater efficiency of the iron/persulfate system over simple persulfate decomposition in producing diacetoxylation. Thus the transition metal additive may be simply providing a suitably stabilized form of $SO_4^{\cdot -}$ which effectively increases its concentration, or possibly by performing as an oxidant itself in the mechanism. Alternatively, the Fe(III) ion may be complexed to the intermediate β-acetoxy radical and stabilizing the radical, step 6b. Such an explanation has been advanced previously where Fe(III) promoted higher bimolecular radical coupling of alkyl radicals.[29]

This concept of increasing the effective concentration of either the radical or sulfate radical anion appears to be verified by the following experiment. The usual mixture of alkene, persulfate and acetic acid were heated to reflux while irradiating the reaction with a Hanovia ultraviolet quartz light source filtered through Pyrex. The photolytic decomposition of persulfate at this wavelength will necessarily be low;[30] nonetheless, the $SO_4^{\cdot -}$ concentration was increased so that a 45% yield of diacetate was realized compared to 10% without irradiation.

The possible oxidation of the β-acetoxyalkyl radical by Fe(III) to a carbonium ion was considered despite the fact that this is not commonly observed in aqueous solution.[31] When dioctanoyl peroxide was allowed to decompose in refluxing acetic acid containing ferric ammonium sulfate, heptane (3%), tetradecane (2%) and heptanol (16%) were identified as products. The poor material balance does not allow a strong statement, however it does appear that in acetic acid solution some oxidation of primary alkyl radicals by Fe(III) can take place.

The conversion of alkyl sulfates, as in steps 7 and 8, to acetates has been demonstrated. Sodium dodecylsulfate was quantitatively converted to dodecyl acetate by refluxing with potassium bisulfate in acetic acid. Sodium dodecylsulfate was relatively stable in acetic acid in the absence of bisulfate. Thus contrary to the implications of a Russian report, alkylsulfates are not stable to the present reaction conditions.[10] The intermediacy of hydroxyacetates (step 7) provides a suitable substrate material for oxidative cleavage as is observed in the acidic reaction product. The 1,2-diacetates, on the other hand, were found to be stable to further oxidation by the Fe(II)/persulfate system. Hydroxyacetates were observed by gas chromatography of reaction mixtures which had not been treated in the usual way with acetic anhydride before workup.

The proposed mechanism is consistent with the stereochemistry and lack of rearrangement seen in the reaction. β-Acetoxy radicals have been felt to be partially bridged or to rapidly interconvert between the two isomeric β-acetoxy radicals via the symmetrical intermediate 7.[32] Attack of $SO_4^{\cdot -}$ on a β-acetoxy radical should favor anti-addition on steric grounds. The lack of rearrangement in the norbornene acids 1 and 2 illustrate the lack of carbonium ion character in any intermediate. The corresponding 2-norbornyl radicals are known not to rearrange rapidly.[33] The formation only of 4 and not 6 from 2 requires that the acetate moiety in 4 be introduced in a fashion which would make formation of the bislactone 6 impossible. The hydrolysis of an *exo*-sulfate in 8 would nicely satisfy this requirement.



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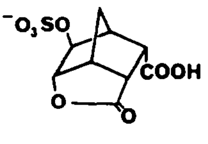

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The iron(II)/persulfate/acetic acid system constitutes a new oxidation system which effectively converts alkenes to 1,2-diacetates. The iron(II) additive appears not to operate as a catalyst for persulfate decomposition as it does in aqueous solution, but instead to operate later in the final carbon-oxygen bond forming step. Thus the results are very different from those of Fe(II) containing aqueous solutions or the common Ag(I)/persulfate/solvent systems in which Ag(II) is involved as the principal oxidant.

EXPERIMENTAL

Melting points were determined with an Electrothermal apparatus and are uncorrected. ^{1}H NMR spectra were obtained on a Varian HFT-80 (80 MHz) or a Nicolet 300 MHz instrument. Chemical shifts are reported in parts per million relative to internal tetramethylsilane in deuteriochloroform unless specified otherwise. Mass spectra were obtained with an AE1 Kratos MS-30 (electron impact) or a Finnigan 4000 (chemical ionization) spectrometer. Infrared spectra were obtained on a Beckman 4250 spectrophotometer. Gas chromatography was performed with a Varian 3700 model equipped with FID's and a Hewlett-Packard 3390A integrator. The columns used were 5% Carbowax 20M on 100/120 mesh Chromosorb W, 0.3 cm x 6 m; 10% SF-96 on 80/100 mesh Chromosorb W, 0.3 cm x 6 m; or a silver nitrate/ethylene glycol on 80/100 mesh Chromosorb P to determine alkenes. Chromatography refers to medium pressure liquid chromatography (FMI pump, silica gel column, refractive index detector, Altex model 156) with ethyl acetate/hexane elution.

Starting alkenes were commercially obtained except *cis*-4-octene which was prepared by a literature method and found to be 97% *cis*-4-octene contaminated by 3% of the trans isomer.[34] Ammonium persulfate and all metal catalysts were commercially available.

The products in Table 3 were identified by comparison of experimental and literature spectral properties (NMR, IR), b.p. or m.p., and in some cases either M.S. or G.C. retention time versus an authentic sample. Literature references for the nontrivial diacetates are entry 6[35] 8[20], 9[36].

General Procedure for Data in Tables 1 and 2. 1-Decene (1.5 mmol) and dodecane (0.75 mmol) along with the transition metal additive and ammonium persulfate amounts listed in the entries were brought to reflux in acetic acid (7 ml) under N_2. After refluxing for 6 hrs the slurry was cooled, poured onto water (20 ml), and extracted with petroleum ether (3 x 6 ml). The combined extracts were washed with satd. $NaHCO_3$ (1 x 20 ml), dried ($MgSO_4$) and filtered. Product yields were determined by GC using appropriate response factors.

General Procedure for Data in Table 3. The alkene (40 mmol), ammonium persulfate (100 mmol) and ferrous sulfate heptahydrate (10 mmol) were heated to the listed temperature in acetic acid (125 ml) for 2-4 hrs. Acetic anhydride (2 ml) was then added to the hot reaction slurry 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 (3 x 100 ml). The combined organic layers were extracted with water and satd. $NaHCO_3$ before drying ($MgSO_4$) and evaporating the solvent. Products were purified by distillation, recrystallization or chromatography.

Isomerization of *Cis*-4-Octene. *Cis*-4-octene (40 mg) was dissolved in acetic acid (3 ml), sulfuric acid added (1 drop) and the mixture heated to 90° C for 28 hrs. By GC using the silver nitrate column, the initial cis/trans ratio (97:3) had been converted to 14:86. No isomerization was detected when the sulfuric acid was omitted.

Acetic Acid Addition to Norbornene. Norbornene (168 mg) and potassium bisulfate (61 mg) were heated to reflux under N_2 in acetic acid. After 5 hrs the reaction was worked up in the usual way. The reaction mixture was spiked with decane and analyzed by GC. No norbornene remained and a calculated yield of 84% of *exo*-2-norbornyl acetate was obtained using the appropriate response factor.

Complete Material Balance Experiment. The reaction was run according to the general procedure of Table 3 with 1-decene (0.73 g) except that acetic anhydride was not added to the hot reaction mixture which had been performed under threefold dilution. The products obtained after dilution of the reaction mixture with water and ether extraction were refluxed in 6N KOH for 12 hrs. The hydrolyzed mixture was acidified to pH = 1 with HCl, satd. with NaCl, and extracted with ether (5 x 40 ml). The combined extracts were washed with brine, dried ($MgSO_4$), and evaporated. The crude products were dissolved in ether, treated with an excess of diazomethane, and then refluxed with acetic anhydride (4 ml) and pyridine (1 ml) under N_2 for 12 hrs. The acetylated reaction mixture was diluted with 0.5 N HCl (100 ml) and extracted with ether (4 x 35 ml). The combined ether extracts were washed with water (3 x 40 ml), satd. $NaHCO_3$ (2 x 40 ml), dried ($MgSO_4$) and evaporated to give the crude product. Chromatography yielded a nonpolar fraction containing 1-decene and unidentified telomer (90 mg, approx. 13%), methyl nonoate (32 mg, 16%), 2-decyl acetate (21 mg, 2%), 1,2-decyl diacetate (728 mg, 56%), γ-dodecalactone (92 mg, 9%), and a polar fraction containing polyacetoxylated material 86 mg, approx 4%).

Photolytic Decomposition of Persulfate. 1-Decene (1.46 g) and ammonium persulfate (4.56 g) were heated to reflux in acetic acid (50 ml) while irradiating through the Pyrex flask with a Hanovia ultraviolet quartz lamp. After 3 hrs the light was turned off, acetic anhydride (15 ml) added, and the mixture allowed to cool. After the usual workup dodecane (0.300 g) was added and the reaction mixture analyzed by GC. The diacetate was the major product (calcd 1.14 g, 45%) along with trace amounts (≤ 1%) of several monoacetate products.

Hydrolysis of Sodium Dodecylsulfate. Sodium dodecylsulfate (0.50 g), ferric ammonium sulfate (0.21 g), and potassium bisulfate (0.24 g) were heated to reflux under N_2 in acetic acid. After 3 hrs the reaction was worked up in the usual way, decane (29 mg) added and analyzed by GC. The reaction products were dodecanal (calcd 16 mg), 1-dodecyl acetate (calcd 308 mg, 82%), and an unidentified primary acetate (calcd approx 100 mg, 20%). The unidentified acetate was probably due to an impurity in the starting sodium dodecylsulfate.

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