(CDCl$_3$) δ 1.0–2 0 (m, 15 H), 2.40 (s, 3 H), 3.76 (d, J = 7 Hz, 2 H), 7.1–7.8 (m, 4 H).

Anal. Calcd for C$_{18}$H$_{24}$O$_3$S: C, 67.48; H, 7.55; S, 9.99. Found: C, 67.71; H, 7.35; S, 10.3.

The tosylate was reduced with 0.20 g (0.0052 mol) of lithium aluminum hydride in 20 mL of ether. Purification of the crude product by column chromatography gave 0.15 g (63% yield) of pure *exo*-2-methyl-4-homobrendane (**10x**): ^{1}H NMR (CDCl$_3$) δ 0.9–1.8 (m); ^{13}C NMR (CDCl$_3$) δ$_C$ 15.17 (t), 21.63 (q), 26.11 (t), 27.38 (t), 33.16 (d), 33.81 (t), 38.07 (t), 39.88 (d), 42.46 (d), 44.05 (d), 44.11 (d); mass spectrum *m/e* (rel intensity) 150 (100, M$^+$), 135 (58), 121 (51), 109 (27), 108 (33), 107 (18), 95 (56), 94 (48), 93 (31), 81 (33).

Anal. Calcd for C$_{11}$H$_{18}$: C, 87.92; H, 12.08. Found: C, 87.70; H, 12.22.

Registry No.—1, 49700-65-4; **2**, 66085-39-0; **3**, 66085-40-3; **4**, 66085-41-4; **5**, 66085-42-5; **6**, 16489-35-3; **7**, 50529-80-1; **8**, 66085-43-6; **9n**, 66085-44-7; **9n** tosylate, 66085-45-8; **9x**, 66140-51-0; **9x** tosylate, 66140-52-1; **10n**, 66085-46-9; **10x**, 66140-53-2; **11**, 66085-47-0; **12**, 61559-34-0; **13**, 50529-94-7; **14**, 66085-48-1; **15**, 43000-53-9; **16**, 51027-87-3; 2-Me-Ad, 700-56-1; 1-Me-Ad, 768-91-2; 2-chloro-4-homobrendane, 66085-49-2; homoadamantane, 281-46-9; *endo*-2,8-trimethylenebicyclo[3.3.0]octane, 28099-09-4.

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Metal Ion Oxidation. 6.[1] Oxidative Acetoxylation of Aromatic Compounds by Silver(II) Complexes in Acetic Acid[2]

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Silver(II) complexes with nitrogen-containing ligands oxidize aromatic compounds (anisole, substituted anisoles, biphenyl, naphthalene, and hexamethylbenzene) in 0.5 M KOAc/HOAc yielding acetoxy derivatives (nuclear or side-chain acetates). Anisole and biphenyl give mainly ortho and para acetates. Results from the competitive oxidation of 4-substituted anisoles gave a Hammett ρ value of −3.4. Nuclear substitution did not show any deuterium isotope effect, whereas side-chain substitution of 4-methoxytoluene gave a k_H/k_D value of 5.9. Oxidation of benzene in trifluoroacetic acid gave phenol after hydrolysis of the reaction product. It is suggested that silver(II) reacts by removing one electron from the aromatic substrate, yielding a radical cation in the initial step. The synthetic utility of the reaction is demonstrated in a catalytic process using either presynthesized bis(2,2'-bipyridine)silver(II) peroxodisulfate or a mixture of silver(I) acetate and 2,2'-bipyridine in the presence of excess potassium peroxodisulfate. Acetates are produced with catalyst efficiencies between 1500 and almost 10 000%.

Although Ag(II) is a very strong oxidant[3] its use as a reagent in organic synthesis has been limited. The oxide, AgO, and the bis(2-pyridine carboxylate), Ag(pic)$_2$, are known to oxidize a variety of organic compounds in aqueous acidic or basic media.[4] More recently it has been shown that AgO dissolved in trifluoroacetic acid (TFA) could affect oxidation of aliphatic hydrocarbons[5] and coupling of phenolic substrates.[6] Kinetic studies have been reported on the oxidation of carboxylic acids by Ag(II)[7–9] or by Ag(I) and peroxodisulfate anion, S$_2$O$_8{}^{2-}$.[10] In the latter study it was shown that Ag(II), obtained by the action of S$_2$O$_8{}^{2-}$ on Ag(I), was the primary oxidant.

In a preliminary report we described the reaction between some aromatic compounds and bis(2,2'-bipyridine)silver(II)

peroxodisulfate, Ag(bpy)$_2$S$_2$O$_8$, in acetic acid containing sodium acetate.[11] The major products were arenes acetoxylated in nuclear and/or side-chain (α) positions. Methyl-substituted arenes also gave benzaldehydes. The stoichiometry of the reaction seemed to follow eq 1.

$$3ArH + 2Ag(II) + 2S_2O_8{}^{2-} + 3OAc^- \rightarrow 3ArOAc + 2Ag(I) + 4SO_4{}^{2-} + 3H^+ \quad (1)$$
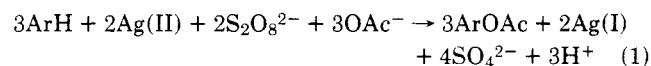
As an example, 4-methoxytoluene was converted into a mixture of 4-methoxybenzyl acetate and 4-methoxybenzaldehyde in a yield of almost 300% based on Ag(II)[12] by Ag(bpy)$_2$S$_2$O$_8$. This indicated that Ag(II) as well as S$_2$O$_8{}^{2-}$ were involved in the overall reaction. The removal of one electron from the

Table I. Acetoxylation of 4-X-anisoles by $Ag(bpy)_2S_2O_8$

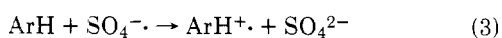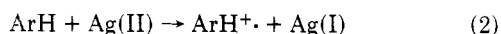| X	Registry no.	Reaction time, h	Product	Yield (4)[a]	Registry no.
OMe	150-78-7	2	1	190	27257-06-3
F	459-60-9	5	2	105[b]	1200-06-2
t-Bu	5396-38-3	6	1	190	66037-02-3
H	100-66-3	6	1	135[c]	66037-03-4
Cl	623-12-1	12	1	155	66037-04-5
Br	104-92-7	16	1	106	104-93-8

[a] GLC yield. [b] Based on a one-electron reaction. [c] The acetoxyanisoles were formed in a o:m:p ratio of 68:1:31.

Table II. Isomer Distribution in Oxidative Acetoxylation

Substrate	Oxidant	Relative amount of acetates		
		o	m	p
Anisole	$Ag(bpy)_2S_2O_8$	68.0	0.6	31.4
Anisole	$Ag(phen)_2S_2O_8$	68.6	1.4	30.0
Anisole	$Ag(py)_4S_2O_8$	72.9	2.8	24.3
Anisole	$Ag(pic)_2$	65.6	1.9	32.5
Anisole	$Ag(bpy)_2(CF_3SO_3)_2$	69.9	1.7	28.4
Anisole	Anodic[a]	67.4	3.5	29.1
Biphenyl	$Ag(bpy)_2S_2O_8$	21.3	b	78.7
Biphenyl	$Ag(phen)_2S_2O_8$	22.8	b	77.2
Biphenyl	$Ag(py)_4S_2O_8$	20.5	b	79.5
Biphenyl	$Ag(pic)_2$	21.5	b	78.5
Biphenyl	$Ag(bpy)_2(CF_3SO_3)_2$	20.9	b	79.1
Biphenyl	Anodic[a]	30.7	0.9	68.4

[a] Data taken from ref 17. [b] Less than 0.1% of the meta formed.

arene is probably the primary reaction step and could take place either by the action of Ag(II) as shown in eq 2 or by the sulfate radical anion, $SO_4^-\cdot$, as shown in eq 3. The latter species is a strong oxidant and is formed by the decomposition of $S_2O_8{}^{2-}$ by heat,[13] by a catalyst,[13] by pulse radiolysis,[14] or photochemically.[15] Ag(I) ion is known to be an efficient catalyst[16] (eq 4).

$$ArH + Ag(II) \rightarrow ArH^+\cdot + Ag(I) \qquad (2)$$

$$ArH + SO_4^-\cdot \rightarrow ArH^+\cdot + SO_4{}^{2-} \qquad (3)$$

$$S_2O_8{}^{2-} + Ag(I) \rightarrow SO_4^-\cdot + SO_4{}^{2-} + Ag(II) \qquad (4)$$
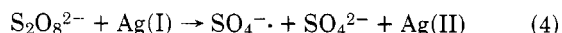
We now present an extensive study on the acetoxylation of arenes by different Ag(II) complexes. The synthetic use of these reactions is demonstrated by the catalytic action of Ag(II) in the presence of an excess of potassium peroxodisulfate.

Results

Products. In our earlier report[11] we found that oxidation of anisole, biphenyl, naphthalene, 1,4-dimethoxybenzene, and mesitylene by $Ag(bpy)_2S_2O_8$ resulted in the formation of nuclear acetates in yields ranging from 42 to 190%. We now use mainly 4-substituted anisoles as substrates, since they react with Ag(II) at convenient rates making them suitable for mechanistic studies. Oxidation with $Ag(bpy)_2S_2O_8$ in general gave one product (eq 5 and Table I), 4-fluoroanisole
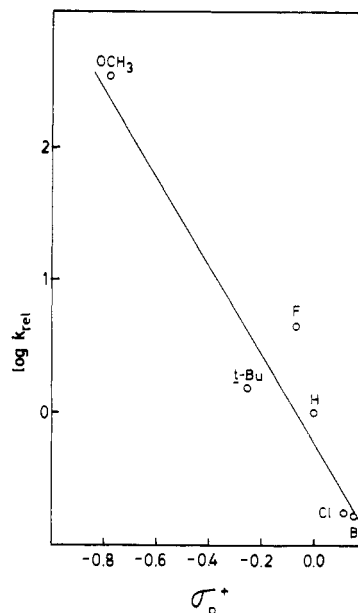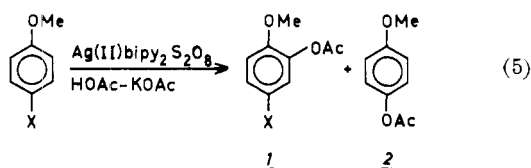
Figure 1. Hammett correlation for competitive acetoxylation of 4-substituted anisoles.

being an exception (see Discussion). The reactions were carried out by adding $Ag(bpy)_2S_2O_8$ to a solution of the substrate in fivefold excess in 0.5 M KOAc/HOAc at room temperature. The reaction was complete when the dark-brown color of the slurry (due to the Ag(II) complex) had changed to colorless.

Isomer Distribution. Anisole and biphenyl were chosen for a detailed study of the isomer distribution in oxidative acetoxylation by different Ag(II) complexes. The results are shown in Table II. Besides the $Ag(bpy)_2S_2O_8$ complex we have studied the corresponding 1,10-phenanthroline (phen) and pyridine (py) complexes. Since it is important from a mechanistic point of view to include Ag(II) complexes containing nonoxidizing counterions we have studied two such Ag(II) complexes, namely $Ag(pic)_2$ and the trifluoromethane sulfonate, $Ag(bpy)_2(CF_3SO_3)_2$. In Table II we have also included data from anodic acetoxylation.[17] No significant difference is observed between different oxidants. We have also compared the oxidation of 4-methoxytoluene by $Ag(bpy)_2S_2O_8$ and $Ag(bpy)_2(CF_3SO_3)_2$, respectively, in KOAc/HOAc. Both oxidants produced a mixture of 4-methoxybenzyl acetate and 4-methoxybenzaldehyde (ratio 3:1) in a quantitative yield based on Ag(II). The same products, although in different ratio and lower yield, are obtained by the action of $Mn(OAc)_3$ in HOAc,[18] $Mn(OAc)_3$ in H_2SO_4/HOAc,[19] $Co(OAc)_3$ in LiCl/HOAc,[20] or by anodic oxidation in HOAc.[17]

Competition Experiments. We initially tried to measure the rate of oxidation of 4-substituted anisoles by $Ag(bpy)_2(CF_3SO_3)_2$ by following the disappearance in Ag(II) spectrophotometrically. However, we had to abandon this technique due to poor reproducibility of the results.[21] Instead we determined the relative rates of oxidation using the same Ag(II) complex, chosen in order to avoid $S_2O_8{}^{2-}$ as a counterion. The reactions were carried out by adding $Ag(bpy)_2(CF_3SO_3)_2$ to a solution of two substrates, each in a tenfold excess, in 0.5 M KOAc/HOAc. The mixture was stirred at room temperature until colorless and the ratio of the products was determined by GLC. The results are shown in Figure 1 as a Hammett plot of log k_X/k_H vs. the substituent constant σ_p^+,[22] yielding a ρ value of -3.4 (correlation coefficient = 0.95). This may be compared with a ρ value of -2.4 obtained in $Co(OAc)_3$ oxidation of 4-substituted toluenes,[20] or a ρ value of -2.4 from the reaction of $SO_4^-\cdot$ with substituted benzenes in aqueous solution.[14] Both these processes are assumed to be electron-transfer oxidations.

$$\text{(eq 5)}$$

Table III. Small-Scale[a] and Preparative-Scale[b] Catalytic Acetoxylation[j]

Substrate	Catalyst	Product	Yield (%) based on Ag(II)[c]	Consumed substrate[d]
1,4-Dimethoxybenzene	Ag(pic)$_2$	2-Acetoxy-1,4-dimethoxybenzene	4930	
1,4-Dimethoxybenzene	Ag(py)$_4$S$_2$O$_8$	2-Acetoxy-1,4-dimethoxybenzene	1680	
1,4-Dimethoxybenzene	Ag(phen)$_2$S$_2$O$_8$	2-Acetoxy-1,4-dimethoxybenzene	8680	
1,4-Dimethoxybenzene	Ag(bpy)$_2$S$_2$O$_8$	2-Acetoxy-1,4-dimethoxybenzene	1880[e]	
1,4-Dimethoxybenzene	Ag(bpy)$_2$S$_2$O$_8$	2-Acetoxy-1,4-dimethoxybenzene	8720	33
Anisole	Ag(bpy)$_2$S$_2$O$_8$	Acetoxyanisoles	5960	39
4-Bromoanisole	Ag(bpy)$_2$S$_2$O$_8$	2-Acetoxy-4-bromoanisole	5560	40
4-tert-Butylanisole	Ag(bpy)$_2$S$_2$O$_8$	2-Acetoxy-4-tert-butylanisole	1470[f]	29[f]
4-Methoxytoluene	Ag(bpy)$_2$S$_2$O$_8$[i]	4-Methoxybenzyl acetate	7540[g]	35[g]
		4-Methoxybenzaldehyde	2270[g]	12[g]
Hexamethylbenzene	Ag(bpy)$_2$S$_2$O$_8$[i]	Pentamethylbenzyl acetate	5370[g]	
		Pentamethylbenzyl alcohol	1660[g]	
Naphthalene	Ag(bpy)$_2$S$_2$O$_8$	Acetoxynaphthalenes	6760[h]	

[a] Catalyst (0.1 mmol), K$_2$S$_2$O$_8$ (10 mmol), Ba(OAc)$_2$·H$_2$O (4 mmol) and substrate (10 mmol) in 0.5 M NaOAc/HOAc (20 mL) at 40 °C. [b] Carried out on a scale 20 times the small-scale reactions. The catalyst can be replaced by AgOAc and 2,2'-bipyridine. [c] GLC yields in small-scale reactions. [d] Yields of isolated products in preparative reactions. [e] In the absence of Ba(II). [f] At 30 °C. [g] Carried out under argon and with the addition of Ac$_2$O. [h] The 1- and 2-acetoxynaphthalenes were formed in a ratio of 95:5. [i] Using AgOAc and 2,2'-bipyridine as catalysts the amount of aldehyde formed decreased to a nonsignificant level. [j] Registry No.—4-Methoxytoluene, 104-93-8; hexamethylbenzene, 87-85-4; naphthalene, 91-20-3; Ag(pic)$_2$, 14783-00-7; Ag(py)$_4$S$_2$O$_8$, 15810-50-1; Ag(phen)$_2$S$_2$O$_8$, 22750-33-0; Ag(bpy)$_2$S$_2$O$_8$, 28226-64-4; 4-methoxybenzyl acetate, 104-21-2; 4-methoxybenzaldehyde, 123-11-5; pentamethylbenzyl acetate, 19936-85-7; pentamethylbenzyl alcohol, 484-66-2.

Isotope Effects. It has previously been shown that anodic acetoxylation of anisole, deuteriated in the ring,[17] or trifluoroacetoxylation of deuteriated benzene[23] by Co(III) trifluoroacetate occur with the same rates as with the protiated compounds. We have used Ag(bpy)$_2$(CF$_3$SO$_3$)$_2$ in 0.5 M KOAc/HOAc to study the acetoxylation of mesitylene-2,4,6-d_3. A comparison between nuclear and α substitution in the deuteriated and the protiated mesitylene showed no isotope effect (k_H/k_D = 1.1 ± 0.2). Using the same oxidant we studied the α acetoxylation of a mixture of equal amounts of 4-methoxytoluene and 4-methoxytoluene-α,α,α-d_3. By determining the deuterium content in 4-methoxybenzyl acetate by MS a k_H/k_D value of 5.9 ± 0.2 was calculated. This value may be compared to those obtained in Mn(OAc)$_3$ oxidation (5.1)[18] and anodic acetoxylation (2.6)[17] of the same compounds.
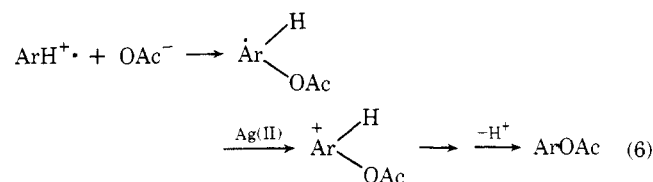
The Effect of Acetate Ion. In our preliminary report[11] we noted that the rate of oxidation with Ag(bpy)$_2$S$_2$O$_8$ in HOAc increased significantly when NaOAc was present. We attributed this effect to the buffer capacity of NaOAc, since the reaction produces protons (as H$_2$SO$_4$). These might have a deleterious influence on the Ag(II) complex, e.g., by protonation of the bipyridine ligand. Although part of the rate increase might be due to the buffer capacity of acetate ions we now believe that most of the rate increase is caused by the increase in solubility of the Ag(II) complex in HOAc that the acetate ion causes. Thus the solubility of Ag(bpy)$_2$S$_2$O$_8$ increased from 0.01 to 0.03 M when the concentration of KOAc in HOAc was increased from 0.5 to 1.0 M.

Reaction in TFA. In several reports it has been shown that the oxidative power of metal ions is greatly increased by carrying out reactions in TFA instead of HOAc, e.g., Co(III),[20,23,24] Mn(III),[24] Pb(IV),[24-26] and Ce(IV).[27] In some cases ESR spectra of radical cations have been observed in TFA.[23,28] Using Ag(bpy)$_2$(CF$_3$SO$_3$)$_2$ in TFA at −10 °C we tried to obtain an ESR spectrum of the radical cation of 1,4-di-tert-butylbenzene. Although the information we obtained indicated that the radical cation was formed, the spectrum was poorly resolved, probably due to the instability of the Ag(II) complex in TFA. We also carried out a preparative experiment with the same Ag(II) complex in TFA using benzene as the substrate and obtained (after hydrolysis of the reaction mixture) phenol in a 17% yield, based on Ag(II).
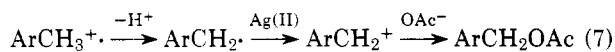
Catalytic Reactions. When the oxidative acetoxylation of aromatic compounds by Ag(II) complexes is carried out with added K$_2$S$_2$O$_8$ the formation of acetoxylated arenes is catalytic in Ag(II). Furthermore we have found that the reactions can be carried out starting with AgOAc, 2,2'-bipyridine, and K$_2$S$_2$O$_8$. We also noticed a profound effect on the yields when Ba(OAc)$_2$ was present in the reaction mixture, the yields being considerably higher in its presence. Since SO$_4^{2-}$ is formed during the reaction and could inhibit the reaction by precipitation of Ag$_2$SO$_4$, it is probable that Ba(II) removes SO$_4^{2-}$ as BaSO$_4$. In view of the high catalytic activity of this system the reaction might be of synthetic value. Results from small-scale experiments and some preparative experiments are shown in Table III.

Discussion

Mechanism. Judging from the results it seems evident that the oxidation with Ag(II) in the absence of S$_2$O$_8^{2-}$ follows the same mechanism as that proposed for Co(III) and Mn(III) oxidations,[29] i.e., eq 2 is the rate-determining step. The isomer distribution from the acetoxylation of anisole and biphenyl is the same for Ag(II) and the anode reactions. The Hammett correlation gave a ρ value of −3.4 indicating an electron-transfer reaction.[14,20] The oxidation in TFA gave results supporting an electron-transfer reaction, although the evidence was not clear cut. The product from the oxidation of benzene (phenol after hydrolysis of the initially formed phenyl trifluoroacetate) is the same that is obtained by Co(III)[23] and anodic oxidation,[30] respectively, in TFA. The possibility that Ag(II) oxidizes acetate ion to give the acetoxy radical that subsequently reacts with the aromatic substrate is ruled out in the same way as in anodic acetoxylation,[31] although radical substitution may have electrophilic character as shown for isopropoxylation of aromatic substrates (ρ = −2.3).[32] The radical cation (eq 2) will be trapped by acetate ion yielding an acetoxycyclohexadienyl radical. This species is rapidly oxi-

$$ArH^{+}\cdot + OAc^{-} \longrightarrow \dot{Ar}\underset{OAc}{\overset{H}{\diagup}}$$

$$\xrightarrow{Ag(II)} \overset{+}{Ar}\underset{OAc}{\overset{H}{\diagup}} \xrightarrow{-H^{+}} ArOAc \quad (6)$$

dized by Ag(II) to a cation that forms the product after loss of a proton (eq 6). The last step is fast as shown by the absence of a deuterium isotope effect. Oxidative substitution in the side chain, as in 4-methoxytoluene or hexamethylbenzene, takes place according to

$$\text{ArCH}_3{}^+\cdot \xrightarrow{-\text{H}^+} \text{ArCH}_2\cdot \xrightarrow{\text{Ag(II)}} \text{ArCH}_2{}^+ \xrightarrow{\text{OAc}^-} \text{ArCH}_2\text{OAc} \quad (7)$$
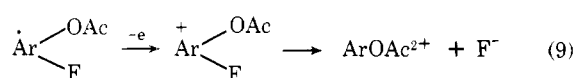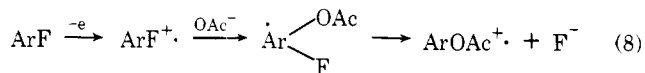
The first step in eq 7, loss of a proton from the radical cation, is the slow step as shown by the deuterium isotope effect for substitution in 4-methoxytoluene. The effect is comparable to that obtained in Mn(III) oxidation.[18]

When the oxidation of the aromatic substrates is carried out with Ag(II) and $S_2O_8{}^{2-}$ present, the mechanism is less clear cut. Some recent studies have convincingly shown that $SO_4{}^-\cdot$, formed by radiolytic[14,33] or metal ion catalytic[34] decomposition of $S_2O_8{}^{2-}$, is capable of oxidizing aromatic substrates in aqueous solutions. Methoxylated benzene radical cations have been observed.[33] However, the same redical cations have also been generated by Ag(II).[33] Hydroxycyclohexadienyl radicals, intermediates in $SO_4{}^-\cdot$ oxidation of aromatic substrates, have also been observed.[35] Thus, although our reaction conditions are different we cannot rule out the possibility that $SO_4{}^-\cdot$ oxidizes aromatic substrates in KOAc/HOAc. We have also tried to acetoxylate anisole with $K_2S_2O_8$ in KOAc/HOAc. No acetoxyanisoles were formed. The addition of Cu(II) to this system did not change the result. Recent studies have shown that some metal ions promote the formation of phenols in the $SO_4{}^-\cdot$ oxidation[34] and in the radical-induced hydroxylation[36] of benzene derivatives.

Comparison with Anodic Acetoxylation. A comparison of products from oxidation of aromatic substrates by other metal ion oxidants is not useful, since the same substrates have only been used in a few cases. We have already mentioned the similarity between Ag(II), Co(III),[20] and Mn(III)[18] oxidation of 4-methoxytoluene and the Ag(II) and Co(III)[23] oxidation of benzene in TFA. On the other hand Ag(II) and anodic oxidations may be compared. The similarities are striking. The isomer distributions in the acetoxylation of anisole and biphenyl are the same. The product distributions from the acetoxylation of mesitylene,[11,37] naphthalene,[11,37] or 4-methoxytoluene[17] and from the trifluoroacetoxylation of benzene[30] by Ag(II) or by the anode are also the same. Some of the nuclear acetates have been prepared by anodic acetoxylation for reference purposes and the yields are comparable to those obtained by Ag(II) acetoxylation.

The result from the Ag(II) acetoxylation of 4-fluoroanisole is of particular interest, since the anodic acetoxylation[38] yields the same product, 4-acetoxyanisole, i.e., an anomalous substitution product. On the other hand 4-chloroanisole and 4-bromoanisole respectively yield the normal product by both oxidants. In the anodic reaction of 4-fluoroanisole we have shown that the usual reaction mechanism for anodic substitution, analogous to eq 2 and 6, is not valid.[38] Instead we have suggested that fluoride ion is lost at some intermediate stage, e.g., as shown in eq 8 and 9, and we believe it is reasonable to assume that the same is valid for Ag(II) oxidation. However, we have not been able to explain satisfactorily the reduction of the 4-acetoxyanisole radical cation or dication, respectively, to the final product. The possibility exists that these reactive species oxidize either the starting material or the solvent. An analogous substitution reaction has recently been found in nucleophilic photosubstitution of 4-fluoro-, 4-chloro- and

$$\text{ArF} \xrightarrow{-e} \text{ArF}^+\cdot \xrightarrow{\text{OAc}^-} \underset{\overset{\displaystyle |}{\text{F}}}{\text{Ar}}\!\!<\!\!\overset{\text{OAc}}{} \longrightarrow \text{ArOAc}^+\cdot + \text{F}^- \quad (8)$$

$$\underset{\overset{\displaystyle |}{\text{F}}}{\text{Ar}}\!\!<\!\!\overset{\text{OAc}}{} \xrightarrow{-e} \underset{\overset{\displaystyle |}{\text{F}}}{\text{Ar}}\!\!<\!\!\overset{\text{OAc}}{} \longrightarrow \text{ArOAc}^{2+} + \text{F}^- \quad (9)$$

4-bromoanisole, respectively, by cyanide ion or hydroxide ion.[39] There is, however, one major difference between the photosubstitution reaction and the oxidative reactions described above. While the former reaction yields the anomalous substitution products from all three haloanisoles the latter reactions produce the normal substitution product from 4-chloro- and 4-bromoanisole.

Synthetic Utility. The catalytic reactions can be carried out starting with either AgOAc, 2,2′-bipyridine, and $K_2S_2O_8$ or with presynthesized $\text{Ag(bpy)}_2S_2O_8$. The yields, based on Ag(II), are high and the reactions might be particularly useful for the preparation of nuclear acetates of activated aromatic derivatives, such as alkoxy- and hydroxy-substituted ones. The difference between the Ag(II) and the anodic acetoxylation reactions is small with regard to product yields. From the experimental point of view, somewhat more sophisticated equipment is needed in the anodic reactions. $S_2O_8{}^{2-}$ has also been used as cooxidant in Pd(II)-catalyzed acetoxylation of arenes.[40] This reaction, however, is different with respect to mechanism (metalation instead of electron transfer) and product distribution.[41]

Experimental Section

The Ag(II) complexes were prepared according to literature procedures: $\text{Ag(bpy)}_2S_2O_8$,[42] $\text{Ag(py)}_4S_2O_8$,[42] $\text{Ag(phen)}_2S_2O_8$,[43] Ag(pic)_2,[44] $\text{Ag(bpy)}_2(\text{CF}_3\text{SO}_3)_2$.[45] 4-Chloroanisole and 4-*tert*-butylanisole were prepared by methylation of the corresponding phenols using dimethyl sulfate.[46] 4-Methoxytoluene-α,α,α-d_3 was prepared according to a literature method.[18] Mesitylene-2,4,6-d_3 was obtained by equilibrating mesitylene three times with a mixture of D_2O and D_2SO_4. Anhydrous acetic acid was frozen out twice before use. Other compounds were of high commercial quality.

Acetoxyanisoles, acetoxybiphenyls, acetoxynaphthalenes, 4-methoxybenzyl acetates, 4-methoxybenzaldehyde, pentamethylbenzyl acetate, and pentamethylbenzyl alcohol were available from earlier work.[17,37] 2-Acetoxy-1,4-dimethoxybenzene was obtained in 68% yield by anodic oxidation of 1,4-dimethoxybenzene.[47] By the same procedure we obtained 2-acetoxy-4-chloroanisole (27% yield) and 2-acetoxy-4-bromoanisole (50% yield) by anodic oxidation of 4-chloroanisole and 4-bromoanisole, respectively. 2-Acetoxy-4-chloroanisole was identified by NMR and MS and by hydrolyzing it into the phenol followed by reaction with 3,5-dinitrobenzoyl chloride yielding the 3,5-dinitro benzoate, mp 171–172 °C (lit mp 171–171.5 °C[48]). 2-Acetoxy-4-bromoanisole, obtained as a solid, mp 64–65 °C (lit. mp 63–64 °C[49]), was identified by NMR and MS.

GLC analysis was done with a Hewlett-Packard Model 6830 A instrument equipped with an electronic integrator on a 2 m × 0.3 cm 5% NPGS on Chromosorb W column. Product yields were calculated from the GLC data after calibration of the authentic samples against a standard. Preparative GLC was carried out with an Aerograph Model A-700 preparative gas chromatograph on a 6 m × 1 cm 20% SE-30 on Chromosorb W column. NMR spectra were recorded on a Varian A 60 spectrometer. MS analysis was done with a LKB Model 9000 mass spectrometer. ESR spectra were recorded on a Varian E-3 spectrometer at −10 °C and at a pressure of 0.01 mmHg.

Small-Scale Reactions with Ag(II) Complexes. The following procedure was used for product studies, isomer distribution studies, and competitive experiments: The Ag(II) complex (2 mmol) was added to a solution of 0.5 M KOAc/HOAc (20 mL) containing the aromatic substrate (10 mmol). The mixture was stirred at room temperature until it became colorless. Dichloromethane was added and the precipitate was filtered off. The filtrate was washed repeatedly with water. The organic phase was then analyzed by GLC. The small-scale catalytic reactions were carried out under the same conditions at 40 °C for 17 h using the Ag(II) complex (0.1 mmol), $K_2S_2O_8$ (10 mmol), $\text{Ba(OAc)}_2\cdot H_2O$ (4 mmol), and the aromatic substrate (10 mmol) in 0.5 M NaOAc/HOAc (20 mL).

Preparative-Scale Catalytic Oxidations. To a solution of the aromatic substrate (200 mmol), $\text{Ba(OAc)}_2\cdot H_2O$ (80 mmol), in 0.5 M NaOAc/HOAc (400 mL) was added $\text{Ag(bpy)}_2S_2O_8$ (2 mmol) and $K_2S_2O_8$ (200 mmol). Instead of the Ag(II) complex AgOAc (2 mmol) and 2,2′-bipyridine (4 mmol) can be used. The slurry was stirred vigorously for 17 h at 40 °C. The oxidations of 4-methoxytoluene and hexamethylbenzene, respectively, were carried out under an argon atmosphere with the addition of Ac_2O (80 mmol). The reaction mixture was then allowed to cool down to room temperature whereupon

water (400 mL) was added. After filtration of the precipitate the solution was washed three times with dichloromethane. The combined organic phases were washed several times with water and dried over anhydrous sodium sulfate. Dichloromethane was then removed by evaporation in vacuo. The isolation of the products is described below.

Oxidation of 1,4-Dimethoxybenzene. The reaction residue was purified by column chromatography on silica gel. Elution with benzene yielded 2-acetoxy-1,4-dimethoxybenzene, recrystallized from ligroin (13.0 g; 66.3 mmol), mp 67–69 °C (lit. mp 68–69 °C[47]).

Oxidation of 4-Bromoanisole. Distillation at reduced pressure gave 4-bromoanisole (20.0 g; 107 mmol). Column chromatography of the residue on silica gel using carbon tetrachloride as an eluent yielded 2-acetoxy-4-bromoanisole, recrystallized from pentane (10.0 g; 40.8 mmol), mp 64–65 °C (lit. mp 63–64 °C[49]).

Oxidation of 4-*tert*-Butylanisole. The starting material (17.0 g; 103.6 mmol) was collected by distillation at reduced pressure. Further distillation had to be interrupted due to decomposition of the product. Instead, 2-acetoxy-4-*tert*-butylanisole (6.4 g; 28.8 mmol) was isolated by preparative GLC and identified by NMR and MS.

Oxidation of 4-Methoxytoluene. Distillation of the reaction residue gave 4-methoxytoluene (3.4 g; 27.8 mmol), 4-methoxybenzaldehyde (3.0 g; 22.1 mmol; bp 125–128 °C (14 mmHg)), and 4-methoxybenzyl acetate (11.1 g; 61.7 mmol; bp 130–14. °C (14 mmHg).

Oxidation of Anisole. The crude reaction mixture was subjected to distillation in a concentric tube column (Fischer Spaltrohr system with 40 theoretical plates) yielding anisole (6.8 g; 63 mmol), 2-acetoxyanisole (5.2 g; 31.3 mmol; bp 104–106 °C (10 mmHg)), and 4-acetoxyanisole (3.6 g; 21.7 mmol; bp 111–112 °C (9 mmHg)).

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