

Metal Ion Oxidation. IV.¹ Oxidative Acetoxylation of Arenes by Bis-(2,2'-bipyridine)-silver(II) Peroxydisulfate in Acetic Acid

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Organic complexes of silver(II) are known to be strong oxidants.² The stability is dependent on the nature of the ligands as well as the acidity of the medium employed. Some of these complexes have been shown to be effective in the oxidation of carboxylic acids,³ alkyl-arenes⁴⁻⁶ and alcohols.⁴⁻⁶

The direct displacement of hydrogen by an acetoxy group in oxidation reactions is of synthetic importance.⁷⁻⁹ We now wish to report a new route to aryl and benzyl acetates using bis-(2,2'-bipyridine)-silver(II) peroxydisulfate,¹⁰ **1**, in the oxidative acetoxylation of aromatic compounds. When **1** was stirred with an excess of anisole in glacial acetic acid for 65 h at room temperature the three isomeric acetoxyanisoles were formed in 31 % yield, based on silver(II). (It is assumed that 2 Ag(II) ions are required to form one molecule of aryl acetate.) However, since the brown color of **1** had not disappeared the reaction had not gone to completion.

A remarkable effect was observed when the reaction was repeated in the presence of 0.5 M sodium acetate. After 17 h the reaction was complete as indicated by the change in color from brown to yellow. The yield of acetoxyanisoles was now 157 %. This shows that the peroxydisulfate ion must be involved in the overall reaction. In a control experiment it was shown that no reaction occurred when potassium peroxydisulfate was employed in the absence of silver(II) or silver(I) ion. We therefore assume that the peroxydisulfate ion in **1** is utilized for reoxidizing silver(I) ions and that every peroxydisulfate ion is capable of oxidizing two silver(I) ions.¹⁰ The latter assumption was borne out by the fact that 4-methoxytoluene was oxidized by **1** in the presence of sodium acetate yielding 290 % of a mixture of 4-methoxybenzyl acetate and 4-methoxybenzaldehyde in a ratio of 76:24. Assuming that 2 Ag(I) ions are oxidized by one peroxydisulfate ion the theoretical yield is 300 % based on silver(II). Table 1 contains additional data for several compounds.

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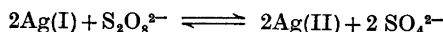
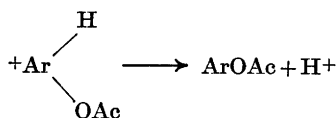
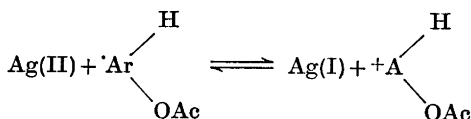
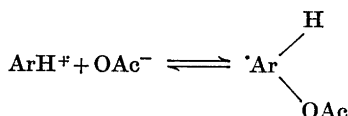
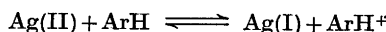
** Prepared in the same way as the corresponding pyridine complex; see Palmer, W. G., Ed., *Experimental Inorganic Chemistry*, Cambridge University Press, Cambridge 1965, p. 158.

Table 1. Product yields in the Ag(bipy)₂S₂O₈ oxidation of arenes in 0.5 M NaOAc/HOAc based on Ag(II).

Compound	Reaction time ^a h	Yield of ArOAc %
Anisole	17	157 (<i>o:m:p</i> = 68:1:31)
Biphenyl	22	55 (<i>o:p</i> = 22:78) ^b
Naphthalene	5	190 (<i>α:β</i> = 95:5)
1,4-Dimethoxybenzene	2	183
Mesitylene	65	42 ^c

^a Complete reaction. ^b 0.1 % *meta* isomer. ^c 3,5-Dimethylbenzaldehyde (7 %) and 3,5-dimethylbenzyl acetate (18 %) were also formed.

The isomer distribution in the silver(II) oxidative acetoxylation of aromatic compounds shown in Table 1 is similar to that obtained in anodic acetoxylation.¹¹ If the instability of the acetoxy radical¹² is also taken into account, it appears safe to conclude that the initial step in the oxidation of aromatic compounds by silver(II) in acetic acid is the transfer of one electron from the aromatic substrate to the silver(II) ion analogously to the corresponding anodic process.⁷ The proposed reaction sequence for the formation of acetoxyarenes compounds in the silver(II) oxidation is shown below. The same mechanism has been suggested



for several reactions involving oxidation by metal ions.^{1,13-19} It has been suggested that in aqueous systems the sulfate anion radical, which is an intermediate in the decomposition of peroxydisulfate ions,²⁰ reacts with aromatic compounds giving cation radicals.²¹ Although a similar reaction is possible in the acetic acid

system we consider it unlikely, since no acetoxy-aromatic compounds were formed when potassium peroxydisulfate was stirred in a mixture of acetic acid and an aromatic compound even at elevated temperatures. The effect of sodium acetate on the reaction rate is probably caused by its buffer capacity, since protons are produced in the reaction.

Our assumption that the peroxydisulfate ion reoxidizes silver(I) ions led us to investigate the possibility of running the reaction catalytically in silver(II) by using an excess of peroxydisulfate ion. Thus, when **1** was stirred in 0.5 M sodium acetate/acetic acid containing naphthalene in the presence of an excess of potassium peroxydisulfate * a mixture of α - and β -acetoxy-naphthalenes in a ratio of 95:5 was obtained in a 2700 % yield based on silver(II) and a 22 % yield based on peroxydisulfate, respectively. A similar oxidation of 4-methoxytoluene produced a mixture of 4-methoxybenzaldehyde and 4-methoxybenzyl acetate in a 4000 % yield (21 % based on peroxydisulfate).

We are currently investigating other silver(II) complexes than that used in the experiments described above. The tetrapyridine complex of silver(II) peroxydisulfate turned out to be an even stronger oxidant, but its use in acetic acid is limited due to oxidative decarboxylation of the solvent. We have also found that it is possible to acetoxy-ate aromatic compounds using silver(I) acetate in the presence of 2,2'-bipyridine and potassium peroxydisulfate.

Experimental. Compound **1** was prepared in the same way as the corresponding tetrapyridine complex. Acetic acid was frozen out twice before use. Other compounds were of high commercial purity. Reaction mixtures were analyzed by GLC with a Varian 1400 gas chromatograph on a 2.5 m \times 0.3 cm 5 % NPGS on Chromosorb W column or a 3 m \times 0.3 cm 10 % APL on Chromosorb P column. The products were identified by comparison with authentic samples. Yields were calculated by integration of the GLC peaks after calibration of the authentic samples against a standard.

A solution of the aromatic substrate (10 mmol) and the complex in 20 ml 0.5 M sodium acetate in acetic acid was stirred at room temperature. Ether was then added and the salts were filtered off. The filtrate was washed with water, dried over anhydrous sodium sulfate and analyzed by GLC. The results are shown in Table 1.

In the catalytic oxidations a suspension of $K_2S_2O_8$ (10 mmol), **1** (0.1 mmol), aromatic substrate (20 mmol), and 40 ml 0.5 M NaOAc/HOAc was stirred at room temperature during 17 h. The reaction mixture was worked up as above.

* The Ag(II) complex and potassium peroxydisulfate are practically insoluble in acetic acid.

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1. Nyberg, K. and Wistrand, L. G. *Chem. Scr.* 6 (1974) 234. Part III.
2. McMillan, J. A. *Chem. Rev.* 62 (1962) 65.
3. Anderson, J. M. and Kochi, J. K. *J. Amer. Chem. Soc.* 92 (1970) 1651.
4. Lee, J. B. and Clarke, T. G. *Tetrahedron Lett.* (1967) 415.
5. Syper, L. *Tetrahedron Lett.* (1967) 4193.
6. Azoo, J. A., Bacon, R. G. and Gupta, K. K. *J. Chem. Soc. C* (1970) 1975.
7. Ebersson, L. and Nyberg, K. *Accounts Chem. Res.* 6 (1973) 106.
8. Ebersson, L. and Jönsson, L. *Chem. Commun.* (1974) 885.
9. Rawlinson, D. J. and Sosnovsky, G. *Synthesis* (1973) 567.
10. Frønes, S. and Östman, C. O. *Acta Chem. Scand.* 10 (1956) 320.
11. Ebersson, L. *J. Amer. Chem. Soc.* 89 (1967) 4669.
12. Braun, W., Rajkenbach, L. and Eirich, F. R. *J. Phys. Chem.* 66 (1962) 1591.
13. Andrusis, Jr., P. J., Dewar, M. J. S., Dietz, R. and Hunt, R. L. *J. Amer. Chem. Soc.* 88 (1966) 5473.
14. Heiba, E. I., Dessau, R. M. and Koehl, Jr., W. J. *J. Amer. Chem. Soc.* 91 (1969) 6830.
15. Norman, R. O. C., Thomas, C. B. and Willson, J. S. *J. Chem. Soc. Perkin Trans. 1* (1973) 325.
16. Norman, R. O. C., Thomas, C. B. and Ward, P. J. *J. Chem. Soc. Perkin Trans. 1* (1973) 2914.
17. Elson, I. H. and Kochi, J. K. *J. Amer. Chem. Soc.* 95 (1973) 5060.
18. Kochi, J. K., Tang, R. T. and Bernath, T. *J. Amer. Chem. Soc.* 95 (1973) 7114.
19. Ledwith, A. and Russel, P. J. *Chem. Commun.* 1974 291.
20. House, D. A. *Chem. Rev.* 62 (1962) 185.
21. Walling, C. and Camaioni, D. M. *J. Amer. Chem. Soc.* 97 (1975) 1603.

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