

BISPYRIDINESILVER PERMANGANATE  $[Ag(C_5H_5N)_2]MnO_4$ : AN EFFICIENT OXIDIZING  
REAGENT FOR ORGANIC SUBSTRATES

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Summary Bispyridinesilver permanganate is an easily prepared crystalline relatively stable compound, soluble in organic solvents; its uses as an oxidizing agent of organic compounds in benzene are described.

Potassium permanganate in aqueous media is a commonly used oxidizing reagent in organic synthesis<sup>1</sup>. However, this reagent is unstable in aqueous solutions and many organic substrates are not soluble in aqueous media. To surmount these problems, several reagents; potassium permanganate dicyclohexyl-18-crown-6<sup>2</sup>, benzyl (triethyl) ammonium permanganate<sup>3</sup>, and tetrabutylammonium permanganate<sup>4</sup> are prepared and used in the oxidation of organic compounds. All of these reagents without exception are very strong oxidants with no selectivity.

Now we wish to report the use of bispyridinesilver permanganate as a mild and selective oxidant in the oxidation of organic substrates. Bispyridinesilver permanganate<sup>5</sup>, a purple crystalline compound is soluble in polar solvents such as acetone, chloroform, and dichloromethane. It however, slowly oxidizes these solvents. It is sparingly soluble in benzene, and very soluble in pyridine in which it is much more stable. The reagent is easily and cheaply prepared in good yield (90%) by adding pyridine (3 mole) to a solution of potassium permanganate (1 mole) in distilled water at 10°C, and adding silver nitrate (1 mole) in ten times its weight of distilled water. The purple crystalline precipitate is washed with cold-distilled water and then with dry benzene for several times and dried over anhydrous calcium chloride. This reagent can be stored for days in the absence of light. Analytically pure material<sup>6</sup> is obtained as purple needles by crystallization from acetone-benzene, m.p. (104-105°C) decomposed. The visible spectrum in pyridine,  $\lambda_{max}$  576( $\epsilon$  1780), 552( $\epsilon$  2730), 529( $\epsilon$  2790) 510( $\epsilon$  2130), 491( $\epsilon$  1410), 474( $\epsilon$  900), 458( $\epsilon$  660), is similar to that of permanganate in aqueous solution and the i.r. spectrum, like that of potassium permanganate<sup>7</sup> exhibits a strong band at 900  $cm^{-1}$ . This reagent to our observation is insensitive to hammer blows, but ignites at 80°C.

In a typical small scale reaction substrate (0.01 mole) is dissolved in dry benzene (25 ml) and dry oxidizing agent (0.01-0.02) mole is added in portion with stirring. After complete addition of oxidizing reagent the reaction mixture is refluxed for (0.25-2) hours. It is then filtered and the solid material washed with methylenechloride for several times.

The solvent is evaporated and the product purified by column chromatography (benzene, silica gel or carbontetrachloride, aluminum oxide).

Oxidative coupling of some aromatic amines<sup>8</sup> and production of orthoaldehydes from their corresponding alcohols are not efficient reactions with manganese dioxide<sup>9,10</sup>. With bispyridine-silver permanganate the yields of some of these reactions are improved drastically. The results of the experiments and some of those obtained by using manganese dioxide are tabulated in the tables (I and II).

To the synthetic organic chemist bispyridine-silver permanganate is a valuable addition to the presently available reagents. Investigation of the oxidizing ability of compounds with general formula  $[ML_n](MnO_4)_m$  are under way.

Table (I)

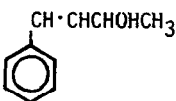
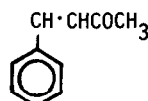
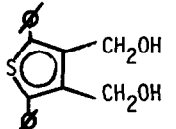
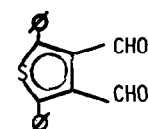
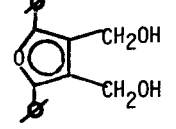
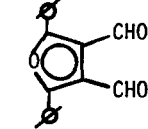
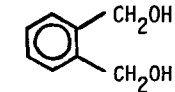
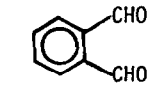

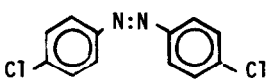

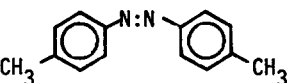
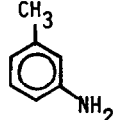
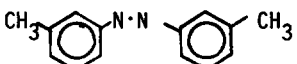
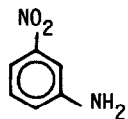
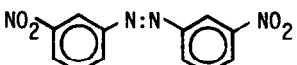
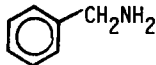
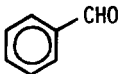
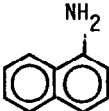
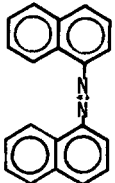
Substrate	Product <sup>a</sup>	Reaction time (hr) [Ag(PY) <sub>2</sub> ] <sub>2</sub> MnO <sub>4</sub>	Yield <sup>b</sup>	Reaction time (hr) MnO <sub>2</sub>	Yield
Benzyl alcohol	Benzaldehyde	0.5	100	3	26.7 <sup>11</sup>
Benzhydrol	Benzophenone	0.5	98	2	87 <sup>8</sup>
Piperonal	Piperonal	1	81	—	—
Citronellol	Citronella	1	90	—	—
Hydroquinone	Quinone	0.5	90	—	—
		1	80	—	—
		0.75	95	8	20 <sup>12</sup>
		1	90	16	20-40 <sup>9,10</sup>
		1	95	8	20 <sup>12</sup>

Table (II)

Substrate	Product <sup>a</sup>	Reaction time (hr) [Ag(PY) <sub>2</sub> ]MnO <sub>4</sub>	Yield <sup>b</sup>	Reaction time (hr) MnO <sub>2</sub>	Yield
		0.25	85	6	87 <sup>8</sup>
		1.5	89	6	87 <sup>8</sup>
		1.5	90	—	—
		1	85	24	0 <sup>8</sup>
		0.5	95	24	34 <sup>13</sup>
		2	40	24	0 <sup>8</sup>

<sup>a</sup>Products were characterized by comparison with authentic samples (i.r. spectrum, thin layer, and m.p.).

<sup>b</sup>All yields refer to isolated products.

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## REFERENCES AND FOOT NOTES;

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