

OXIDATION OF BENZENE AND ALKYL BENZENES BY XENON TRIOXIDE CATALYZED

Cr(VI) OXO COMPOUNDS OR Mn AND Fe PORPHYRIN COMPLEXES

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In previous work [1], we have used XeO_3 for the oxidation of aromatic and alkylaromatic compounds. A solution of 0.73 mole/liter benzene in 3.8:1 acetonitrile-water was oxidized by $0.85 \cdot 10^{-2}$ mole/liter xenon trioxide at 64°C over 5 h to $0.73 \cdot 10^{-2}$ mole/liter phenol. The reaction proceeds after a significant induction period, which is markedly reduced by the addition of $1.6 \cdot 10^{-4}$ mole/liter CrO_3 ($0.8 \cdot 10^{-2}$ mole/liter phenol is formed after 4 h in this case). The hydroxylation of benzene by XeO_3 is also induced photochemically at 20°C . The irradiation of a solution of 0.64 mole/liter benzene and $0.74 \cdot 10^{-2}$ mole/liter XeO_3 in 4.6:1 acetonitrile-water using the entire emission of a high-pressure 1000-W mercury lamp leads to the formation of $0.54 \cdot 10^{-2}$ mole/liter phenol over 3 h. The addition of CrO_3 accelerates the photochemical process. A total of $0.24 \cdot 10^{-2}$ mole/liter of a mixture of cresol isomers and $\leq 0.1 \cdot 10^{-3}$ mole/liter $\text{C}_6\text{H}_5\text{CHO}$ was formed in the oxidation of 0.60 mole/liter toluene by $0.82 \cdot 10^{-2}$ mole/liter XeO_3 in the presence of $1.55 \cdot 10^{-4}$ mole/liter CrO_3 at 64°C . Under the same conditions $\text{C}_6\text{H}_5\text{C}_2\text{H}_5$ gives $0.15 \cdot 10^{-2}$ mole/liter of a mixture of ring-hydroxylated ethylbenzene isomers and $0.9 \cdot 10^{-3}$ mole/liter acetophenone. In the presence of a tetraphenylporphyrin (TPP) complex, $2.0 \cdot 10^{-4}$ mole/liter TPPMnOCOCH_3 , 0.75 mole/liter ethylbenzene in 2.9:1 acetone-water is slowly oxidized (here and subsequently, over 290 h) by $1.0 \cdot 10^{-2}$ mole/liter xenon trioxide to $0.29 \cdot 10^{-2}$ mole/liter acetophenone. The yield of the ring-hydroxylated products did not exceed $0.86 \cdot 10^{-3}$ mole/liter. TPPMnCl in acetonitrile-water gives a somewhat lower yield of acetophenone ($0.17 \cdot 10^{-2}$ mole/liter). TPPFeCl in aqueous acetone is even less active and gives only $0.49 \cdot 10^{-3}$ mole/liter acetophenone. The oxidation of $\text{C}_6\text{H}_5\text{C}_2\text{H}_5$ in the absence of a catalyst gives only $0.32 \cdot 10^{-3}$ mole/liter acetophenone. Apparently, XeO_3 donates an oxygen atom [1-3] transferred by the metalloporphyrin catalyst to a substrate with C-H bonds.

LITERATURE CITED

1. A. E. Shilov and G. B. Shul'pin, *Usp. Khim.*, 56, 754 (1987).
2. R. H. Holm, *Chem. Rev.*, 87, 1401 (1987).
3. I. Tabushi, *Coord. Chem. Rev.*, 86, 1 (1988).