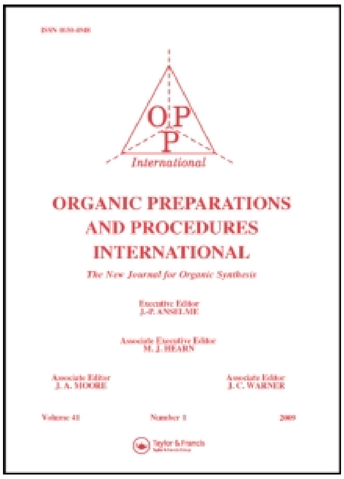

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THE SELECTIVE OXIDATION OF ETHYLBENZENES

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THE SELECTIVE OXIDATION OF ETHYLBENZENES

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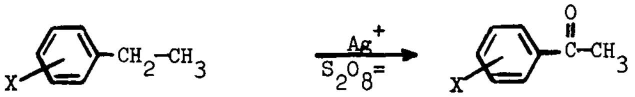
The silver ion/persulfate couple has been used as an oxidizing agent for alcohols,[1] amines,[2] and vic-glycols.[3] We report the use of this reagent to oxidize selectively ethylbenzene derivatives to the corresponding acetophenones in aqueous media. This method offers the advantage of using water as a solvent and only a catalytic amount of silver ion.



The oxidations were conducted by stirring an aqueous slurry of the hydrocarbon and silver ion/persulfate couple at 65-70°C. The reactions were usually complete in 2-3 hrs; p-methoxyethylbenzene was oxidized in 3 hrs at room temperature.

The use of co-solvents such as acetone, acetonitrile, dimethylformamide and dioxane was investigated. While they offered the advantage of a homogeneous reaction mixture, they significantly decreased the selectivity of the oxidation. In these solvent systems, complex mixtures of oxidation products were formed.

A 2:1 molar ratio of persulfate to hydrocarbon was optimum. The silver nitrate catalyst was used at a concentration of 1.25 to 2.5 mole per cent based on hydrocarbon.

The effect of substituents on the aromatic ring was examined (Table I). The data indicate that the reaction is facilitated by electron donating substituents. Evidence of oxidation of the nitro compounds was indicated by a small amount of carbonyl absorption in the crude reaction mixture, however, no acetophenone derivatives were isolated.

The conversion of hydrocarbon to ketone appears to be a clean reaction on the basis of glc data. In the case of ethylbenzene, a small amount (∿ 3%) of styrene was detected. This material was not isolated and it is possible that it could have polymerized during the reaction. Styrene derivatives were not detected in the other examples.

TABLE I

OXIDATION OF ETHYLBENZENE DERIVATIVES

$$X\text{-}C_6H_4CH_2CH_3 \longrightarrow X\text{-}C_6H_4COCH_3$$

X	% CONVERSION	% YIELD
H	90	73[a)]
p-OCH_3	> 95	80[b)]
p-Br	35	55[c)]
p-O_2CCH_3	53	62[d)]
p-NO_2	< 5	0
o-NO_2	< 5	0

a) bp 86-8°C (15 mm); b) 141-142°C (16 mm), mp 37-9°C;
c) mp 49-51°C; d) mp 52-4°C.

EXPERIMENTAL

The following procedures are representative of the oxidation method.

Preparation of Acetophenone

A mixture of 21.2 g. (0.2 mole) of ethylbenzene and 89.0 g. (0.4 mole) of ammonium persulfate in 400 ml of water was heated with stirring in an oil bath at 50-55°C. A solution of 0.8 g (0.005 mole) of silver nitrate in 2 ml of water was added. The internal temperature slowly rose to 70°C in 0.75 hrs, and was maintained between 65-70° for 2 hrs. The reaction mixture was cooled to room temperature and extracted with ether. The ether extract was dried (Na_2SO_4), filtered, and evaporated. The residual oil was distilled to give 2.1 g. (0.02 mole) of ethylbenzene bp 44-9° (15 mm) and 15.8 g (0.132 mole) of acetophenone bp 86-8° (15 mm). The yield was 73% based on recovered starting material. Glc analysis indicated the presence of $\sim$ 3% of styrene (identified by injecting an authentic sample of styrene).

Preparation of p-Methoxyacetophenone

A mixture of 13.7 g. (0.1 mole) of p-methoxyethylbenzene, 46.0 g. (0.2 mole) of ammonium persulfate and 0.4 g (0.0024 mole) of silver nitrate in 200 ml of water was stirred at room temperature. An exothermic reaction occurred and the internal temperature rose to 50°C. The mixture was then allowed to cool to room temperature. The total reaction time was 3.5 hrs. The product was extracted into chloroform. The extract was dried (Na_2SO_4) and evaporated to give a dark oil. The oil was distilled to give 11.9 g (0.079 mole), 79%, of product bp 141-2° (16 mm). The material solidified on standing mp 37-39°.

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