

FACILE CONVERSION OF ELECTRON RICH BENZYLIC HYDROCARBONS TO CARBONYL
COMPOUNDS BY PEROXYDISULPHATE AND COPPER IONS

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Abstract: A convenient method for the conversion of electron rich benzylic hydrocarbons to carbonyl compounds is reported.

We wish to report a new, facile and efficient conversion of electron rich benzylic hydrocarbons to carbonyl compounds by stoichiometric amounts of peroxydisulphate, in the presence of catalytic amounts of copper ions in aqueous acetonitrile medium, under nearly neutral conditions. The results are summarized in the Table 1.

There has been considerable mechanistic and synthetic **interest in** the reaction of single electron oxidants with aromatic substrates. Many of the reagents studied, like ceric ammonium nitrate (CAN)¹, manganic acetate (MA)², cobaltic acetate (CA)³, ceric trifluoro acetate (CT FA)⁴ and silver (II) complexes⁵ give an embarassingly complex mixture of products, with the possible exception of CAN. It is not surprising, therefore that barring a few exception not many synthetically useful procedures have resulted from the use of single electron oxidants.

Sometimes ago we had observed dramatic differences in the oxidising abilities of CAN⁶ and ceric ammonium sulphate (CAS)⁷, for the oxidation of aromatic substrates. By the simple expedient of using an unobstrusive anion, the yield of the quinone could be increased three to four fold with same substrates. A similar synthetically attractive procedure was developed with manganic sulphate (MS)⁸ (MA itself gives mixtures).

Pursuing the same line of reasoning we have explored the synthetic potentialities of peroxy disulphate - copper system under nearly neutral conditions in aqueous acetonitrile medium. This study, as well as the previous reports from this laboratory, emphasize the beneficial role of unobstrusive anions in keeping the product pattern simple. When, anions like acetate, trifluoroacetate are used, they give rise to a number of species of radicals, which themselves react with aromatic substrates to give a mixture of products.

While it would be premature to discuss the detailed mechanism, at this stage, the general pattern can be easily recognized. Peroxydisulphate radical formed thermally, converts Cu (II) to Cu (III) species, which in turn, oxidises the aromatic substrates to the cation radicals⁹. As is well known the cation radical undergo a variety of reactions, delicate balance among which is controlled by the acid strength of the medium, and by many other factors as well (scheme 1).

Table 1. Oxidation of electron rich benzylic hydrocarbons with peroxydisulphate - copper system ^{a,b}.

No.	Substrates ^c	Product ^d	Yield (%)
1.	p - Ethyl anisole	p - Methoxy acetophenone	86
2.	o - Ethyl anisole	o - Methoxy acetophenone	82
3.	p - n - Propyl anisole	p - Methoxy propiophenone	85
4.	6 - Methoxytetralin	6 - Methoxytetralone	45
		+	
		2 - Methoxynaphthalene	10
5.	p - Methoxytoluene	p - Methoxy benzaldehyde	70
		p - Methoxy benzoic acid	18
6.	o - Methoxytoluene	o - Methoxy benzaldehyde	64
7.	4 - Bromo - o - cresol methyl ether	5 - Bromo - 2 - methoxy benzaldehyde	51
8.	4 - Bromo - o - cresol ethyl ether	5 - Bromo - 2 - ethoxy benzaldehyde	50

a, The mole ratio of peroxydisulphate was 2.0

b, The mole ratio of copper sulphate was 0.2

c, The mole ratio of pyridine used in entries 5-8 was 2.0

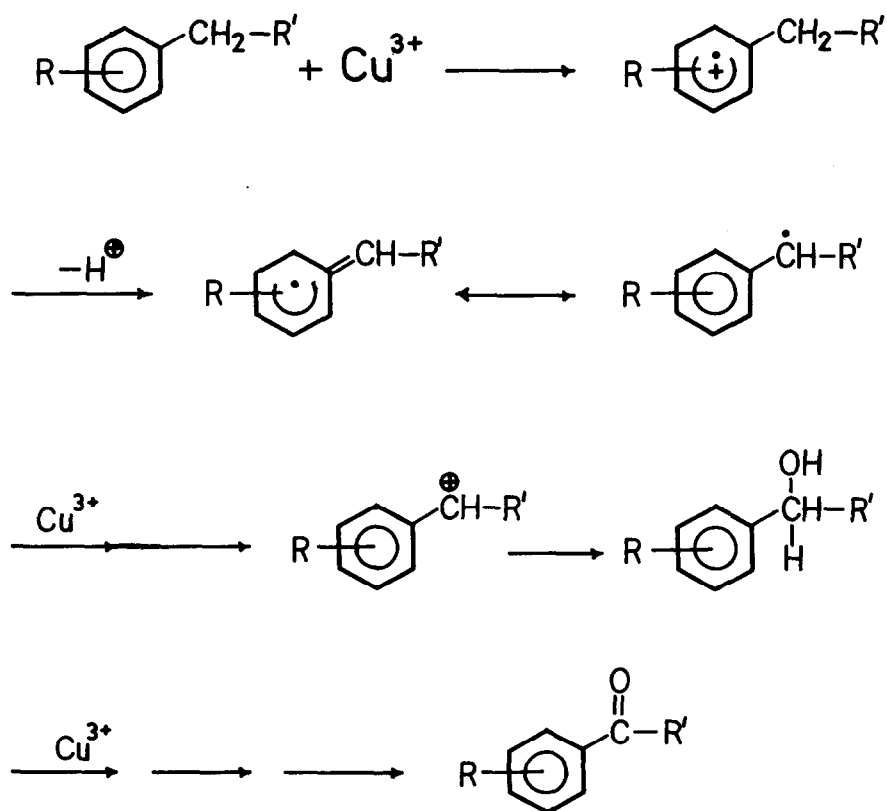
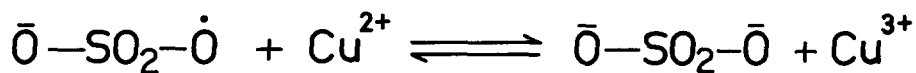
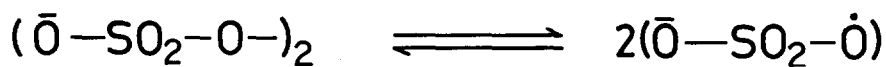
d, The products were isolated by preparative T.L.C.

[Silicagel/chloroform - hexane (40-60°) 1:3] and identified on the basis of their IR and NMR spectra.

Oxidation of p-Ethyl anisole : Typical preparative Scale Procedure:

A solution of p-ethylanisole (5.5 gm, ca. 40 mmol) in 140 ml of acetonitrile was added to a solution of potassium peroxydisulphate (21.6 gm, ca. 80 mmol) in 140 ml water and copper sulphate (2 gm, ca. 8 mmol). The resulting mixture was stirred at 65-70° for 3 hr. The reaction mixture was then extracted with ether and the ether extracts were washed (water), dried (sodium sulphate) and concentrated to give the crude product which was distilled under vacuum to give p-methoxy acetophenone (B.p 120-122° at 10 mm, m.p 37-38°). Yield 5.22 gm (86%) IR 1680 cm^{-1} NMR 2.4 s(3H), 3.9 s(3H), 6.9 d(2H), 7.8 d(2H) δ .

Scheme-1



Oxidation of p-Methoxytoluene : Typical small scale procedure :

A solution of p-methoxytoluene (0.49 gm, ca. 4 mmol) in 30 ml of acetonitrile was added to the solution of potassium peroxydisulphate (2.16 gm, ca. 8 mmol) in 20 ml of water and copper sulphate (0.2 gm, ca. 0.8 mmol). To the resulting solution pyridine (0.64 gm, ca. 8 mmol) was added and stirred at 65-70° for 3 hr. The reaction mixture was extracted with ether. From the ether extract, after removal of the solvent the crude material was obtained. The products were separated by TLC using 1:3 chloroform/hexane (40-60°). Yield p-methoxybenzaldehyde 0.387 gm (70%) IR 2735, 1695 cm⁻¹, NMR 3.95 s(3H), 6.95 d(2H), 7.75 d(2H) 9.85 s(1H) and p-methoxybenzoic acid 0.11 gm (18%) m.p. 182-183°.

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(Received in UK 27 August 1980)