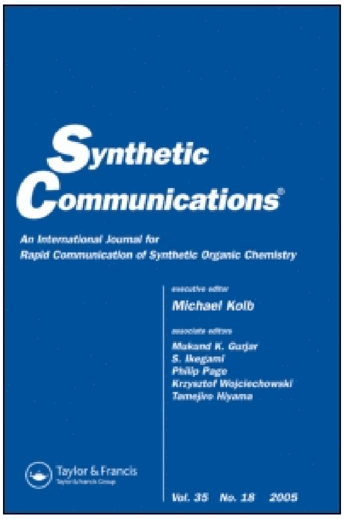

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Oxidation of Alkenes by Peroxydisulphate-copper Sulphate

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OXIDATION OF ALKENES BY PEROXYDISULPHATE-COPPER SULPHATE

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Abstract: A novel oxidative cleaved product and addition product were obtained from the oxidation of alkenes with peroxydisulphate-copper(II) systems.

Oxidation of benzylic hydrocarbons, eletron rich benzylic hydrocarbons and halophenols with peroxydisulphate in the presence of copper (II), iron (III), cobalt (II) and nickel (II) in aqueous acetonitrile or aqueous acetic acid or acetic acid was recently reported by Bhatt and Perumal[1-4], Walling et al.[5] and Minisci et al.[6]. In continuation of our studies with peroxydisulphate, now I wish to report a novel and efficient conversion of alkenes to carbonyl compounds and carboxylic acids by peroxydisulphate in the presence of copper sulphate in aqueous acetonitrile. The results are summarized in Table 1.

In some conditions, cyclohexene was oxidized by peroxydisulphate - copper (II) to afford cyclopentanecarboxaldehyde[6,7]. According to our standard conditions, reaction of cyclohexene with a 2 molar ratio of peroxydisulphate in 80% aqueous acetonitrile medium at 80°C gives 42% of cyclopentanecarboxaldehyde (1) and 25% of 1,2-cyclohexanediol cyclic sulphate (3), whereas by using a 3:1 molar ratio of peroxydisulphate and cyclohexene in 50%

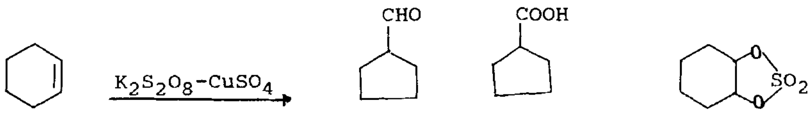
Table 1: Oxidation of alkenes with peroxydisulphate

Entry	Substrate	Products	Yield %
1	Cyclohexene	Cyclopentanecarboxylic acid 1,2-Cyclohexanediol cyclic sulphate	52 23
2	Cyclopentene[a]	1,2-Cyclopentanediol cyclic sulphate[b]	24
3	Cycloheptene	Cyclohexanecarboxlic acid	56
4	1-Phenyl-1-cyclohexene	4-Benzoyl-n-pentanoic acid	62
5	1-Phenyl-6-methyl-1-cyclohexene	4-Benzoyl-n-hexanoic acid	65
6	Styrene	Benzoic acid Benzaldehyde	52 18
7	α-Methylstyrene	Acetophenone	82
8	1,1-Diphenylethylene	Benzophenone	85

a, The reaction was carried out at 45°C with stirring for 3 h. then at 80°C with stirring for 3 h. b, ^1H NMR 1-2.1(m,6H), 5-5.2(m,2H), ^{13}C NMR 21.7, 31.85, 85.95.

aqueous acetonitrile medium at 80°C, 52% of cyclopentanecarboxylic acid (2) and 23% of addition product (3) are formed (Scheme 1).

SCHEME 1



1 2 3

The products were isolated and identified by GC, IR, proton and carbon-13 NMR.

We have proposed that copper (III) species are involved in the oxidation of aromatic substrates to aromatic cation radicals[1,3,4]. A plausible explanation for the formation of the products in the present study is that the alkenes are oxidized by a copper (III) species to cation radical which undergoes 1,3 dipolar addition reaction with sulphate radical anion to give addition product(3). The alkene radical cation or the addition product is further oxidized by either sulphate radical anion or copper (III) species to afford the oxidative cleavage product.

Oxidation of cyclohexene: Typical procedure

A solution of cyclohexene (4.1 g, 50 mmol) in 140 ml of acetonitrile was added to a solution of potassium peroxydisulphate (40.5 g, 150 mmol) in 140 ml of water and copper sulphate (4 g, 16 mmol). The resulting mixture was stirred at 80°C for 4 h. The organic layer was separated and the aqueous layer was extracted twice with ether. The combined organic extracts were dried over sodium sulphate and concentrated to give the crude products. The crude products were separated with saturated sodium carbonate solution and ether. The sodium carbonate portion was acidified with dilute hydrochloric acid and extracted with ether, dried and evaporated to give the crude acid. The crude acid was distilled under vacuum to give cyclopentanecarboxylic acid, Bp 130°C at 3 mm; yield 2.96 g (52%), ^{1}H NMR 1.5-2.0 (m, 8H), 2.4-2.9 (m, 1H), 11.9 (s, 1H), ^{13}C NMR 25.53, 29.67, 43.52, 183.29. The ether portion was dried and distilled under vacuum to give 1,2-cyclohexanediol cyclic sulphate , Bp 170°C at 3mm, yield; 2 g, (23%), IR 1770-1650 cm^{-1} ^{1}H NMR 0.9-2.6 (m, 8H), 5.5-5.8

(m,2H), ^{13}C NMR cis 19.62, 26.79, 82.42, Trans 22.61, 27.71, 87.72.

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