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Copper Catalyzed Oxidation of Tetralin to 1-(tert-Butylperoxy)-Tetralin by Aqueous tert-Butylhydroperoxide Under Phase Transfer Conditions.

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Abstract: Selective α- peroxidation of tetralin by TBHP is catalyzed by copper salts with the aid of quaternary ammonium compounds in an aqueous-organic biphasic system.

Dialkyl peroxides are important components in the polymer industry serving as radical initiators in polymerization, cross linking and curing processes[1]. Other functions of dialkyl peroxides in organic synthesis focus on the oxyfunctionalization of organic substrates and the induced decomposition of the peroxides which have synthetic applications [2,3].

The metal ion -prompted decomposition of alkyl hydroperoxides can be utilized as a method for introducing the alkylperoxy group into various substrates [2,4].

Tert-butylperoxidaion of tertiary benzylic carbon (ArCHRR') was firstly proposed by Kharasch[4] who reported the reaction of TBHP with Cumene in the presence of copper, cobalt or manganese salt at 70°C to afford tert-butyl-1-cumyl peroxide. This system suffers from a parallel non productive catalytic decomposition of TBHP which causes rather low yields of the peroxide product.

Muzart recently reported a t-butylperoxidation of tertiary benzylic carbon, triphenylmethane, with aqueous TBHP catalyzed by chromium oxide[5]. Low selectivity (37%) to t-butylperoxy-1,1,1-triphenylmethane was observed.

Only small amounts (1%-5%) of t-butylperoxy tetralin were obtained in oxidation of tetralin in the above system[6]. It has been stated that secondary dialkyl peroxides are not stable in the oxidation conditions and consequently give rise to carbonyl compounds[7].

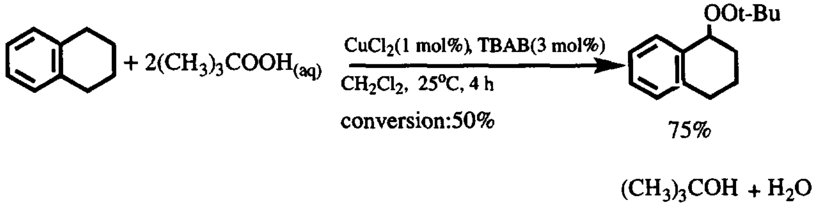
We have now found that by using an aqueous/organic two phase system at room temperature, and in the presence of quaternary ammonium phase transfer catalyst, copper salts are active catalyst precursors which generate an active catalytic system for the TBHP peroxidation of tetralin. 1-(tert-Butylperoxy)-tetralin was obtained in good selectivity. No unproductive decomposition of TBHP was observed.

We have previously proposed this novel catalytic system for the selective oxidative dehydrogenation of alcohols[8].

In a typical procedure we have mixed 3.43 g of tetralin (26.2 mmol) in 10 ml methylene chloride with 3.40 g of TBHP (70% in water, 26.2 mmol) in the presence of 0.28 g tetra-n-butylammonium bromide (TBAB)(0.79 mmol,3 mol%) and 35.2 mg $CuCl_2$ (0.26 mmol, 1 mol%) at 25°C for 4 h. Quantitative GC analysis of the reaction mixture showed 50% conversion of tetralin with 75% selectivity to 1-(tert butyl peroxy)- tetralin (eq.1). Other products were 1-tetralone, small amounts of 1-tetralol, naphthalene and 1,2,3,4-tetrahydro-1-keto-4-hydroxy naphthalene.

All the reaction products were positively identified by GCMS and by comparison with authentic standards. The reaction proceeds according to the following equation (eq.1).

(1)



Using 2:1 ratio of TBHP to tetralin, as the stochiometry of the reaction demands, led to higher conversion but with poorer selectivity for 1-(tert-butylperoxy)-tetralin.

1-(tert-Butylperoxy)-tetralin can be purified by flash chromatography using silica gel 60 (Merck ,particular size 0.040-0.063 mm) and a gradient of petroleum Ether/EtOAc (100 to 90/10) as a carrier. over 90% yield of 1-(tert-butylperoxy)-tetralin was obtained. 1-(tert-Butylperoxy)-tetralin was identified by comparison of It's spectral data with those of the literature values^5.

Total oxidation rate as well as product selectivity were found to be rather sensitive to the reaction conditions. The presence of both catalysts was essential.

No reaction was detected in the absence of copper and less than 8% conversion was monitored without the TBAB under the conditions of reaction (1).

Similar conversions and selectivities were obtained by modifying the amounts of the catalysts (1-3 mole% $CuCl_2$ with 1.8 mole% TBAB and 0.5-3 mole% TBAB with 1 mole% $CuCl_2$).

Subjecting the dialkyl peroxide product to the same reaction conditions, in the presence of an excess of aqueous TBHP, indicate that 1-(tert-butylperoxy) tetralin is a potential intermediate to tetralone and di-oxidation products when using an excess of TBHP . Thus, an excess of aqueous TBHP led to higher conversions but lower selectivity to 1-(tert-butylperoxy)- tetralin. In addition dihydroxy-naphthalene and naphthoquinone were also obtained in considerable amount (about 10% each). The choice of the organic solvent has substantial influence on the peroxidation efficiency and selectivity of tetralin. Best results were achieved in aqueous-methylene chloride two phase system. With other solvents e.g acetic acid,THF,CH_2Cl_2, in the absence of water , Hexane-H_2O, lower rate, conversion and selectivity were found.

Similar observations were found when indane was exposed to the conditions of reaction (1). The major product was 1-(tert-butylperoxy)- indane which was produced in 70% selectivity after 6 h with 50% conversion of indane.

In view of literature data^9 we envisage a mechanism based on simple redox steps between copper salts and free radical intermediates (scheme 1).

$$(1)\quad Cu(II) + t\text{-}BuO_2H \longrightarrow Cu(I) + t\text{-}BuO_2 + H^+$$

$$(2)\quad Cu(I) + t\text{-}BuO_2H \longrightarrow Cu(II)OH + t\text{-}BuO$$

$$(3)\quad Cu(II)OH + t\text{-}BuO_2H \longrightarrow Cu(II)O_2Bu\text{-}t + H_2O$$

$$(4)\quad t\text{-}BuO + RH \longrightarrow t\text{-}BuOH + R$$

$$(5)\quad R + Cu(II)O_2Bu\text{-}t \longrightarrow RO_2Bu\text{-}t + Cu(I)$$

scheme 1

First, formation of Cu(I) by oxidation of TBHP by Cupric salt (step no.1). Second, reduction of TBHP by cuprous salt to oxy radical (step no.2). Third, chain transfer reaction between oxy radical intermediate and hydrogen donor substrate (step no. 4). Fourth, Cupric salt oxidation of carbon type radical formed in the chain transfer step (step no.5).

Oxidation of diphenylmethane and fluorene in the above system resulted mainly in formation†of the corresponding ketones. Only low quantity (5%) of tert-butyl peroxidation of benzylic group have been observed from these starting compounds. We believe that 1-(tert-butylperoxy)- fluorene and 1-(tert-butylperoxy)- diphenyl methane are potential intermediates in the oxidation of fluorene and diphenyl methane to the corresponding carbonyl compounds. The absence of those peroxides in considerable amount can be attributed to their more active benzylic hydrogen subjected to abstraction by an oxy free radical in the oxidizing system.

The importance in synthetic applications of these peroxides lies on their ability to decompose to valuable compounds[10].

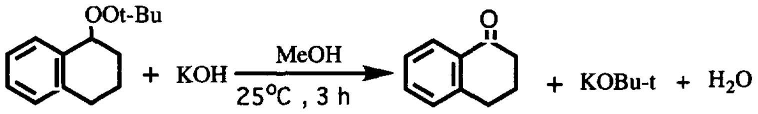
We have investigated the decomposition of 1-(tert-butylperoxy)- tetralin in various conditions. Thus, when 1-(tert-butylperoxy)- tetralin was subjected to catalytic amount of $CuCl_2$ and TBAB in dichlorobenzene at 60°C, 78% conversion was achieved in 2 h leading to 68% selectivity of 1-tetralone and 32% selectivity of 1-tetralol. No transformation of the dialkyl peroxide is detected in the absence of TBAB. Application of TBAB as a single catalyst led to the same transformation but with a considerably lower efficiency.

Subjection of 1-(tert-butylperoxy)- tetralin to concentrated H_2SO_4 at 10°C[11] led to 100% conversion in 15 min with 77% yield of 1-tetralone and 23% yield of 1,2- tetralene.

Primary and secondary dialkylperoxides are well known to decompose with the generation of ketone and alkoxy anion in the presence of bases such as potassium hydroxide, sodium ethoxide or piperidine[12]. We obtained the best results when subjecting the dialkylperoxide to basic catalysis.

Upon mixing 2.88 g of 1-(tert-butylperoxy)- tetralin with 3.67 g KOH dissolved in 20 ml methanol at room temperature for 3 h, we found 92% conversion to tetralone with 100% selectivity. The reaction could be continued to 100% conversion of 1-(tert-butylperoxy)- tetralin. Tetralone then can be purified by it's simple extraction to organic solvent followed by It's distillation (0.3 mm, 65°C-70°C) for further purification. The reaction proceeds according to the following equation (eq.2).

(2)



Combining the two methods provides a highly selective two stage procedure for preparing tetralone. The first stage is oxidation of tetralin with aqueous TBHP (1:1 ratio of TBHP to Substrate) in the presence of $CuCl_2$ and TBAB, in methylene chloride at 25°C. Followed by the decomposition of 1-(tert-butylperoxy)- tetralin under basic conditions.

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