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New Catalysts for the Conversion of Cumene Hydroperoxide into Phenol

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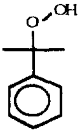
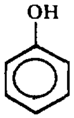
Abstract: *Several copper and iron salts are good catalysts for the conversion of cumene hydroperoxide into phenol.* © 1997 Published by Elsevier Science Ltd.

The conversion of cumene hydroperoxide into phenol under acidic conditions, is an important industrial process.[1] In the recent patent literature, new acid based procedures are still reported.[2,3]

The conversion of cumene hydroperoxide into acetophenone and cumyl alcohol under the influence of simple copper or iron salts is also a well known phenomenon.[4,5] There are not many examples of metal catalysed reactions where phenol is formed,[3,6] and relatively high temperatures are often involved.

We first studied the reaction of cumene hydroperoxide with $Cu(ClO_4)_2 6H_2O$ in acetonitrile (30 mL), expecting to see fragmentation into acetophenone and methyl radicals. However, the product was phenol[7] in high yield (**Table 1**).

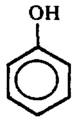
Table 1: Formation of phenol in presence of $Cu(ClO_4)_2 6H_2O$

	Cu^{II}		Yield %	$t_{1/2}$	Turn over
0.50	0.50	0.41	82	60'	0.82
1.00	0.10	0.925	92.5	30'	9.25
1.00	0.05	0.89	89	20'	17.8
5.39	0.10	4.52	80	45'	45.2

The solvent acetonitrile has a major influence on the reaction. The addition of pyridine (2mL) or water (2 mL) completely inhibits the reaction. Likewise, ethanol and THF as solvents behaved in the same way.

The fragmentation of cumene hydroperoxide was especially efficient and fast with a variety of iron salts (**Table 2**). The reactions were carried out at room temperature, but decreasing the temperature to 0°C also permitted fast reactions ($t_{1/2}$ about 30 min).

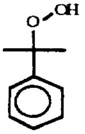
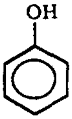
Table 2: Decomposition of the hydroperoxide with different iron salts.

iron salts		half life ($t_{1/2}$)
$Fe(ClO_4)_3$ n H_2O	1.01	< 5 min
$FeCl_3$	1.0	< 5 min
$Fe(ClO_4)_2$	1.1	< 5 min
$FeCl_3$, 2 CH_3CN[8]	0.97	< 5 min

Cumene hydroperoxide 1 mmol, iron salt 0.1 mmol, CH_3CN 30 mL at room temperature.

Using Fe^{III} perchlorate, the reaction gave impressive turn-overs of nearly one thousand (**Table 3**).

Table 3: Use of catalytic amount of $Fe^{III}(ClO_4)_3$ nH_2O

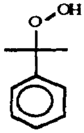
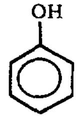
Fe^{III}			yield %	Turn over
0.10	1.0	0.91	91.0	9.1
0.01*	1.08	1.04	95.6	104
0.10	9.29	8.61	92.7	86.1
0.01*	10.2	9.31	91.0	931

* A solution of iron salt (0.01 mmol) in acetonitrile was prepared (25 mL). 1 mLof the previous solution is added to the cumene hydroperoxide in solution in 29 mL of acetonitrile.

The volume of solvent could be decreased to 10 mL of acetonitrile. With less solvent, the reaction is exothermic and even explosive (**Table 4**, entries 8 and 9), and the yields decreased.

Other solvents were also examined. Methylene dichloride was comparable to acetonitrile and toluene also gave an excellent yield of phenol.

Table 4: Variation of the amount of solvent

Entry	Fe^{III}		CH_3CN		Yield %	Turn over
1	$Fe(ClO_4)_3nH_2O$ 0.01 mmol	1.08 mmol	30 mL	1.04 mmol	96.3	104
2	$Fe(ClO_4)_3nH_2O$ 0.01 mmol	1.10 mmol	10 mL	1.01 mmol	91.8	101
3	$Fe(ClO_4)_3nH_2O$ 0.01 mmol	1.00 mmol	5 mL	0.92 mmol	92	92
4	$Fe(ClO_4)_3nH_2O$ 0.01 mmol	10 mmol	30 mL	9.31 mmol	93.1	931
5	$Fe(ClO_4)_3nH_2O$ 0.01 mmol	10 mmol	10 mL	9.63 mmol	96.3	963
6	$FeCl_3$ 0.01 mmol	1.00 mmol	1 mL	0.94 mmol	94	94
7	$FeCl_3$ 2 CH_3CN 0.01 mmol	1.00 mmol	1 mL	0.88 mmol	88	88
8	$FeCl_3$ 2 CH_3CN 0.01 mmol	5.00 mmol	1 mL	0.27 mmol	5.4	27
9	$FeCl_3$ 2 CH_3CN 0.01 mmol	1 mmol	0 mL	0.17 mmol	17	17

In the fragmentation of cumene hydroperoxide, the second product is acetone. It would, therefore, be advantageous to use this solvent for the reaction. As shown in **Table 5**, the reaction proceeds in acetone more slowly than in acetonitrile, but the yields are comparable. If 0.1 mmol of ferric chloride is added in acetone, then the $t_{1/2}$ returns to 5 minutes.

Table 5 : amount of acetone

Volume of acetone (x)	phenol	$t_{1/2}$	Yield %	Turn over
3 mL	0.89	45'	98.05	89
5 mL	0.96	60'	98.9	96
10 mL	0.95	60'	91	95

Cumene hydroperoxide 1 mmol, $FeCl_3$ 0.01 mmol, Acetone x mL, at room temperature.

This method is an efficient way to produce phenol from the cumene hydroperoxide under mild conditions. Actually, 1 mmol of the cumene hydroperoxide is converted into phenol with 100% yield in the following simple and mild conditions: 0.1 mmol of $FeCl_3$ in 5 ml of acetone, at room temperature, in less than 5 minutes.

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REFERENCES

1 - Kislina, I.S.; Sysoeva, S.G., Vinnik, M.I.; Bushmakin, L.G. *Kinet. Katal.* **1990**, *31*, 535-539. *Ibid*, **1989**, *30*, 229-232.
2 - Zakoshansky, V.M.; Griaznov, A.K. *Eur. Pat. Appl EP* **1995**, 670, 296.
3 - Blackbourn, R.L.; Allan, E.D.; Le, L.B.; Patel, S. **1996**, *U.S. US* 5, 463, 136.
4 - Kochi, J.K. *J. Am. Chem. Soc.* **1963**, *85*, 1958-1968. Immamura, S.; Fukumoto, K. *Nippon Kagaku Kaishi*, **1973**, *3*, 573-8. Emanuel, O.N.; Kitaeva, D.Kh; Skibida, I. P. *Izv. Akad. Nauk. SSR. Ser. Khim*, **1976**, *1*, 46-50. Barton, J.; Horanska, V. *Makromol. Chem.* **1972**, *157*, 87-101. Casemier, J.H.; Nieuwenhuys, B.E.; Sachtler, W. M. H. *J. Catal.* **1973**, *29*, 367-373.
5 - Chenier, J.H.B.; Howard, J.A.; Tait, J.C. *Can. J. Chem.* **1977**, *55(10)*, 1644-1652.
6 - Klyueva, N.D.; Muratova, G.E.; Kushlinskii, A.I.; Sokolov, A. V. *Zh. Anal. Khim.* **1967**, *22(2)*, 29-40. Kurusu, Y.; Matsumura, Y.; Ishii, N. *Nippon Kagaru, Kaishi*, **1979**, *3*, 383-388. Cornelia, I.; Maria, B.; Carpen, A. *Rev. Chim.* **1984**, *35(2)*, 109-116. Timofeev, S.V.; Smirnova, A.L.; Blyumberg, E.A. *Kinet. Katal.* **1991**, *32(6)*, 1371-1376.
7 - In order to prove that the product was really phenol, a derivative from 2,4-dinitrobenzoic acid was synthetized and compared with an authentic sample. To 30 mL of acetonitrile containing 0.1 mmol of $Fe(ClO_4)_3nH_2O$, cumene hydroperoxide (10.4 mmol) was added. At the end of the reaction, the mixture was poured into a saturated solution of $NaHCO_3$ and extracted with ether. The organic phases were dried over $MgSO_4$, filtered and concentrated by rotavapor. The product obtained was put in solution with dicyclohexyl carbodiimide (1.05 eq) in anhydrous THF (30 mL) at 0°C. 2,4-Dinitrobenzoic acid (1 eq) in solution in THF was added dropwise. The reaction mixture was stirred overnight at room temperature. The precipitate was filtered over silica. The filtrate was concentrated by rotavapor. The residue was recrystallised twice from hot methanol. Yellow crystals were obtained: yield, 90% (crude), 29 % (recrystallised); mp= 123-129°C, ^1H NMR ($CDCl_3$), 8.89 (d, 1H), 8.575 (d, 1H), 8.05 (d, 1H), 7.22-7.45 (m, 5H); ^{13}C NMR ($CDCl_3$), 119.86, 120.957, 126.9, 127.952, 129.79, 131.415, 132.5, 150.019, 162.238; IR (KBr) 1745.66 cm-1 ($\gamma_{C=O}$).
The authentic sample prepared in the same way, from the commercial phenol, give a yellow crystalline compound with the same caracteristics. The mixed melting point of the two products was 122-130°C.
8- Hathaway, J.; Holah, D.G. *J. Chem. Soc.* **1964**, 2408.

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