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Tetrahedron Letters

Tetrahedron Letters 46 (2005) 8013–8015

A novel and selective catalytic oxidation of hydrocarbons to ketones using chloramine-T/O_2/Fe(TPP)Cl system

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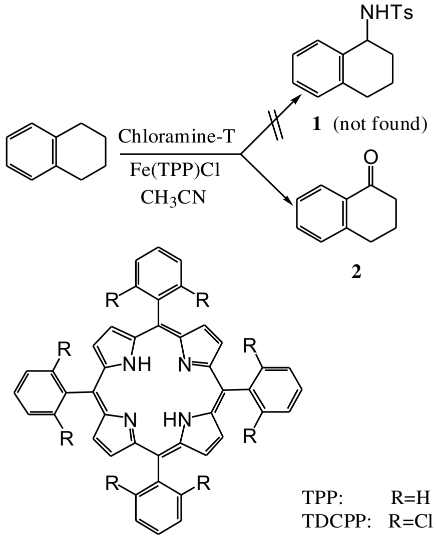
Received 28 July 2005; revised 9 September 2005; accepted 12 September 2005
Available online 26 September 2005

Abstract—A novel and highly selective oxidation of hydrocarbons to the corresponding ketones using the Fe(TPP)Cl/chloramine-T/O_2 system was described.

Catalytic oxidation of hydrocarbons to alcohols or carbonyls is an important transformation in both organic synthetic chemistry and industry.[1] A number of oxygenation systems composed of a variety of oxygen donors such as Bu_4NHSO_5,[2] $PhI(OAc)_2$,[3] PhIO,[4] NaOCl,[5] H_2O_2,[6] pyridine *N*-oxide[7] and periodates,[8] in combination with different metalloporphyrin catalysts have been employed for the oxidation of hydrocarbons. Metalloporphyrins promoted oxidations of alkanes with oxygen and acetaldehyde have also been reported.[9] However, these metalloporphyrins-catalyzed methods usually give the mixture of alcohols and carbonyls. In addition, most of the other traditional metallic and metal-free organic catalysts used for oxidation of hydrocarbons could not yield single product, neat alcohols or carbonyls.[10] Recently, we found that chloramine-T combined with air or oxygen as an oxidant could selectively convert hydrocarbons to ketones using metalloporphyrins as a catalyst at room temperature, and no alcohol was detected in this oxidation system. To the best of our best knowledge, it is the first example for oxidation of alkanes using chloramine-T. Herein, we disclose the results of this research.

Originally, we intended to amidate tetralin with chloramine-T as a nitrene source via metalloporphyrin catalyzed aziridination of alkenes and amidation of saturated C–H bonds.[11] However, when the Fe complex of *meso*-tetrakisphenyl porphyrin (TPP) was used as the catalyst, an oxidation product tetralone (**2**) instead of the amidized product **1** was obtained (Scheme 1). It is well known that chloramine-T is not only an aziridination and amidation reagent, but also an efficient oxidant in many reactions.[12]



Scheme 1. Oxidation of tetralin.

Encouraged by this result, we examined the catalytic activity of several metalloporphyrins derived from TPP and *meso*-tetrakis(2,6-dichloro-phenyl)porphyrin (TDCPP) for the aerobic oxidation of tetralin using chloramine-T.[13] As shown in Table 1, the catalytic activity of porphyrin complexes was strongly dependent upon both central metal and ligands. The Fe and Mn complexes with porphyrin ligands showed better catalytic activity (Table 1, entries 2, 3 and 7–11) than

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doi:10.1016/j.tetlet.2005.09.055

Table 1. Oxidation of tetralin catalyzed by different metalloporphyrins with chloramine-T under air[a]

Entry	Catalyst	Solvent	Yield (%)[b]
1	None	CH_3CN	5
2	Mn(TPP)Cl	CH_3CN	77
3	Fe(TPP)Cl	CH_3CN	81
4	Co(TPP)	CH_3CN	43
5	Ni(TPP)	CH_3CN	40
6	Ru(TPP)CO	CH_3CN	57
7	Mn(TDCPP)Cl	CH_3CN	50
8	Fe(TDCPP)Cl	CH_3CN	58
9	Fe(TPP)Cl	CH_2Cl_2	9
10	Fe(TPP)Cl	THF	16
11	Fe(TPP)Cl	DMSO	38

[a] Tetralin (2 mmol) was oxidized by chloramine-T (1 mmol) and air (1 atm) in the presence of metalloporphyrins (5 mol %) in solvent (5 mL) at room temperature for 24 h.

[b] Yields were determined by GC analyses based on tetralin used.

the corresponding Co, Ni and Ru complexes (Table 1, entries 4–6). The complex Fe(TPP)Cl in acetonitrile was found to be the most effective catalyst (Table 1, entry 3). The Fe and Mn complexes of chlorinated porphyrin ligand had lower catalytic activity due to their slight solubility in acetonitrile. The solvent effects were also investigated. Acetonitrile was superior to other solvents due to its good solubility to chloramine-T.

The reaction conditions are further optimized, and the results were summarized in Table 2. Both chloramine-T (Table 2, entry 1) and air or molecular oxygen (Table 2, entry 2) were found to be necessary to this oxidation system. Increasing the amount of chloramine-T from 0.2 to 0.5 equiv could increase the yields (Table 2, entries 3–6), but further increase led to a significant reduction in the yields (Table 2, entries 7–9). The amount of catalyst was also examined. Fe(TPP)Cl (5–10 mol %) was found to be the most effective (Table 2, entries 5, 10 and 11). The temperature had no obvious effect on the reaction (Table 2, entries 5 and 12).

Table 2. Oxidation of tetralin with different amounts of Fe(TPP)Cl and chloramine-T[a]

Entry	Chloramine-T amount (mol equiv)	Fe(TPP)Cl amount (mol equiv)	Yield[b] (%)
1	0	0.05	3
2	0.5[c]	0.05	11
3	0.2	0.05	42
4	0.4	0.05	69
5	0.5	0.05	81
6	0.5[d]	0.05	84
7	0.6	0.05	72
8	0.75	0.05	68
9	1.0	0.05	54
10	0.5	0.01	55
11	0.5	0.10	87
12	0.5[e]	0.05	82

[a] Typically tetralin (2 mmol) was oxidized with different amounts of chloramine-T and Fe(TPP)Cl under air atmosphere (1 atm) in acetonitrile (5 mL) at room temperature for 24 h.

[b] Yields were determined by GC analyses based on tetralin used.

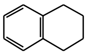
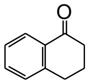
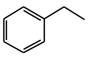
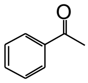
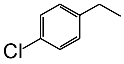
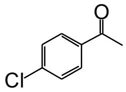
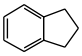
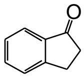
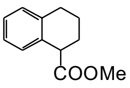
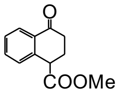
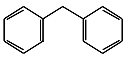
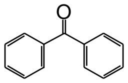
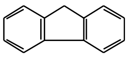
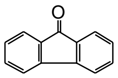
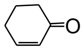
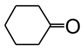
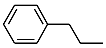
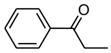
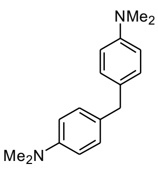
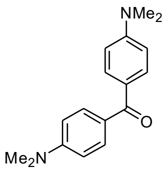
[c] Reaction under N_2 atmosphere.

[d] Reaction under O_2 atmosphere.

[e] Reaction at 80 °C.

Using the optimized reaction conditions, the catalytic oxidation of various hydrocarbons was investigated. As shown in Table 3, tetralin and other aryl-substituted alkanes were oxidized into the corresponding aromatic ketones in good conversions (Table 3, entries 1–7, 11 and 12). The oxidation of toluene gave benzaldehyde (26% conversion) along with a small amount of benzoic acid (Table 3, entry 8). The oxidation of cyclohexene offered cycohexenone in moderate conversion (52%) (Table 3, entry 9). Although inactive cyclohexane only gave 13% conversion, the result had a significant improvement compared with the industrial process (about 3–7% conversion).[14] It was noteworthy that no alcohol was detected in all cases.

Table 3. Oxidation of different hydrocarbons using the chloramine-T/O_2/Fe(TPP)Cl system[a]

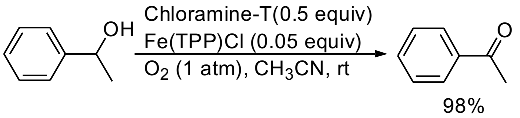
Entry	Substrate	Product	Yield (%)
1			83[b,d] 87[c]
2			67[c]
3			63[b]
4			78[b]
5			72[b]
6			84[b]
7			86[b]
8	$PhCH_3$	PhCHO $PhCO_2H$	23[c] 3[c]
9			52[c]
10			13[c]
11			62[b]
12			71[b]

[a] Typically reactions were carried out with substrate (2 mmol), chloramine-T (1 mmol) and Fe(TPP)Cl (5 mol %) in acetonitrile (5 mL) under O_2 atmosphere (1 atm) at room temperature for 24 h.

[b] Isolated yields.

[c] Yields was determined by GC analyses based on substrates used.

[d] Reaction for 48 h.



Scheme 2. Oxidation of 1-phenylethanol.

We also tested the activity of the chloramine-T/O_2/Fe(TPP)Cl system for oxidation of alcohol to carbonyl. As shown in Scheme 2, 1-phenylethanol could be transformed almost quantitatively into 1-phenylethanone.

In conclusion, we have developed a novel and efficient oxidation system for the selective oxidation of hydrocarbons to ketones. Using the chloramine-T/O_2/Fe(TPP)Cl system, aryl- or vinyl-substituted alkanes could be oxidized to the corresponding benzylic and ketones in good yields with excellent selectivity.

Acknowledgements

Authors would like to thank the National Natural Science Foundation of China (No. 20272051) as well as the Teaching and Research Award Program for Outstanding Young Teachers in Higher Education Institutions of MOE, PR China.

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