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Tetrakis(pyridine)silver(II) Peroxodisulfate, $[Ag(py)_4]S_2O_8$, a Reagent for the Oxidative Transformations

Habib Firouzabadi,* Peyman Salehi, and Iraj Mohammadpour-Baltork
Chemistry Department, Shiraz University, Shiraz, Iran
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Synopsis. Tetrakis(pyridine)silver(II) peroxodisulfate oxidizes aromatic aldehydes to carboxylic acids, benzylic alcohols to carbonyl compounds, aromatic thiols, and allylaryl thioethers to arylsulfonic acids and benzylic carbon–hydrogen bonds to carbonyl groups. α-Hydroxycarboxylic acids and phenylacetic acids are decarboxylated to produce carbonyl compounds. Dibenzyl ether and its sulfur analogue are converted to their corresponding ester and the thioester, respectively.

Peroxodisulfate ion $S_2O_8^{2-}$ is a strong oxidant with a redox potential equal to 2.01 volts in aqueous solution. The kinetics and the mechanism of peroxodisulfate oxidations have been extensively studied and reviewed.[1)] Electron-transfer processes and the effects of counter cations: Ag^+, Cu^{2+}, Pb^{4+}, Co^{2+}, Mn^{2+}, Ce^{3+}, Fe^{3+}, Fe^{2+}, Ni^{2+} have been also investigated.[1—9)] Conversion of aliphatic ketones to diketones,[10)] fragmentation of phenyl-substituted alcohols and ethers,[11)] oxidations of nucleic acid bases[12)] and carboxylic acids,[13)] aromatic hydroxylation,[14)] oxidation of unsaturated aliphatic and alkylaryl alcohols,[15)] and alkenes,[16,17)] acetoxylation of methylbenzenes,[18)] oxidation of thymines,[19,20)] and allyl alcohols[9)] and also conversion of electron-rich benzylic hydrocarbons to carbonyl compounds[21)] are mostly performed in aqueous acidic or basic solutions in the presence of $S_2O_8^{2-}$ ion.

In recent years we have introduced reagents which are effective for the oxidative transformation of several functional groups in organic solvents and most of them are performed under aprotic conditions.[22—29)] In a recent communication, we have reported that tetrakis(pyridine)silver(II) peroxodisulfate is an effective oxidant for the oxidation of benzylic carbon–hydrogen bonds in acetonitrile.[30)]

In this paper we report the potential of this reagent for the oxidation of several classes of organic compounds.

Results and Discussion

Tetrakis(pyridine)silver(II) peroxodisulfate was easily prepared from aqueous solution of silver nitrate, potassium peroxodisulfate, and pyridine.[31)] Reactions with this reagent were performed well in dry acetonitrile or in acetonitrile in the presence of a catalytic amount of water (1 : 20) at room temperature or under reflux conditions. The other solvents such as benzene and dichloromethane could be used but the yields and the rates of the reactions were lower. Oxidation of benzylic methyl and methylene groups proceeded well with this reagent in acetonitrile with a catalytic amount of water at room temperature or in dry acetonitrile under reflux conditions. Tetrakis(pyridine)silver(II) peroxodisulfate oxidizes benzylic methyl and methylene groups in both activated and non-activated aromatic compounds to give carbonyl groups (Table 1, Entries 1—10). Ben-

Table 1.

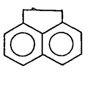
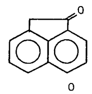
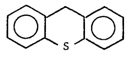
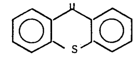
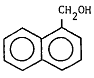
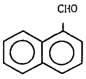
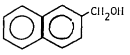
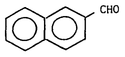
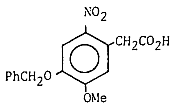
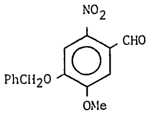
Entry	Substrate	Product	mp or bp/°C[32,33)]	Reaction time/h	Oxidant/Substrate	Yield/%[a,b)]
1	Toluene	Benzaldehyde	175—178	3	3	85
2	*p*-Bromotoluene	*p*-Bromobenzaldehyde	55—58	7	3	90
3	*o*-Bromotoluene	*o*-Bromobenzaldehyde	—	7	3	60
4	*p*-Nitrotoluene	*p*-Nitrobenzaldehyde	104—107	10	3	30
5	*m*-Nitrotoluene	*m*-Nitrobenzaldehyde	55—57	20	3	Trace
6	Ethylbenzene	Acetophenone	202—204	2.5	3	98
7	Diphenylmethane	Benzophenone	47—50	3	3	60
8	Anthrone	Anthraquinone	280—283	3	3	60
9			117—119	1	1.5	60
10			207—210	0.4	3	60
11	Benzyl bromide	Benzaldehyde	176—179	8	3	45
12	Benzyl chloride	Benzaldehyde	175—178	8	3	40
13	$PhCH_2OCH_2Ph$[c,d)]	 $Ph\underset{\underset{O}{\Vert}}{C}OCH_2Ph$	—	0.75	3	70
14	$PhCH_2SCH_2Ph$	 $Ph\underset{\underset{O}{\Vert}}{C}SCH_2Ph$	36—38	0.5	3	40
15	Benzyl alcohol[c,d)]	Benzaldehyde	175—178	0.75	1.5	100
16	*p*-Nitrobenzyl alcohol	*p*-Nitrobenzaldehyde	103—106	3	3	60

Table 1. (Continued)

Entry	Substrate	Product	mp or bp/°C$^{32,33)}$	Reaction time/h	Oxidant / Substrate	Yield/%$^{a,b)}$
17	*p*-Methoxybenzyl alcohol	*p*-Methoxybenzaldehyde	245—248	3	3	65
18			—	3	3	45
19			59—61	3	3	50
20	Benzhydrol$^{c,d)}$	Benzophenone	48—50	0.3	1	100
21	Benzoin	Benzil+Benzoic acid	91—94+120—122	2.5	3	25+75
22	4,4′-Dichlorobenzoin	4,4′-Dichlorobenzil	—	3	3	50
23	Furoin	Furil	162—164	3	3	55
24	Cinnamyl alcohol	Cinnamaldehyde	—	6	3	80
25	Phenylacetic acid	Benzaldehyde	176—179	0.75	3	45
26	*p*-Benzyloxyphenylacetic acid	*p*-Benzyloxybenzaldehyde	68—71	1	3	45
27			—	1	3	50
28	α-Hydroxyphenylacetic acid	Benzaldehyde	175—178	2	3	50
29	Benzilic acid$^{c,d)}$	Benzophenone	47—49	0.25	3	95
30	Benzaldehyde$^{c,d)}$	Benzoic acid	121—123	6	3	100
31	*p*-Chlorobenzaldehyde$^{c,d)}$	*p*-Chlorobenzoic acid	238—240	8	3	70
32	*p*-Bromobenzaldehyde$^{c,d)}$	*p*-Bromobenzoic aid	250—252	6	3	85
33	*p*-Methoxybenzaldehyde$^{c,d)}$	*p*-Methoxybenzoic acid	180—183	4	3	70
34	*m*-Nitrobenzaldehyde$^{c,d)}$	*m*-Nitrobenzoic acid	138—141	6	3	60
35	*m*-Methoxybenzaldehyde$^{c,d)}$	*m*-Methoxybenzoic acid	98—101	8	3	50
36	Phthaldehydic acid$^{c,d)}$	Phthalic acid	200(decomp)	5	3	80
37	*o*-Nitrobenzaldehyde$^{d)}$	*o*-Nitrobenzoic acid	144—146	4	3	40
38	Thiophenol	Benzenesulfonic acid	—	2	3	75
39	*m*-Methylthiophenol	*m*-Methylbenzenesulfonic acid	—	2	3	80
40	Benzylthiol	Benzylsulfonic acid	—	2	3	50
41	Phenylallyl thioether	Benzenesulfonic acid	—	2	3	55
42	*m*-Methylphenylallyl thioether	*m*-Methylbenzenesulfonic acid	—	2.5	3	65
43	Styrene	Benzaldehyde	176—179	4	3	75
44	*trans*-Stilbene	Benzil	93—95	3	3	100

a) Yields reported are isolated ones. b) Compared with those of authentic samples (IR, NMR, mp). c) Room temperature. d) Solvent CH_3CN/H_2O:20/1.

zyl bromide and chloride were also oxidized to benzaldehyde (Table 1, Entries 11, 12). Dibenzyl ether and its sulfur analogue were converted to their ester and thioester, respectively (Table 1, Entries 13, 14).

Oxidations of benzylic alcohols were performed in refluxing dry acetonitrile or in acetonitrile in the presence of a catalytic amount of water at room temperature. (Table 1, Entries 15—20). Carbon-carbon bond cleavage occurred in the oxidation of benzoin, and benzoic acid was isolated as the major product from the reaction mixture (Table 1, Entry 21). The oxidation of 4,4′-dichlorobenzoin and furoin produced their diketones as the sole product (Table 1, Entries 22, 23). Cinnamyl alcohol was converted to cinnamaldehyde (Table 1, Entry 24). α-Hydroxycarboxylic acids and phenylacetic acids underwent oxidative decarboxylation and produced their corresponding carbonyl compounds (Table 1, Entries 25—29). This reagent oxidized selecttively benzylic aldehydes, and converted them to the corresponding carboxylic acids (Table 1, Entries 30—37). Thiols were oxidized to the corresponding sulfonic acids (Table 1, Entries 38—40). Carbon-sulfur bond cleavage occurred in allylaryl thioethers, and arylsulfonic acids produced in good yields (Table 1, Entries 41, 42). Styrene was transformed to benzaldehyde, and *trans*-stilbene produced benzil in a quantitative yield (Table 1, Entries 43, 44).

Conclusions

In this paper we have explored the utility of tetrakis(pyridine)silver(II) peroxodisulfate as an oxidizing agent for a number of synthetically important transformations. The ease of preparation, neutrality of the reaction media, stability, and the mildness of the reagent are advantages which should be mentioned. The results are quite reproducible and the reactions could be proceeded very easily on medium to large-scale operations.

Experimental

Oxidation products were characterized by comparison with authentic samples (IR, ^{1}H NMR, TLC, and mp). Melting points are not corrected. All yields refer to isolated products.

Tetrakis(pyridine)silver(II) peroxodisulfate was prepared according to the reported procedures.[31]

General Procedures for the Oxidation of Substrates with Tetrakis(pyridine)silver(II) Peroxodisulfate. To a solution of a substrate (0.02—0.2 mol) in 80 ml acetonitrile or acetonitrile/water (20/1), tetrakis(pyridine)silver(II) peroxodisulfate (0.03—0.6 mol) was added and stirred at room temperature or refluxed for 0.25—20 h. The progress of the reaction was monitored by TLC (eluent: CCl_4/MeOH). The reaction mixture was left at room temperature for 30 min and filtered. In the case of carboxylic and sulfonic acids, a few drops of concentrated hydrochloric acid was added before filtration. The solid material was washed with acetonitrile three times (each 80 ml). The filtrates were combined together and evaporated on a rotatory evaporator. The resulting crude material was purified by column chromatography (silica gel). The oily sulfonic acids were isolated as their sodium salts by the addition of saturated sodium bicarbonate solution.

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