α-Naphthyltriphenylphosphonium Peroxodisulfate: A Selective and Regenerable Reagent for Oxidation of Organic Compounds

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Alcohols, hydroquinones, tetrahydropyranyl ethers, trimethylsilyl ethers, oximes, semicarbazones, and phenylhydrazones were efficiently converted to the corresponding carbonyl compounds using α-naphthyltriphenylphosphonium peroxodisulfate (NTPPPODS) in acetonitrile at reflux conditions. This reagent could be regenerated and reused, which represents significant advantages over the known reagents.

INTRODUCTION

The oxidation of organic compounds under mild conditions has found valuable applications in modern organic synthesis. So far, significant improvments have been achieved by the use of new oxidizing agents.[1–8] Unfortunately, many of the reagents mentioned in literature suffer from at least one of the following disadvantages: cost of preparation, hygroscopicity, photosensitivity, instability, lack of selectivity, and tedious work-up procedure with accompanying reagent decomposition.

The peroxodisulfate ion is one of the strongest oxidizing agents and its standard redox potential in aqueous solution is about 2.01V, but there are only a few reports concerning the capability of peroxodisulfate for oxidative transfomations.[9–16]

In connection with our ongoing work on the application of peroxodisulfate based oxidants to the selective oxidation of organic

(NTPPPODS)
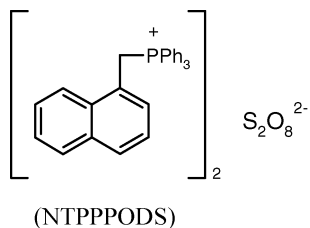
FIGURE 1

compounds,[9,17] we report here the oxidation of structurally different alcohols, hydroquinones, tetrahydropyranyl ethers, trimethylsilyl ethers, oximes, semicarbazones, and phenylhydrazones using α-naphthyltriphenylphosphonium peroxodisulfate in acetonitrile at reflux conditions. α-Naphthyltriphenylphosphonium peroxodisulfate (NTPPPODS, Figure 1) as an oxidant can overcome most of the above-mentioned disadvantages for the oxidation of organic compounds.

RESULTS AND DISCUSSION

α-Naphthyltriphenylphosphonium peroxodisulfate was readily prepared from an aqueous solution of α-naphthyltriphenylphosphonium chloride and potassium peroxodisulfate at room temperature and characterized spectroscopically, as well as by elemental analysis. The content of active oxidizing agent ($S_2O_8^{2-}$) was determined by titrimetric method.[18] This reagent is a stable white powder, which can be stored for months without losing its activity.

The effect of solvent on the oxidation reaction was evaluated by carrying out the oxidation in different solvents. Oxidation of benzyl alcohol with α-naphthyltriphenylphosphonium peroxodisulfate was carried out in dichloromethane, chloroform, tetrahydrofuran, *n*-hexane, acetonitrile, and in a mixture of water and acetonitrile (70:30) at reflux temperature. The results are presented in Table I.

As indicated in Table I, a 1:0.5 molar ratio of benzyl alcohol and α-naphthyltriphenylphosphonium peroxodisulfate in acetonitrile or in a mixture of water and acetonitrile gave excellent yield of benzaldehyde within five minutes.

In addition, the effect of temperature on this reaction was studied by carrying out the oxidation of benzyl alcohol at lower temperatures; longer reaction time was necessary to achieve complete conversion to benzaldehyde, however.

In order to evaluate the general applicability of this method we have treated benzylic, allylic and aliphatic alcohols,

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TABLE I Oxidation of Benzylalcohol in Different Solvents Using NTPPPODS[a]

Solvent	Reaction time (min)	Yield (%)[b]
CH_3CN	2	98
H_2O/CH_3CN (70/30)	5	96
$CHCl_3$	60	4
CH_2Cl_2	60	5
n-C_6H_{12}	60	0
THF	60	0

[a]Reactions were carried out at reflux conditions using substrate/oxidant (2:1).
[b]Yields refer to isolated products or GC.

hydroquinones, tetrahydropyranyl and trimethylsilyl ethers with α-naphthyltriphenylphosphonium peroxodisulfate in refluxing acetonitrile. The results are shown in Table II.

It is evident from Table II, that aromatic substrates, including bezylic alcohols as well as tetrahydropyranyl and trimethylsilyl ethers, were rapidly oxidized to the corresponding carbonyl compounds in excellent yields under the reaction conditions, whereas aliphatic compounds needed longer reaction time for oxidation.

It is noteworthy that, unlike other hydrolytic oxidative methods, the major drawback of overoxidation of the resulting aldehydes was not observed under this reaction conditions. α,β-Unsaturated derivatives are oxidized very efficiently without affecting the olefinic bond and the reaction is essentially chemoselective (Table II).

It is interesting to mention that NTPPPODS can selectivly oxidize hydroquinones in the presence of alcohols in refluxing chloroform. When an equimolar mixture of hydroquinone and a benzylic or an aliphatic alcohol was treated with NTPPPODS, only the hydroquinone was oxidized, while the alcohol remained unaffected (Scheme 1).
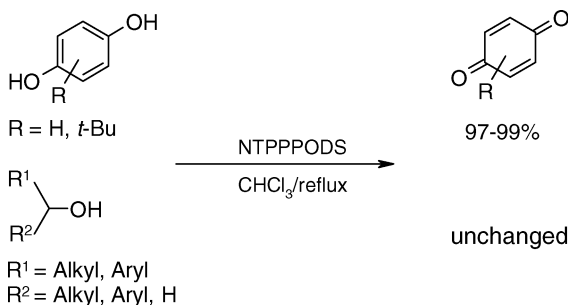

R = H, *t*-Bu

NTPPPODS
$CHCl_3$/reflux

97–99%

R^1
R^2 OH

R^1 = Alkyl, Aryl
R^2 = Alkyl, Aryl, H

unchanged

SCHEME 1

TABLE II Oxidation of Alcohols and Hydroquinones and Oxidative Deprotection of Trimethylsilyl and Tetrahydropyranyl Ethers with NTPPPODS[a]

Substrate	Product	Reagent /substrate	Time (min)	Yield (%)[b,c]
$C_6H_5CH_2OH$	C_6H_5CHO	0.5	2	98
p-$MeOC_6H_4CH_2OH$	*p*-$MeOC_6H_4CHO$	0.5	2	95
o-$ClC_6H_4CH_2OH$	*o*-ClC_6H_4CHO	0.5	3	97
p-$ClC_6H_4CH_2OH$	*p*-ClC_6H_4CHO	0.5	2	99
p-$BrC_6H_4CH_2OH$	*p*-BrC_6H_4CHO	0.5	4	97
p-$NO_2C_6H_4CH_2OH$	*p*-$NO_2C_6H_4CHO$	1	15	65
$C_6H_5CH(OH)CH_3$	$C_6H_5COCH_3$	0.5	3	95
$C_6H_5CH(OH)CH_2CH_3$	$C_6H_5COCH_2CH_3$	0.5	4	97
$(C_6H_5)_2CHOH$	$(C_6H_5)_2CO$	0.5	2	95
$C_6H_5CH_2CH_2OH$	$C_6H_5CH_2CHO$	1	20	93
$CH_3(CH_2)_5CH_2OH$	$CH_3(CH_2)_5CHO$	1	20	84
$CH_3(CH_2)_6CH_2OH$	$CH_3(CH_2)_6CHO$	1	20	87
$C_6H_5CH=CHCH_2OH$	$C_6H_5CH=CHCHO$	1	10	95
Cyclohexanol	Cyclohexanone	1	15	89
Hydroquinone	Quinone	0.5	2	99
tert-Butylhydroquinone	*tert*-Butylquinone	0.5	2	95
$C_6H_5CH_2OSiMe_3$	C_6H_5CHO	0.5	3	98
$(C_6H_5)_2CHOSiMe_3$	$(C_6H_5)_2CO$	0.5	5	96
p-$ClC_6H_4CH_2OSiMe_3$	*p*-ClC_6H_4CHO	0.5	4	99
p-$BrC_6H_4CH_2OSiMe_3$	*p*-BrC_6H_4CHO	0.5	3	97
p-$NO_2C_6H_4CH_2OSiMe_3$	*p*-$NO_2C_6H_4CHO$	1	40	74
$C_6H_5CH_2CH_2OSiMe_3$	$C_6H_5CH_2CHO$	1	30	92
$CH_3(CH_2)_5CH_2OSiMe_3$	$CH_3(CH_2)_5CHO$	1	40	81
$CH_3(CH_2)_6CH_2OSiMe_3$	$CH_3(CH_2)_6CHO$	1	45	84
$C_6H_5CH=CHCH_2OSiMe_3$	$C_6H_5CH=CHCHO$	0.5	5	86
Hydroquinone trimethylsilylether	Quinone	0.5	3	94
tert-Butylhydroquinone trimethylsilylether	*tert*-Butylquinone	0.5	2	98
$C_6H_5CH_2OTHP$	C_6H_5CHO	0.5	10	96
$(C_6H_5)_2CHOTHP$	$(C_6H_5)_2CO$	0.5	12	95
o-$ClC_6H_4CH_2OTHP$	*o*-ClC_6H_4CHO	0.5	8	95
p-$MeC_6H_4CH_2OTHP$	*p*-MeC_6H_4CHO	0.5	10	94
p-$BrC_6H_4CH_2OTHP$	*p*-BrC_6H_4CHO	0.5	8	93
$CH_3(CH_2)_5CH_2OTHP$	$CH_3(CH_2)_5CHO$	1	30	87
$CH_3CH=CHCH_2OTHP$	$CH_3CH=CHCHO$	0.5	17	91
Cyclohexanol tetrahydropyranyl ether	Cyclohexanone	1	25	90

[a]Reactions were carried out in water and acetonitrile (70/30) at reflux temperature.

[b]All products were characterized spectroscopically (^{1}H NMR, IR) and showed physical and spectral data in accordance with their structures and also in accord with those of authentic samples.

[c]Yields refer to pure isolated products; the eluent in column chromarography was EtOAc/*n*-hexane (1:5) for alcohols, and EtOAc/*n*-hexane (1:10) for TMS and THP ethers.

As summarized in Table III, our experiments show, that oximes, phenylhydrazones and semicarbazones can be deprotected to the corresponding aldehydes and ketones in water and acetonitrile (70/30) at reflux temperature.

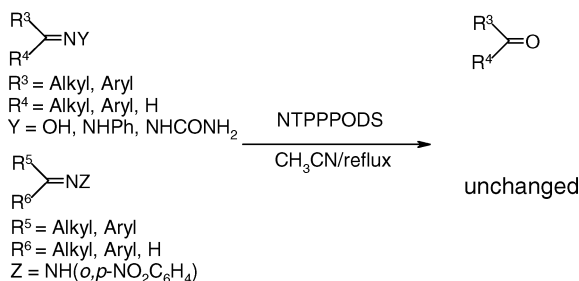**TABLE III Deprotection of Phenylhydrazones, Oximes and Semicarbazones to the Corresponding Carbonyl Compounds Using NTPPPODS[a]**

Substrate	Product	Reagent /substrate	Time (min)	Yield (%)[b,c]
$4C_6H_5CHNNHC_6H_5$	C_6H_5CHO	1.5	15	96
o-$ClC_6H_4CHNNHC_6H_5$	o-ClC_6H_4CHO	1.5	15	95
p-$ClC_6H_4CHNNHC_6H_5$	p-ClC_6H_4CHO	1.5	12	94
p-$MeOC_6H_4CHNNHC_6H_5$	p-$MeOC_6H_4CHO$	1.5	12	96
p-$MeC_6H_4CHNNHC_6H_5$	p-MeC_6H_4CHO	1.5	12	94
p-$NO_2C_6H_4CHNNHC_6H_5$	p-$NO_2C_6H_4CHO$	1.5	45	78
$(C_6H_5)_2CNNHC_6H_5$	$(C_6H_5)_2CO$	1.5	18	95
$C_6H_5CH_2CH_2CHNNHC_6H_5$	$C_6H_5CH_2CH_2CHO$	1.5	40	83
Cyclohexanone Phenylhydrazone	Cyclohexanone	1.5	30	85
$C_6H_5CH{=}CHCHNNHC_6H_5$	$C_6H_5CH{=}CHCHO$	1.5	25	91
C_6H_5CHNOH	C_6H_5CHO	2	20	96
p-MeC_6H_4CHNOH	p-MeC_6H_4CHO	2	18	93
p-$MeOC_6H_4CHNOH$	p-$MeOC_6H_4CHO$	2	15	97
m-$ClC_6H_4C(CH_3)NOH$	m-$ClC_6H_4COCH_3$	2	20	93
o-$ClC_6H_4C(CH_3)NOH$	o-$ClC_6H_4COCH_3$	2	18	94
p-$NO_2C_6H_4C(CH_3)NOH$	p-$NO_2C_6H_4COCH_3$	2	60	81
$(C_6H_5)_2CNOH$	$(C_6H_5)_2CO$	2	20	97
$C_6H_5CH_2CH_2CHNOH$	$C_6H_5CH_2CH_2CHO$	2	40	87
Cyclohexanone Oxime	Cyclohexanone	2	45	85
$C_6H_5CH{=}CHCHNOH$	$C_6H_5CH{=}CHCHO$	2	20	91
$C_6H_5CHNNHCONH_2$	C_6H_5CHO	1.5	20	96
p-$ClC_6H_4CHNNHCONH_2$	p-ClC_6H_4CHO	1.5	20	91
o-$ClC_6H_4CHNNHCONH_2$	o-ClC_6H_4CHO	1.5	20	95
p-$BrC_6H_4CHNNHCONH_2$	p-BrC_6H_4CHO	1.5	20	93
m-$MeOC_6H_4CHNNHCONH_2$	m-$MeOC_6H_4CHO$	1.5	15	95
p-$MeOC_6H_4CHNNHCONH_2$	p-$MeOC_6H_4CHO$	1.5	18	92
o-$NO_2C_6H_4CHNNHCONH_2$	o-$NO_2C_6H_4CHO$	1.5	55	78
$(C_6H_5)_2CNNHCONH_2$	$(C_6H_5)_2CO$	1.5	20	96
$C_6H_5CH_2CH_2CHNNHCONH_2$	$C_6H_5CH_2CH_2CHO$	1.5	30	92
$C_6H_5CH{=}CHCHNNHCONH_2$	$C_6H_5CH{=}CHCHO$	1.5	25	92

[a]Reactions were carried out in water and acetonitril (70/30) at reflux temperature.

[b]All products were characterized spectroscopically (^{1}H NMR, IR) and showed physical and spectral data in accordance with their structures and also in accord with those of authentic samples.

[c]Yields refer to pure isolated products; the eluent in column chromarography was EtOAc/n-hexane (1:4).

Similarly, this reagent can selectively deprotect oximes, semicarbazones, and phenylhydrazones in the presence of 2,4-dinitrophenylhydrazones to the coreesponding carbonyl compounds in refluxing acetonitrile. When an equimolar mixture of an oxime, a semicarbazone, or a phenylhydrazone and 2,4-dinitrophenylhydrazone was treated with NTPPPODS, the oxime, semicarbazone or phenylhydrazone were deprotected but 2,4-dinitrophenylhydrazone remained unchanged (Scheme2).

R^3 = Alkyl, Aryl
R^4 = Alkyl, Aryl, H
Y = OH, NHPh, NHCONH$_2$

NTPPPODS

CH$_3$CN/reflux

R^5 = Alkyl, Aryl
R^6 = Alkyl, Aryl, H
Z = NH(o,p-NO$_2$C$_6$H$_4$)

unchanged

SCHEME 2

Another interesting feature of this method is, that the α-naphthyltriphenylphosphonium cation could be recycled and reused for regeneration of the reagent. On completion of the reaction, the residual solid materials were collected, dissolved in DMSO, and treated with freshly prepared aqueous K$_2$S$_2$O$_8$ to give α-naphthyltriphenylphosphonium peroxodisulfate quantitatively (Scheme 3).

K$_2$S$_2$O$_8$ (aq)

(NTPP)$_2$ S$_2$O$_8$　　　(NTPP)$_2$ SO$_4$

Substrate　　　　　　　　　　　　　　Product
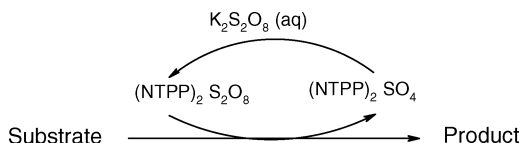
SCHEME 3

In conclusion, we have developed a convenient and efficient method for oxidation of structurally different alcohols, hydroquinones, tetrahydropyranyl ethers and trimethylsilyl ethers to the corresponding carbonyl compounds and the regeneration of carbonyl compounds from oximes, phenylhydrazones and semicarbazones. Our new method has significant advantages over the existing methods such as selective and recyclable procedure, high yields and mild reaction conditions.

EXPERIMENTAL

All the alcohols and hydroquinones were purchased from Fluka and Merck. The reactions were monitored by TLC using silica gel plates. The products were purified by flash column chromatography on silica gel (Merck; 230–400 mesh) and were identified by comparison of their IR and ^{1}H NMR spectra and physical data with those of authentic samples. ^{1}H NMR spectra were measured at 90 MHz with a JEOL JNM-EX 90 spectrometer with tetramethylsilane as an internal reference and DMSO-d_6 as solvent. IR spectra were recorded with a Pye-unicam SP 1100 spectrophotometer. Elemental analyses were performed on a LECO 250 instrument.

Preparation of α-Naphthyltriphenylphosphonium Peroxodisulfate (NTPPPODS)

To an aqueous solution of α-naphthyltriphenylphosphonium chloride (0.878 g, 2 mmol, 10 mL) was added an aqueous solution of potassium peroxodisulfate (0.32 g, 1.2 mmol). The mixture was stirred at room temperature for 20 min. The resulting white solid product was filtered, washed with cooled distilled water (10 mL) and dried in vacuum desiccators. Yield 0.969 g, 97%; m.p. = 221–223°C.^{1}H NMR (DMSO): δ = 5.61 (d, J = 16.3 Hz, 4H, CH$_2$), 7.02–8.27 (m, 44H, arom. H). IR (KBr) ν(cm^{-1}): 1290, 1260, 1092, 1058, 700, 685, 590, 554; Elemental analysis: Calcd for C$_{58}$H$_{48}$P$_2$S$_2$O$_8$: C, 69.72%; H, 4.84%; S, 6.41%, Found: C, 69.75%; H, 4.79%; S, 6.38%.

General Procedure for Oxidation of Alcohols, Hydroquinones Tetrahydropyranyl and Trimethylsilyl Ethers, and Deprotection of Oximes, Phenylhydrazones and Semicarbazones

A mixture of the substrate (1 mmol), acetonitrile (10 mL) and NTPP-PODS (0.5-2 mmol), were placed in a round bottomed flask and stirred for the specified time (Tables II and III) at reflux conditions. After completion of the reaction (monitored by TLC), the reaction mixture was cooled to room temperature and filtered. The solid material was washed with acetonitrile (10 mL). From the combined filtrates the solvent was evaporated under reduced pressure and the resulting crude material was purified on a silica-gel column with an appropriate eluent. The pure carbonyl compounds were obtained in 65–99% yield.

Regeneration of α-Naphthyltriphenylphosphonium Peroxodisulfate

The used reagent was washed with diethyl ether (2 × 10 mL). The filter cake was dissolved in DMSO (5 mL) and added dropwise to a freshly

prepared aqueous solution of potassium peroxodisulfate. The mixture was stirred at room temperature for 20 min. Then, the solid material was separated by filtration, repeatedly washed with water to remove the free peroxodisulfate, and dried in a vacuum desiccator over calcium chloride to obtain the regenerated reagent.

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