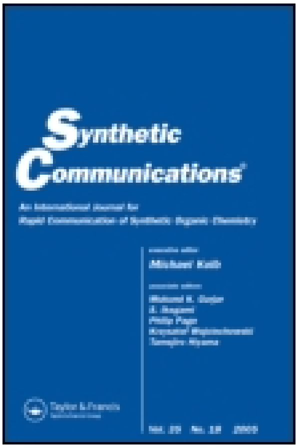

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Selective Oxidation of Benzylic Alcohols and Ethers and Oxidative Cleavage of Benzylic Tetrahydropyranyl and Trimethylsilyl Ethers to Their Carbonyl Compounds by Dinitrogen Tetroxide–Impregnated Activated Charcoal (N_2O_4/Charcoal)

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Abstract: Benzylic alcohols and ethers were oxidized to their corresponding carbonyl compounds using dinitrogen tetroxide impregnated on activated charcoal (N_2O_4/charcoal) in CH_2Cl_2 at room temperature. Efficient oxidative cleavage of trimethylsilyl (TMS) and tetrahydropyranyl (THP) ethers to their corresponding carbonyl compounds was also performed by this reagent. High selectivity was observed for oxidation of benzylic alcohols and ethers and also trimethylsilyl ethers in the presence of tetrahydropyranyl ethers.

Keywords: Benzylic alcohol, benzylic ether, charcoal, oxidation, tetrahydropyranyl ether, trimethylsilyl ether, N_2O_4

For more than a century, gaseous or liquid dinitrogen tetroxide (N_2O_4) has found wide applications in organic synthesis as an oxidizing, nitrating, and nitrosating agent.[1,2] Apart from difficulties in handling and the corrosive nature of N_2O_4, another limitation of utilizing this versatile reagent in organic synthesis is its high reactivity, which usually causes undesired side reactions and requires low temperature-controlled conditions.[2a] To remove these drawbacks, we

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have prepared and used different organic, inorganic, and polymeric complexes of N_2O_4 for nitrosation and nitration reactions.[3] Recently, we reported N_2O_4 impregnated on activated charcoal (N_2O_4/charcoal) as an efficient, cheap, and safe reagent for the selective and heterogeneous oxidation of sulfides to sulfoxides and also disulfides to thiosulfonates.[3c] This reagent is stable in refrigeration for months without loosing its activity.

Now we report the use of N_2O_4/charcoal as a mild reagent for the oxidation of benzylic alcohols and ethers, and also THP and TMS ethers to their corresponding carbonyl compounds.

Using this reagent, heterogeneous oxidation of benzylic alcohols to their corresponding carbonyl compounds was performed in good to excellent yields at room temperature in CH_2Cl_2 without any overoxidation to carboxylic acids (Scheme 1, Table 1).

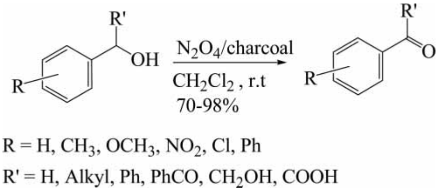
We observed that this method is very convenient for oxidation of primary and secondary benzylic alcohols in the presence of aliphatic ones.

The chemoselectivity of the method was shown by performing a competitive reaction between benzyl alcohol and cyclohexanol. It was observed that benzyl alcohol was selectively converted to benzaldehyde with N_2O_4/charcoal in excellent yield (95%); however, cyclohexanol remained intact (98%).

The oxidative cleavage of ethers to give aldehydes or ketones is an attractive synthetic route for organic chemists. However, this transformation is usually carried out under forceful reaction conditions using a wide range of oxidizing agents such as chromic acid/acetic acid,[4] cerium(IV) sulfate/acetic acid,[5] silver(II) oxide,[6] uranium hexafluoride,[7] cerium(IV) ammonium nitrate coupled with sodium bromate,[8] trityl tetrafluoroborate,[9] silica gel supported metal nitrates, [10] and N_2O_4 in the presence of silica gel.[11]

We investigated the applicability of the N_2O_4/charcoal system as a new source of N_2O_4 for oxidation of benzylic ethers. It was found that oxidative cleavage of benzylic ethers to their corresponding carbonyl compounds can be performed with this reagent in CH_2Cl_2 at room temperature under aprotic and neutral conditions (Scheme 2, Table 2). This transformation is again highly selective for benzylic ethers and alkyl ethers remain unreacted.

Because of the importance of direct conversion of trimethylsilyl (TMS) and tetrahydropyranyl (THP) ethers to carbonyl compounds,[12b,13–15] we studied the applicability of using N_2O_4/charcoal for this transformation (Scheme 3, Table 3). This reagent converted various benzylic TMS ethers



Scheme 1.

Table 1. Oxidation of benzylic alcohols to the corresponding aldehydes and ketones with N_2O_4/charcoal in CH_2Cl_2 at room temperature[a]

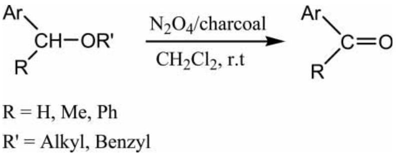
Entry	R	R′	Time/h	Isolated yield %
1	H	H	4	90
2	4-Me	H	3	96
3	2-MeO	H	3	89
4	4-MeO	H	2.5	91
5	2-Cl	H	3.5	85
6	4-Cl	H	4	86
7	2-NO_2	H	8	75
8	4-NO_2	H	8	80
9	4-Ph	H	5	90
10	H	Me	3.5	95
11	H	Et	3.5	98
12	H	Ph	7.5	86
13	H	PhCO	8	70
14	H	CH_2OH	6	90
15	H	COOH	10	70
16	4-Cl	Ph	10	75

[a] All the products are known compounds and were identified by their spectral data.

to their corresponding aldehydes and ketones in CH_2Cl_2 at room temperature. However, because of the resistance of THP ethers, their oxidative deprotections required refluxing $CHCl_3$.

Selective oxidation reactions were also studied by this reagent using binary mixtures. Excellent selectivity was observed for the oxidation of benzylic alcohols (Table 4, entries 1, 2), trimethylsilyl ethers, and benzylic ethers in the presence of THP ethers (Table 4, entries 3–7).

In conclusion, using N_2O_4/charcoal as a cheap, safe, efficient, and easily prepared reagent provides a practical method for the heterogeneous oxidation of benzylic alcohols, ethers, and TMS and THP ethers to their carbonyl compounds without any overoxidation reactions under mild and neutral reaction conditions. The products can be easily obtained by a simple filtration and evaporation of the solvent. In addition, this reagent shows high selectivity



Scheme 2.

Table 2. Oxidative cleavage of benzylic ethers with N_2O_4/charcoal in CH_2Cl_2 at room temperature[a]

Entry	Ar	R	R′	Time/h	Isolated yield %
1	C_6H_5	H	Me	3	93
2	C_6H_5	H	Bu	3	96
3	C_6H_5	H	C_6H_5 CH_2	4	98
4	4-MeO-C_6H_5	H	Me	2.5	90
5	4-MeO-C_6H_5	H	Bu	2	92
6	4-MeO-C_6H_5	H	4-MeO-C_6H_5 CH_2	2	95
7	4-MeC_6H_5	H	Me	3.5	96
8	C_6H_5	CH_3	Bu	8	70
9	C_6H_5	C_6H_5	Me	10	75
10	C_6H_5	C_6H_5	Ph_2CH	10	—[b]

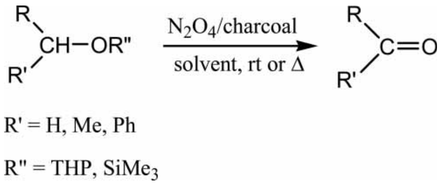
[a] All the products are known compounds and were identified by their spectral data.
[b] No reaction.

for oxidation of benzylic alcohols and ethers and also trimethylsilyl ethers in the presence of THP ones.

EXPERIMENTAL

General

Chemicals were purchased from Merck and Fluka Chemical Companies. The products were characterized by comparison of their physical data with those of known samples or by their spectral data. IR spectra were run on a Shimadzu model 8300 FT-IR spectrophotometer. NMR spectra were recorded on a Bruker Avance DPX-250. Mass spectra were recorded on a Shimadzu GCMS-QP 1000 EX. The purity of the products and the progress of the reactions were accomplished by TLC on silica-gel polygram SILG/UV_{254} plates or by a Shimadzu Gas Chromatograph GC-14A instrument with a flame ionization detector.



Scheme 3.

Table 3. Oxidative deprotection of TMS ethers in CH_2Cl_2 and THP ethers in $CHCl_3$ with N_2O_4/charcoal[a]

Entry	R	R′	R″	Condition	Time/h	Isolated yield %
1	C_6H_5	H	$SiMe_3$	rt	0.5	96
2	4-MeO-C_6H_5	H	$SiMe_3$	rt	0.2	98
3	4-MeC_6H_5	H	$SiMe_3$	rt	0.2	99
4	4-ClC_6H_5	H	$SiMe_3$	rt	0.5	95
5	4-$NO_2C_6H_5$	H	$SiMe_3$	rt	3	90
6	C_6H_5	CH_3	$SiMe_3$	rt	1	96
7	C_6H_5	C_6H_5	$SiMe_3$	rt	—[b,c,d]	98
8	C_6H_5	H	THP	Reflux	1	95
9	4-MeO C_6H_5	H	THP	Reflux	0.5	98
10	4-MeC_6H_5	H	THP	Reflux	0.25	95
11	4-$NO_2C_6H_5$	H	THP	Reflux	3.5	70
12	C_6H_{13}	CH_3	THP	Reflux	2.5	90
13	C_6H_5	C_6H_5	THP	Reflux	3	85

[a] All the products are known compounds and were identified by their spectral data.

[b] The product is diphenyl methanol.

[c] Immediately.

[d] If the reaction is stirred for 8 h, benzophenone is produced in 83% yield.

Table 4. Selective oxidations of different binary mixtures using N_2O_4/charcoal at room temperature

Entry	Substrate	Product[a]	Time/h	Yield %
1	4-Me$C_6H_4CH_2OH$ $C_6H_5CH_2$OTHP	4-MeC_6H_4CHO $C_6H_5CH_2$OTHP	4	90 98
2	4-Cl$C_6H_4CH_2OH$ C_6H_{13}CH(Me)OTHP	4-ClC_6H_4CHO C_6H_{13}CH(Me)OTHP	6	84 95
3	4-Me$C_6H_4CH_2$OTMS $C_6H_5CH_2$OTHP	4-MeC_6H_4CHO $C_6H_5CH_2$OTHP	1	98 99
4	4-Cl$C_6H_4CH_2$OTMS 4-$NO_2C_6H_4CH_2$OTHP	4-ClC_6H_4CHO 4-$NO_2C_6H_4CH_2$OTHP	1	98 100
5	C_6H_5CH(Me)OTMS $C_6H_5CH_2$OTHP	C_6H_5COMe $C_6H_5CH_2$OTHP	2	92 98
6	$(PhCH_2)_2O$ $C_6H_5CH_2$OTHP	PhCHO $C_6H_5CH_2$OTHP	6	95 96
7	$PhCH_2OCH_3$ C_6H_{13}CH(Me)OTHP	PhCHO C_6H_{13}CH(Me)OTHP	5	92 99

[a] All the products are known compounds and were identified by their spectral data.

[b] GC yield using internal standard.

Oxidation of 4-chlorobenzyl alcohol; typical procedure: A solution of 4-chlorobenzyl alcohol (0.285 g, 2 mmol) in CH_2Cl_2 (4 mL) was prepared and N_2O_4/charcoal (0.48 g, 2.2 mmol) was added to this solution at room temperature with stirring. After completion of the reaction (4 h), the mixture was filtered. Evaporation of the solvent followed by chromatography on a short column of silica gel using petroleum ether–acetone (9:1) afforded the 4-chlorobenzaldehyde (0.242 g, 86%); mp 42–44°C [Lit.[3g] mp 42–45°C].

Oxidative cleavage of di(4-methoxybenzyl) ether; typical procedure: To a stirring solution of di(4-methoxybenzyl) ether (0.258 g, 1 mmol) in CH_2Cl_2 (5 mL) was added N_2O_4/charcoal (0.66 g, 3 mmol) at room temperature. After completion of the reaction (2 h), the mixture was filtered. Evaporation of the solvent followed by chromatography on a short column of silica gel using petroleum ether–acetone (9:1) afforded the 4-methoxybenzaldehyde (0.258 g, 95%); bp 247–250°C/760 Torr [Lit.[3g] bp 245–248°C/760 Torr].

Oxidative deprotection of 4-methoxybenzyl trimethylsilyl ether; typical procedure: To a solution of 4-methoxybenzyl trimethylsilyl ether (0.388 g, 2 mmol) in CH_2Cl_2 (6 mL) was added N_2O_4/charcoal (0.88 g, 4 mmol) and the mixture was stirred at room temperature. After completion of the reaction (12 min), the mixture was filtered. The filtrate was applied on a short column of silica gel which was eluted with petroleum ether–acetone (9:1). The solvent was evaporated to give 4-methoxybenzaldehyde (0.267 g, 98%); bp 247–248°C/760 Torr [Lit.[14] bp 247–248°C/760 Torr].

Oxidative deprotection of benzyl tetrahydropyranyl ether; typical procedure: To a solution of benzyl tetrahydropyranyl ether (0.384 g, 2 mmol) in $CHCl_3$ (6 mL) was added N_2O_4/charcoal (0.88 g, 4 mmol) while stirring gently. The reaction was refluxed for 1 h. After completion of the reaction, the mixture was filtered. Chromatography of the crude product on a short column of silica gel eluted with petroleum ether–acetone (9 : 1) gave benzaldehyde (0.202 g, 95%) as colorless liquid; bp 176–178°C/760 Torr [Lit.[3g] bp 175–178°C/760 Torr].

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