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Dinitrogen Tetraoxide Complexes of Iron(III) and Copper(II) Nitrates as Versatile Reagents for Organic Syntheses. Efficient Oxidative Deprotection of Silyl or Tetrahydropyranyl Ethers, Acetals, and Thioacetals

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$Fe(NO_3)_3 \cdot 1.5N_2O_4$ and $Cu(NO_3)_2 \cdot N_2O_4$ are efficient reagents for oxidative deprotection of various silyl and tetrahydropyranyl ethers, acetals, and thioacetals in aprotic organic solvents. $Fe(NO_3)_3 \cdot 1.5N_2O_4$ is also able to perform the reactions efficiently in the absence of solvents at room temperature. Over-oxidation of the products has not been observed in these reactions. A synergic effect of N_2O_4 upon the oxidation abilities of metal nitrates is observed.

Metal nitrates have been used for different purposes in organic syntheses.[1—5] The oxidation ability of metal nitrates is very low and has been extensively studied.[2] For example, $Cu(NO_3)_2 \cdot 3H_2O$ in CCl_4 transforms cyclodecanol to cyclodecanone in only 6% yield.[2a] A similar results has also been reported very recently for the oxidation of benzyl alcohol to benzaldehyde by $Cu(NO_3)_2 \cdot 3\ H_2O$ in CCl_4 and $CHCl_3$. The carbonyl compound was produced in 8 and 9% yield respectively.[5]

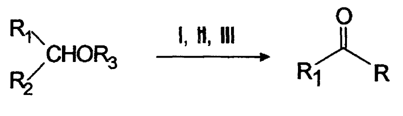
Clayfen and claycop are clay-supported ion(III) and copper(II) nitrates which are introduced as multipurpose reagents for organic synthesis.[1] Clayfen is unstable but may be stored for a few days under pentane. The preparation of the compound also needs some precautions.[1] Claycop is stable at room temperature and could be considered as a practical bench top reagent.[1b]

Hexadecylsilica-supported copper(II) nitrate has been studied for the oxidation of varieties of alcohols and has shown the ability to oxidize primary alcohols in the presence of secondary ones with high chemoselectivity.[5] Varieties of metal nitrates supported on silica gel have also been used for the oxidation of alcohols and oxidative cleavage of ethers.[2,3]

Anhydrous metal nitrates show exceptional reactivity towards organic substrates.[6,7] They are usually unstable and their isolation is difficult.[1,7,8]

Dinitrogen tetraoxide has been used for oxidation of 1,2,4-triazolidine-3,5-diones to the corresponding 3*H*-1,2,4-triazol-3,5(4*H*)-diones,[9] oxidation of benzylic alcohols,[10] conversion of sulfides to their corresponding sulfoxides,[11] oxidation of thiols,[12,13] production of multiple ketones via oxidative deoximation,[14] cleavage of carboxamides to carboxylic acids in the presence of *N*-bromosuccinimide,[15a] dethioacetalization,[15b] and oxidation of ethers in the presence of silica gel.[15c] Recently, we have paid attention to applications of $Cu(NO_3)_2 \cdot N_2O_4$ and $Fe(NO_3)_3 \cdot 1.5N_2O_4$ in organic syntheses. Nitration of phenolic compounds, catalytic coupling of thiols, selective oxidation of thioethers, and oxidation of hydroxy compounds are some examples of the applications of these complexes for functional group transformations.[18]

Now we report that $Cu(NO_3)_2 \cdot N_2O_4$ and $Fe(NO_3)_3 \cdot 1.5N_2O_4$[8,16,17] are able to cause oxidative deprotection of silyl and tetrahydropyranyl ethers, acetals and thioacetals under aprotic conditions with high efficiencies.



1a-r **2a-g, 2r**

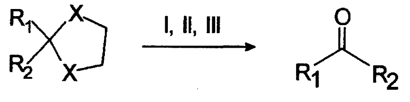
1	R₁	R₂	R₃
a	Ph	H	TMS
b	$4\text{-}CH_3OC_6H_4$	H	TMS
c	$4\text{-}NO_2C_6H_4$	H	TMS
d	Ph	CH_3	TMS
e	Ph	Ph	TMS
f	PhCO	Ph	TMS
g	*n*-C_7H_{15}	H	TMS
h	Ph	H	TBDMS
i	$4\text{-}CH_3OC_6H_4$	H	TBDMS
j	$4\text{-}NO_2C_6H_4$	H	TBDMS
k	Ph	CH_3	TBDMS
l	Ph	Ph	TBDMS
m	PhCO	Ph	TBDMS
n	*n*-C_7H_{15}	H	TBDMS
o	Ph	H	THP
p	Ph	Ph	THP
q	*n*-C_7H_{15}	H	THP
r	C_6H_{13}	CH_3	THP

(I) $Fe(NO_3)_3 \cdot 1.5N_2O_4/CH_2Cl_2$/r.t. (II) $Fe(NO_3)_3 \cdot 1.5N_2O_4$/without solvent/r.t. (III) $Cu(NO_3)_2 \cdot N_2O_4/CCl_4$/r.t.
Scheme 1.

Table 1. Oxidative Deprotection and Cleavage of Trimethylsilyl, *t*-Butyldimethylsilyl, Tetrahydropyranyl Ethers, Acetals, and Thioacetals with (I) $Fe(NO_3)_3 \cdot 1.5N_2O_4$ in CH_2Cl_2, (II) $Fe(NO_3)_3 \cdot 1.5N_2O_4$ in the Absence of Solvents, and (III) $Cu(NO_3)_2 \cdot N_2O_4$ in CH_2Cl_2 or CCl_4

Substrate	Product	mmol oxid/subst.			Time (h)			Yield (%)$^{a)}$			mp (°C) or bp (°C)/Torr	
		I	II	III	I	II	III	I	II	III	Found	Reported
1a	**2a**	2	2	2	—$^{b)}$	—$^{b)}$	0.16	80	83	88	61—62/10	62/10$^{24)}$
1b	**2b**	2	2	2	—$^{b)}$	—$^{b)}$	0.25	85	87	90	247—248/760	248/760$^{24)}$
1c	**2c**	3	3	4	1	0.16	14	100	97	98	106—107	106$^{24)}$
1d	**2d**	2	2	2	—$^{b)}$	—$^{b)}$	0.25	80	88	84	78—79/10	79/10$^{24)}$
1e	**2e**	3	3	2	—$^{b)}$	—$^{b)}$	0.33	85	90	82	48	48$^{24)}$
1f	**2f**	4	4	2	2	—$^{d)}$	0.75	95$^{c)}$	—$^{d)}$	100	95—96	96$^{24)}$
1g	**2g**	2	2	4	0.5	—$^{b)}$	0.25	81	83	86	163/760	163.4/760$^{25)}$
1h	**2a**	2	2	2	—$^{b)}$	—$^{b)}$	0.16	82	80	82	61—62/10	62/10$^{24)}$
1i	**2b**	2	2	2	—$^{b)}$	—$^{b)}$	0.25	92	83	93	246—248/760	248/760$^{24)}$
1j	**2c**	3	3	4	2	0.5	20	100	100	93	105—107	106$^{24)}$
1k	**2d**	2	2	2	—$^{b)}$	—$^{b)}$	0.5	83	85	80	78—79/10	79/10$^{24)}$
1l	**2e**	3	3	4	0.75	—$^{b)}$	0.5	80	85	80	48	48$^{24)}$
1m	**2f**	4	4	2	3.4	—$^{d)}$	1	98$^{c)}$	—$^{d)}$	100	95—96	96$^{24)}$
1n	**2g**	2	2	4	0.75	—$^{b)}$	0.75	85	80	83	162—163/760	163.4/760$^{24)}$
1o	**2a**	1.5	1.5	2	0.16	—$^{b)}$	0.33	84	80	75	61—62/10	62/10$^{24)}$
1p	**2e**	1.5	1.5	2	1	—$^{b)}$	1	86	90	85	48	48$^{24)}$
1q	**2g**	1.5	1.5	4	0.8	—$^{b)}$	0.8	80	83	78	163/760	163.4/760$^{24)}$
1r	**2r**	2	2	4	0.75	—$^{b)}$	1	85	80	82	172—173/760	172/760$^{24)}$
3a	**2a**	1	1	1	—$^{b)}$	—$^{b)}$	—$^{b)}$	80	85	80	61—62/10	62/10$^{24)}$
3b	**2e**	1	1	1	—$^{b)}$	—$^{b)}$	—$^{b)}$	95	97	95	48	48$^{24)}$
3c	**4c**	1	1	1	—$^{b)}$	—$^{b)}$	—$^{b)}$	93	97	93	233—235/760	235/760$^{20a)}$
3d	**4d**	1	1	1	—$^{b)}$	—$^{b)}$	—$^{b)}$	95$^{e)}$	80	95$^{e)}$	155—156/760	155/760$^{20a)}$
3e	**2a**	1	1	1	—$^{b)}$	—$^{b)}$	—$^{b)}$	89	83	94	61—62/10	62/10$^{24)}$
3f	**2e**	1	1	1	—$^{b)}$	—$^{b)}$	—$^{b)}$	98	95	96	48	48$^{24)}$
3g	**4c**	1	1	1	—$^{b)}$	—$^{b)}$	—$^{b)}$	95	90	92	234—235/760	235/760$^{20a)}$
3h	**4d**	1	1	1	—$^{b)}$	—$^{b)}$	—$^{b)}$	80	83	82	155—156/760	155/760$^{20a)}$

a) Isolated yields after column chromatography. b) Reactions occurred immediately. c) Reactions performed in refluxing CCl_4. d) In solid phase only deprotection occurred in the absence of solvents. e) GC yields.



3a-h **2a, 2e, 4c, 4**

3	R_1	R_2	X
a	Ph	H	O
b	Ph	Ph	O
c	$PhCH_2CH_2$	CH_3	O
d	$-(CH_2)_5-$	—	O
e	Ph	H	S
f	Ph	Ph	S
g	$PhCH_2CH_2$	CH_3	S
h	$-(CH_2)_5-$		S

(I) $Fe(NO_3)_3 \cdot 1.5N_2O_4/CH_2Cl_2$/r.t. (II) $Fe(NO_3)_3 \cdot 1.5N_2O_4$/without solvent/r.t. (III) $Cu(NO_3)_2 \cdot N_2O_4/CH_2Cl_2$/r.t.
Scheme 2.

Table 2. Deprotection of Silyl and Tetrahydropyranyl Ethers with (I) $N_2O_4/CH_2Cl_2/-10$ °C and (II) $Cu(NO_3)_2 \cdot 3H_2O/CH_3CN$/r.t.

Substrate	Product	Time/min		Yield/%$^{b)}$	
		I	II	I	II
1a	Benzyl alcohol	—$^{a)}$	5	100	90
1g	1-Octanol	—$^{b)}$	10	100	95
1e	Diphenylmethanol	20	15 h	90	98
1o	Benzyl alcohol	—$^{b)}$	—	100	No reaction

a) Reaction was completed immediately. b) Isolated yields.

Results and Discussion

Functional group protection is important in the synthesis of organic molecules. One way to protect hydroxy groups is to transform the molecules to their corresponding silyl or tetrahydropyranyl ethers.[19] Direct oxidation of these functionalities under mild conditions and in the absence of protic solvents is an important transformation in organic synthesis.

Recently, we have reported oxidative deprotection of trimethylsilyl ethers with varieties of reagents in aprotic organic solvents.[20] *t*-Butyldimethylsilyl ethers are more stable than their trimethylsilyl analogues and they generally resist deprotection and oxidation reactions under mild conditions.[5,19a—c] We have found that both $Fe(NO_3)_3 \cdot 1.5N_2O_4$ and $Cu(NO_3)_2 \cdot N_2O_4$ are very efficient reagents for oxidative deprotection of trimethylsilyl and *t*-butyldimethylsilyl ethers (**1a**—**1n**) to convert them to their corresponding aldehydes or ketones (**2a**—**g**, Scheme 1). $Fe(NO_3)_3 \cdot 1.5N_2O_4$ works

Table 3. Comparison of the Results of $Fe(NO_3)_3 \cdot 1.5N_2O_4/CH_2Cl_2$/r.t. (I), $Fe(NO_3)_3 \cdot 1.5N_2O_4$ (II), and $Cu(NO_3)_2 \cdot N_2O_4$ (III) with Some of Those Reported Which Used Bis(triphenylsilyl)chromate[26] (IV), *N*-Bromosuccinimides[27] (V), CrO_3/H_2SO_4[28,29] (VI), $Ce_2(CrO_4)(NO_3)_6$[20d] (VII),[20c] $Ce_3(H_2IO_6)(NO_3)_9$[20c] (VIII)

Substrate	Product	Yield/%							
		I[a)]	II[a)]	III[a)]	IV	V	VI	VII	VIII
1a	**2a**	80	83	88	—	87	—	85	85
1b	**2b**	85	87	90	—	70	—	92	90
1e	**2e**	85	90	82	98	72	82	85	55

a) Yields are more or less the same, but the rates of the reactions are not comparable. The reaction rates are much faster with I, II, and III.

at room temperature in CH_2Cl_2 or in the absence of solvent with high yields (80—100%, Table 1). $Cu(NO_3)_2 \cdot N_2O_4$ in refluxing CCl_4 converts the silyl ethers efficiently to their carbonyl compounds with high yields (80—100%, Table 1). Both reagents form stable complexes with carbon–carbon double bonds and separate out from the reaction mixture; therefore, they are not recommended for the reaction with these compounds.

The oxidative cleavage of ethers is usually carried out under rather forced conditions which are of somewhat limited applicability.[21] Deprotection of tetrahydropyranyl ethers is generally done by aqueous acids or amberlyst H-15, $MgBr_2$, Me_2AlCl, $LiCl/H_2O$–DMSO, etc.[22] Oxidative cleavage methods of these compounds in aprotic solvents, to the best of our knowledge, are rare in the literature. We have tried this reaction with the reagents in our studies. Both reagents are able to oxidize tetrahydropyranyl ethers (**1o**—**r**) to the corresponding carbonyl compounds (**2a**, **e**, **g**, and **r**, Scheme 1) with high yields (75—90%, Table 1).

Protection of carbonyl compounds is usually performed by their conversion to their corresponding acetals or thioacetals. Regeneration of the carbonyl group from acetals and thioacetals in the absence of protons and under mild conditions is a useful achievement in organic synthesis. Therefore, we have studied deacetalization of several compounds (**3a**—**d**) with $Cu(NO_3)_2 \cdot N_2O_4$ and $Fe(NO_3)_3 \cdot 1.5N_2O_4$ in CH_2Cl_2 at room temperature. Immediate deprotection of acetals (**3a**—**d**) with both reagents in CH_2Cl_2 proceeded efficiently at room temperature with excellent yields (80—95%, Scheme 2, Table 1).

Regeneration of carbonyl compounds from their corresponding thioacetals is not so easy and is a tricky step in organic synthesis.[1a,22] We have tried this reaction with the reagents in our studies. Both $Fe(NO_3)_3 \cdot 1.5N_2O_4$ and $Cu(NO_3)_2 \cdot N_2O_4$ are able to effect dethioacetalization immediately in CH_2Cl_2 to produce the carbonyl compounds (**2a**,**2e**,**4c**—**d**) in high yields (80—98%, Table 1) at room temperature.

Methods which are able to induce chemical transformations in the absence of solvents have gained attention in recent years from different points of views.[23] We have also tried all the above-mentioned reactions with these reagents in the absence of solvent. $Fe(NO_3)_3 \cdot 1.5N_2O_4$ shows promising activities; usually the immediate reaction occurs and the desired products are produced in excellent yields (80—100%, Table 1) at room temperature. $Cu(NO_3)_2 \cdot N_2O_4$ in comparison with its iron analogue is a rather sluggish reagent under solvent-free conditions.

In order to show the synergic effects of N_2O_4 upon the oxidative ability of metal nitrates, we have tried a few reactions with N_2O_4, $Cu(NO_3)_2 \cdot N_2O_4$, and $Fe(NO_3)_3 \cdot 1.5N_2O_4$ separately. Our results show that N_2O_4/CH_2Cl_2, $Cu(NO_3)_2 \cdot 3H_2O$, and $Fe(NO_3)_3 \cdot 9H_2O$ in CH_3CN effect deprotection reactions of the substrates without further oxidation. Similar results are also reported for the cleavage of silyl ethers with Fe(II) and Cu(II) salts.[4] The results are summarized in Table 2. In order to evaluate the performance of our methods for deprotection and oxidative deprotection reaction, we have compared some of our results with some of those reported which used other reagents (Table 3).

In conclusion, the coupling of the two chemical compounds ($Fe(NO_3)_3$ and $Cu(NO_3)_2$ with N_2O_4 gas produces complexes which are stable up to 70 °C in the absence of moisture. The high activities of the complexes of N_2O_4 with $Fe(NO_3)_3$ and $Cu(NO_3)_2$ in the above chemical transformations indicate the enhanced synergistic effect of the two chemical species; metal nitrates and dinitrogen tetraoxide, upon each other. Preparation of the complexes is not time-consuming and the reagents could be stored in capped bottles for months at room temperature without appreciable loss of their activities. The rates of the reactions are usually great and the side products are not formed. The work-up of the reaction mixture is easy and is performed by a simple chromatography through a short column. The yields of products are usually very high. In this paper we have introduced new methods for some useful functional group transformations. Such methods could be considered as practical ones in organic syntheses.

Experimental

General: Chemicals were either prepared in our laboratories or were purchased from Fluka, Merck, B.D.H., Aldirch or Riedel Dehaen AG Chemical Companies. Products were characterized by comparison of their physical data with those of authentic samples. All yields refer to isolated products. IR and UV spectra were recorded on a Perkin Elmer 781 and Pye Unicam 8725 spectrometers. NMR spectra were recorded on a Bruker DPX250. Mass spectra were recorded on a Shimadzu GCMS-QP 1000EX. The purity determination of the substrates and the reaction monitoring were accomplished by TLC on Silica gel polygram SILG/UV 254 plates or GLC on a Shimadzu GC-14A instrument. All solvents were completely dried and predistilled. The yields of the partially volatile carbonyl compounds were also determined by their conversion to their 2,4-dinitrophenylhydrazone derivatives.

Generation of NO_2–N_2O_4 Gas: Lead(II) nitrate (100 g) was crushed into powder and dried under vacuum. The resulting powder was transferred into a one-necked round-bottomed flask (250 ml) which was equipped with an air condenser and a gas trap containing P_2O_5. The flask was heated by a Bunsen burner to generate brownish-red NO_2–N_2O_4 gas, which was used immediately for the subsequent preparation of the metal nitrate complexes.

Preparation of $Fe(NO_3)_3\cdot 1.5N_2O_4$. A solution of anhydrous $FeCl_3$ (16.25 g, 0.1 mol) in EtOAc (100 ml) was prepared in a three-necked round-bottomed flask (250 ml) which was equipped with a magnetic stirrer, gas inlet tube, thermometer and drying tube. The resulting solution was cooled to −10 °C while being stirred. The generated NO_2–N_2O_4 gas (the preceding procedure) was bubbled through this solution for 1 h. The solvent was evaporated under vacuum to give $Fe(NO_3)_3\cdot 1.5N_2O_4$ as a deliquescent brownish solid material (38 g, 100%).

Preparation of $Cu(NO_3)_2\cdot N_2O_4$. A suspension of copper powder (16 g, 0.25 mol) in EtOAc (500 ml) was prepared in a one litter three-necked round-bottomed flask which was equipped with a magnetic stirrer, gas inlet tube, thermometer and a drying tube. The resulting mixture was cooled to −10 °C while being stirred. The generated NO_2–N_2O_4 gas (the preceeding procedure) was bubbled through this solution during a 2 h period. The resulting mixture was stirred for 10 h. The reaction mixture was filtered and the filtrate was evaporated under vacuum to give $Cu(NO_3)_2\cdot N_2O_4$ as a blue deliquescent solid (30.5 g, 44%).

Oxidative Deprotection of Benzhydryl Trimethylsilyl Ether with $Cu(NO_3)_2\cdot N_2O_4$ as a Typical Procedure. To a solution of benzhydryl trimethylsilyl ether (257 mg, 1 mmol) in CCl_4 (4 mL) was added $Cu(NO_3)_2\cdot N_2O_4$ (1.12 g, 4 mmol) and the mixture was magnetically stirred under reflux conditions for 5 min. The progress of the reaction was followed by TLC. The reaction mixture was presorbed on silica gel (5 g) and was applied on a silica gel column and eluted with petroleum ether/acetone (9/1) to afford benzophenone (**2e**), 165 mg, 82%, mp 47—49 (lit,[24] mg 48—50 °C).

Oxidative Deprotection of 4-Nitrobenzyl *t*-Butyldimethylsilyl Ethers with $Fe(NO_3)_3\cdot 1.5N_2O_4$ Under Solvent Free Conditions as a Typical Procedure. A mixture of 4-nitrobenzyl t-butyldimethylsilyl ether (534 mg, 2 mmol) and $Fe(NO_3)_3\cdot 1.5N_2O_4$ (2.28 g, 6 mmol) was prepared. The reaction mixture was magnetically agitated at room temperature for 0.5 h. The progress of the reaction was monitored by TLC. The reaction mixture was mixed with silica-gel (5 g) and was applied on a silica gel pad and eluted with petroleum ether/acetone (9/1). The solvent was evaporated and to the resulting residue for further purification, CH_3OH (3×5 mL) was added and the resulting mixture was evaporated to gain the desired aldehyde (**2c**, 300 mg, 100%, mp 104—106 °C, lit,[24] mp 103—106 °C).

Oxidative Deprotection of Benzyl Tetrahydropyranyl Ether with $Cu(NO_3)_2\cdot N_2O_4$ as a Typical Procedure. A solution of benzyl tetrahydropyranyl ether (384 mg, 2 mmol) in CCl_4 (4 ml) was prepared and $Cu(NO_3)_2\cdot N_2O_4$ (1.12 g, 4 mmol) was added to the solution. The reaction mixture was magnetically stirred under reflux conditions for 20 min. The progress of the reaction was monitored by TLC. The reaction mixture was presorbed on silica gel (5 g) and was applied on a short pad of silica gel and eluted with petroleum ether/acetone (9/1). The solvent was evaporated and the desired aldehyde (**2a**) was isolated (160 mg, 75%, bp 173—176 °C/760 mmHg, lit,[24] bp 175—178 °C/760 mmHg) (1 mmHg = 133.322 Pa).

Oxidative Cleavage of 2-Methyl-2-(2-phenylethyl)-1,3-dithiane as a Typical Procedure. A solution of 2-methyl-2-(2-phenylethyl)-1,3-dithiane (0.764 g, 2 mmol) in CH_2Cl_2 (4 ml) was prepared and $Cu(NO_3)_2\cdot N_2O_4$ (0.56 g, 2 mmol) was added to the solution. The reaction was completed immediately. The resulting mixture was presorbed on silica gel (5 g) and was applied on a short pad of silica gel and was eluted with petroleum ether/acetone (9/1). Evaporation of the solvent afforded the pure ketone (**4c**) in 268 mg, 92%, bp 235 °C/760 mmHg (lit,[20a] bp 233 °C/760 mmHg).

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