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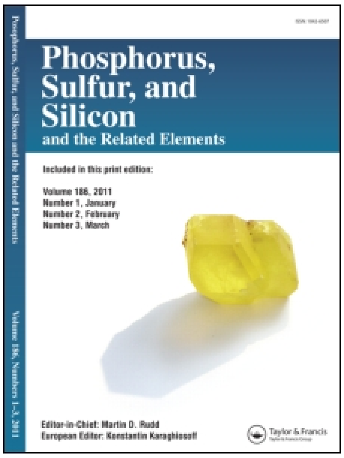

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
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A STUDY OF OXIDATIVE DEPROTECTION OF TRIMETHYLSILYL (TMS) AND TERT-BUTYLDIMEHYLSILYL (TBDMS) ETHERS OF ALCOHOLS WITH POTASSIUM PERMANGANATE ($KMnO_4$) AND BARIUM MANGANATE ($BaMnO_4$) IN THE PRESENCE OF LEWIS ACIDS IN DRY ORGANIC SOLVENTS

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To cite this Article Firouzabadi, Habib , Etemadi, Shahrad , Karimi, Babak and Jarrahpour, Ali Asghar(1999) 'A STUDY OF OXIDATIVE DEPROTECTION OF TRIMETHYLSILYL (TMS) AND TERT-BUTYLDIMEHYLSILYL (TBDMS) ETHERS OF ALCOHOLS WITH POTASSIUM PERMANGANATE ($KMnO_4$) AND BARIUM MANGANATE ($BaMnO_4$) IN THE PRESENCE OF LEWIS ACIDS IN DRY ORGANIC SOLVENTS', Phosphorus, Sulfur, and Silicon and the Related Elements, 152: 1, 141 — 151

To link to this Article: DOI: 10.1080/10426509908031626

URL: http://dx.doi.org/10.1080/10426509908031626

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Phosphorus, Sulfur and Silicon, 1999, Vol. 152, pp. 141-151
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Printed in Malaysia

A STUDY OF OXIDATIVE DEPROTECTION OF TRIMETHYLSILYL (TMS) AND TERT-BUTYLDIMEHYLSILYL (TBDMS) ETHERS OF ALCOHOLS WITH POTASSIUM PERMANGANATE ($KMnO_4$) AND BARIUM MANGANATE ($BAMnO_4$) IN THE PRESENCE OF LEWIS ACIDS IN DRY ORGANIC SOLVENTS

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(Received 04 February, 1999)

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Oxidative deprotection of various trimethylsilyl and tert-butyldimethylsilyl ethers of alcohols with $KMnO_4$ and $BaMnO_4$ in the presence of varieties of Lewis acids in dry acetone and dry acetonitrile at room temperature are studied. $BaMnO_4$ shows more chemoselectivity than $KMnO_4$.

Keywords: Oxidation; Oxidative deprotection: Silyl ethers; Potassium permanganate; Barium manganate; Organic solvents

INTRODUCTION

Conversion of hydroxy functional groups to their corresponding silyl ethers is a strong tool for the protection of hydroxy groups during the multi-step synthesis of organic compounds.[1] One pot oxidation of silyl ethers to the corresponding carbonyl compounds in aprotic organic solvents and under mild reaction conditions is useful for further manipulation of the hydroxy functionality. In the literature, varieties of oxidizing agents, which are reported for this purpose,[2] are extensively reviewed.[3] How-

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* Correspondence Author.

ever, the reported methods may suffer from harsh reaction conditions, expensive reagents, aqueous work-up and low selectivity. Therefore, search for methods, which are not expensive and require non- aqueous work-up and mild reaction conditions are always welcome by synthetic organic chemists.

Potassium permanganate ($KMnO_4$) as an oxidizing agent has been used in organic chemistry for over a century and is one of the most versatile and vigorous of the commonly used oxidants. This reagent has been extensively employed in acid, alkaline, and neutral media. The oxidation of alcohols by permanganate ion has been the subject of extensive studies.[4] It is generally accepted that in acidic or basic media, permanganate ion oxidizes primary alcohols to aldehydes or acids, and secondary alcohols to ketones. However, as reported, $KMnO_4$ may be used in acidic, neutral, or basic aqueous solutions, but not in completely non- aqueous solvents.[5]

The commercially available barium manganate ($BaMnO_4$) which can be regarded as a strong competitor to active MnO_2 has been used for the oxidation of varieties of organic compounds.[4, 6]

In this study, we report deprotection and oxidative deprotection of trimethylsilyl (TMS) and *tert*-butyldimethylsilyl (TBDMS) ethers of alcohols in the presence of Lewis acids in dry solvents such as acetone and acetonitrile at room temperature with $KMnO_4$ and $BaMnO_4$.

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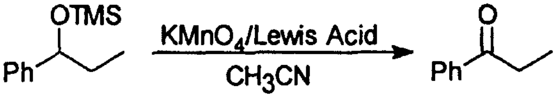
RESULTS AND DISCUSSION

Potassium permanganate ($KMnO_4$) and barium manganate ($BaMnO_4$) are inexpensive commercially available oxidants. Their uses as oxidants for the oxidative deprotection of silyl ethers in aprotic and non-aqueous solvents have not been reported yet. Therefore, study in this area gives useful information about the new applications of the oxidants. For this purpose, first, we have studied the oxidation of several trimethylsilyl ethers in common organic solvents such as; THF, *t*-BuOH, CH_2Cl_2, CH_3CN and CH_3COCH_3, with $KMnO_4$ and $BaMnO_4$. Both reagents are ineffective oxidants for this purpose and the starting materials are isolated intact after several hours.

In recent years, we and the others have reported the effect of Lewis acids, as promoter or catalysts, for the oxidation of organic substrates.[7] Therefore, the effect of Lewis acids upon the reactivity of $KMnO_4$ for the oxidation of 1-trimethylsilyloxy-1-phenyl propane, as a model compound, in dry CH_3CN has been studied. The results are tabulated in Table I.

TABLE I


Lewis Acid	*Reaction Time (min)*	*Yield (%)*
$AlCl_3$	10	100
$ZnCl_2$	10	50
$CeCl_3, 7H_2O$	10	90
$FeCl_3$	10	100
$SnCl_2, 2H_2O$	10	70
$TiCl_3OTf$	10	100

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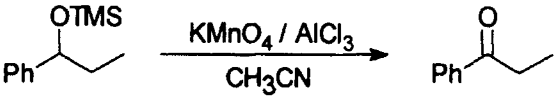
The presented results in the table show that all the Lewis acids in our studies are able to catalyze the reaction with $KMnO_4$. Barium manganate shows also more or less similar results as $KMnO_4$ does We have chosen $AlCl_3$ in this study, which is traditionally a more familiar Lewis acid and is also available in all laboratories.

The nature of the solvent is very important in oxidation reactions. Therefore, we have studied the effects of solvents upon the oxidation abilities of $KMnO_4$ in the presence of $AlCl_3$ for the oxidative deprotection of 1-trimethylsiloxy-1-phenylpropane. *t*-ButOH, CH_3CN, and acetone proved to be good solvents for this purpose. We have used CH_3CN and acetone in this study as aprotic organic solvents (Table II).

TABLE II


Solvent	*Reaction Time (min,)*	*Yield (%)*
THF	60	0
t-BuOH	60	85
CH_2Cl_2	60	20
CH_3CN	3	97
CH_3COCH_3	5	95

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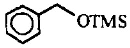
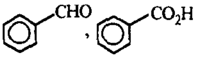
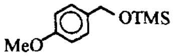
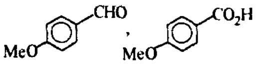
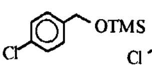
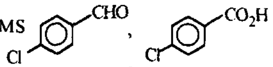
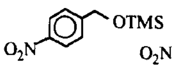
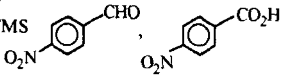
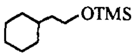
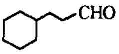
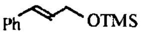
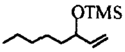
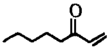
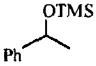
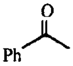
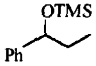
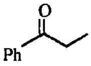
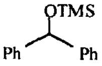
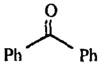
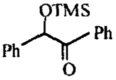
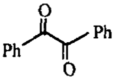
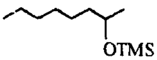
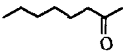
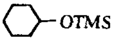
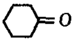
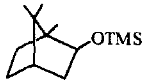
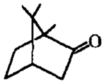
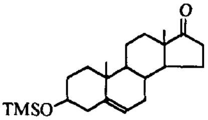
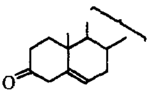
Oxidative Deprotection of TMS and TBDMS Ethers with $KMnO_4$ in the Presence of $AlCl_3$

Primary benzylic TMS ethers are oxidized easily to produce a mixture of the corresponding aldehydes and carboxylic acids with good to excellent total yields (entries 1–4, Table III). The ratio of the formation of aldehydes is usually higher in acetone. Cinnamyltrimethylsilyl ether undergoes oxidation that is accompanied with the cleavage of the carbon-carbon double bond to give benzaldehyde in 70% yield (entries 7, Table III). Therefore, this method is not recommended for the oxidation of this type of substrates. However, non-benzylic allylic trimethylsilyl ether (entry 8, Table III) undergoes oxidative deprotection and the carbon-carbon double bond survives in this reaction and the corresponding ketone is produced in 75% yield. Secondary benzylic TMS ethers are oxidized easily to their corresponding ketones with high yields (entries 9–11, Table III). Oxidation of benzoin trimethylsilyl ether to benzil produced the desired product in 90% yield (entry 12, Table III). Saturated primary and secondary TMS ethers are also oxidized with $KMnO_4$ in the presence of $AlCl_3$. Yields of the carbonyl compounds of the primary silyl ethers are usually much lower than that of the secondary ones (entries 5,6,13–16, Table III). *tert*-Butyldimethylsilyl (TBDMS) ethers are more stable than their trimethylsilyl (TMS) analogues and they generally resist deprotection and oxidation reactions.[1a,3] Oxidation of tert-butyldimethylsilyl (TBDMS) ethers of various alcohols with $KMnO_4$ in the presence of $AlCl_3$ in dry acetone and dry CH_3CN were also investigated at room temperature. Primary benzylic alcohols are converted easily to a mixture of carbonyl compounds and carboxylic acids with good yields (entries 1–4, Table IV). Secondary benzylic alcohols are also transformed to their ketones in high yields (entries 9–11, Table IV). Primary saturated TBDMS ethers are converted to their aldehydes in low yields accompanied with the unreacted starting material (entries 5,6, Table IV). The reactions of the secondary saturated TBDMS ethers proceeded smoothly within a few minutes and the corresponding ketones were obtained in good yields (entries 13–15, Table IV). Cinnamyl TBDMS ether was also oxidized easily with the cleavage of the benzylic double bond, whereas a non-benzylic allyl TBDMS ether was converted to its corresponding carbonyl compound in 80% with the survival of the double bond (entry 8, Table IV).

TABLE III Oxidative Deprotection of TMS Ethers with KMnO$_4$ in the Presence of AlCl$_3$ Acetone and Acetonitrile

Entry	Substrate	Product	Subst./KmnO$_4$/AlCl$_3$	Time(min)	Yield(%)
1			1:1:0.5	10	85,10^{a}
2			1:1:0.5	5	68,25^{a}
3			1:1:0.5	5	70,25^{a}
4			1:1:0.5	15	30,45^{b}
5			1:1:0.5	10	40^{b}
6			1:1:0.5	10	
7		PhCHO	1:1:0.5	10	70^{b}
8			1:1:0.5	10	75^{b}
9			1:0.5:0.2	5	95^{a,b}
10			1:0.5:0.2	5	95^{a,b}
11			1:1:0.5	10	85^{b}
12			1:1:1	10	60^{b}
13			1:1:0.5	10	80^{a,b}
14			1:1:0.5	10	50^{a,b}
15			1:1:0.5	10	85^{a,b}
16			1:1:0.5	10	90^{b}

a) Reactions proceeded in acetone. b) Reaction proceeded in CH$_3$CN

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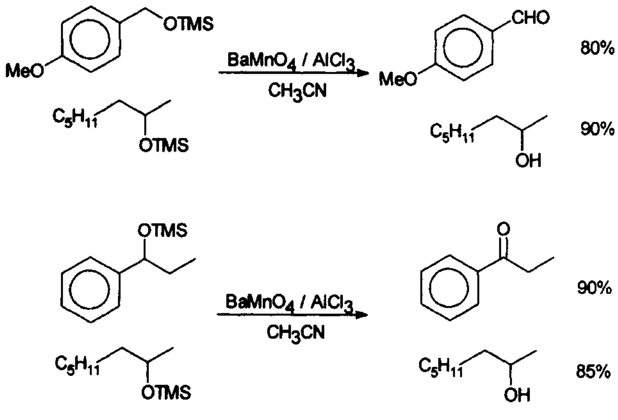
Oxidative Deprotection of Trimethylsilyl (TMS) and *tert*-Butyldimethylsilyl (TBDMS) Ethers with $BaMnO_4$ in the Presence of $AlCl_3$

In contrast to $KMnO_4$, barium manganate oxidation of primary benzylic TMS ethers in the presence of $AlCl_3$ in dry acetone and dry acetonitrile produces the corresponding aldehydes in high yields (entries 1–4, Table V). Barium manganate is a milder reagent than potassium permanganate and MnO_2[7] and even in the presence of $AlCl_3$ is not able to oxidize TBDMS ethers. With $BaMnO_4$, primary and secondary saturated TMS ethers usually undergo deprotection reaction rather than oxidation and usually a mixture of the carbonyl compounds and the alcohols, the major products, are produced (entries 5,6,15,16, Table V). The carbon-carbon double bond of cinnamyl TMS ether survives during oxidation with $BaMnO_4$ and cinnamaldehyde is produced in 90% yield (entry 7, Table V). A non-benzylic allylic TMS ether was converted to its corresponding ketone in 85% plus its alcohol in 10% yields respectively (entry 9, Table V). Secondary benzylic TMS ethers undergo oxidation easily to their ketones with this reagent in excellent yields (entries 10–12, Table V). TMS ether of benzoin is also easily 5 oxidized to benzil with an excellent yield (entry 13, Table V). $BaMnO_4$ is a milder reagent than $KMnO_4$ therefore, it shows some selectivity which is of value in organic synthesis. We have demonstrated this selectivity in the following Scheme.



Oxidant/$AlCl_3$/Subst. 1/Subst. 2 = 2/0.5/1/1

SCHEME

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EXPERIMENTAL

General

Products were characterized by comparison of their physical data with those of authentic samples. All yields refer to isolated products after column chromatography unless otherwise stated. Infrared spectra were recorded on a Perkin Elmer 781 spectrometer. NMR spectra were recorded either on a Hitachi R-2413, 60 MHz NMR spectrometer or were run on a Bruker Avance DPX 250 MHz. Mass spectra were recorded on a Shimadzu GCMS-QP 1000 EX. Melting Points were determined in open capillaries with a Galen-Kamp melting point apparatus.TLC accomplished the purity determination of the substrates and reactions monitoring on silica gel polygram SILG/UV 254 plates. Column Chromatography was carried out using silica gel 60.

All solvents were dried and pre-distilled by drying over molecular sieves 4 A, calcium hydride, or anhydrous calcium sulfate. Zinc chloride was dried in an oven at 110°C for 24 h.

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Oxidative Deprotection of 1-Trimethylsiloxy-1-phenylpropane with $KMnO_4/AlCl_3$ in Acetonitrile

A Typical Procedure

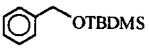
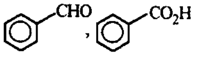
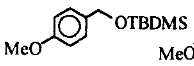
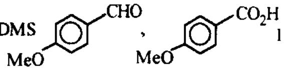
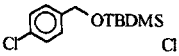
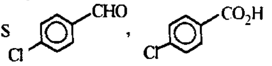
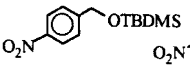
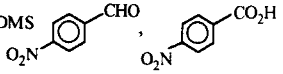
A solution of 1-trimethylsiloxy-1-phenylpropane (208 mg, 1 mmol) in acetonitrile (5 ml) was treated with $KMnO_4$ (79 mg, 0.5 mmol) and $AlCl_3$ (26 mg, 0.2 mmol). The reaction mixture was stirred magnetically for 5 min at room temperature. Then 0.5 g of silica gel was added to the mixture and the solvent was evaporated under reduced pressure. The resulting powder was added on a silica gel pad (2 cm thick). The filter cake was washed with petroleum ether/ethyl acetate (5:1) (50 ml) and the solvent was evaporated to afford ethyl phenyl ketone in 97% yield.

Oxidative Deprotection of 1-t-Butyldimethylsiloxy-1-phenylethane with $KMnO_4/AlCl_3$ in Acetone

A Typical Procedure

A solution of 1-t-butyldimethylsiloxy-1-phenylethane (236 mg, 1 mmol) in acetone (5 ml) was treated with $KMnO_4$ (79 mg, 0.5 mmol) and $AlCl_3$

TABLE IV Oxidative Deprotection of TBDMS Ethers with $KMnO_4$ in the Presence of $AlCl_3$ in Acetone, and Acetonitrile

Entry	Substrate	Product	Subst./$KMnO_4$/$AlCl_3$	Time(min)	Yield(%)
1			1:1:0.5	5	80,15[a]
2			1:1:0.5	5	63,20[b]
3			1:1:0.5	5	75,13
4			1:1:1	10	32,37[a]
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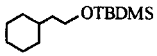
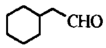
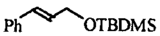
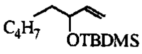
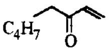
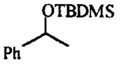
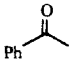
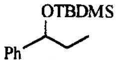
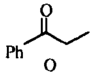
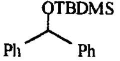
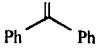
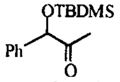
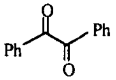
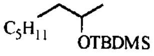
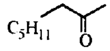
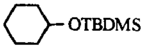
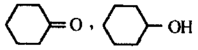
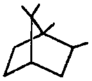
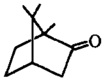
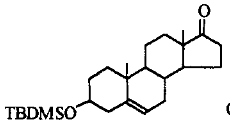
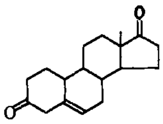
6			1:1:0.5	10	10[b]
7		PhCHO	1:1:0.5	5	70[b]
8			1:1:0.5	10	80[b]
9			1:0.5:0.2	5	96[b]
10			1:0.5:0.2	5	97[b]
11			1:1:0.5	10	85[b]
12			1:1:1	5	35[b]
13			1:1:0.5	10	80[b]
14			1:1:0.5	20	20,10[b]
15			1:1:0.5	10	85[a,b]
16			1:1:0.5	5	70

a) Reactions proceeded in acetone at room temperature. b) Reaction proceeded in CH_3CN at room temperature.

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(26 mg, 0.2 mmol). The reaction mixture was stirred magnetically for 5 min at room temperature. Then 0.5 g of silica gel was added to the mixture and the solvent was evaporated under reduced pressure. The resulting powder was applied on a silica gel pad (2 cm thick). The filter cake was washed with petroleum ether/ethyl acetate (5:1)(50 ml) and the solvent was evaporated to afford acetophenone in 90% yield.

Oxidative Deprotection of 4-Nitrobenzyl Trimethylsilyl Ether with $BaMnO_4/AlCl_3$ in Acetonitrile

A Typical Procedure

A solution of 4-nitrobenzyl trimethylsilyl ether (225 mg, 1 mmol) in acetonitrile (10 ml) was treated with $BaMnO_4$ (512 mg, 2 mmol) and $AlCl_3$ (66 mg, 0.5 mmol). The reaction mixture was stirred magnetically for 20 min at room temperature. Then 0.5 g of silica gel was added to the mixture and the solvent was evaporated under reduced pressure. The resulting powder was applied on a silica gel pad (2 cm thick). The filter cake was washed with petroleum ether/ethyl acetate (5:1) (50 ml) and the solvents were evaporated to afford 4-nitrobenzaldehyde in 70% yield.

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Oxidative Deprotection of Cinnamyl Trimethylsilyl Ether with $BaMnO_4/AlCl_3$ in Acetone

A Typical Procedure

A solution of cinnamyl trimethylsilyl ether (206 mg, 1 mmol) in acetone (10 ml) was treated with $BaMnO_4$ (512 mg, 2 mmol) and $AlCl_3$ (66 mg, 0.5 mmol). The reaction mixture was stirred magnetically for 10 min at room temperature. Then 0.5 g of silica gel was added to the mixture and the solvent was evaporated under reduced pressure. The resulting powder was poured on a silica gel pad (2 cm thick). The filter cake was washed with petroleum ether/ethyl acetate (5:1) (50 ml) and the solvent was evaporated to afford cinnamaldehyde in 90% yield.

Acknowledgements

The authors are grateful to Shiraz University Research Council and National Research Council of I. R. Iran for the support of this work by grant no. 464.

TABLE V Oxidative Deprotection of TMS Ethers with $KMnO_4$ in the Presence of $AlCl_3$ in CH_3CN, and Acetone

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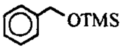
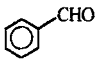
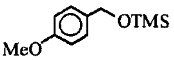
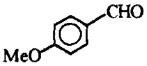
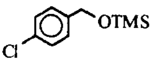
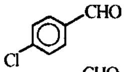
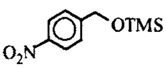
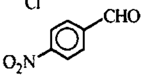
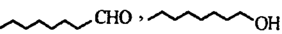
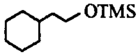
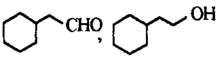
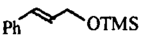
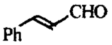
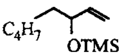
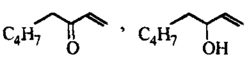
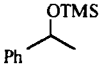
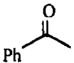
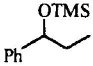
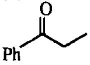
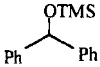
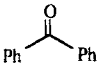
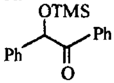
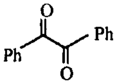
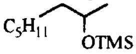
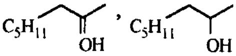
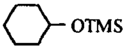
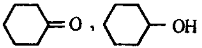
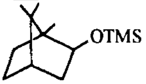
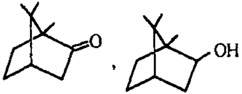
1			1:2:0.5	10	95[a]
2			1:2:0.5	10	93[b]
3			1:2:0.5	5	95[a]
4			1:2:0.5	20	70[a]
5			1:2:0.5	20	10,5[b]
6			1:2:0.5	20	20,60[b]
7			1:2:0.5	10	90[a]
8			1:2:0.5	15	85,10[b]
9			1:2:0.5	10	95[a]
10			1:2:0.5	10	97[a]
11			1:2:0.5	20	95[a]
12			1:2:0.5	5	95[a]
13			1:2:0.5	10	30,65[a]
14			1:2:0.5	20	15,75[b]
15			1:2:0.5	20	20,70[b]

a) Reactions proceeded in acetone at room temperature. b) Reaction proceeded in CH_3CN at room temperature.

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