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DMP-mediated one-pot oxidative olefination of silyl ethers

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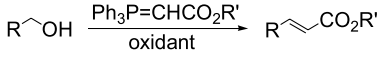
Abstract—Silyl ethers of arylic, allylic, propargylic and unactivated alcohols could be deprotected and oxidized with Dess–Martin periodinane, and the resulting aldehydes could be directly converted to the corresponding α,β-unsaturated esters in one pot with stabilized phosphoranes. Good selectivities were achieved upon a variety of protecting groups of alcohol by using this method. Other advantages of the protocol included simplicity of operations and high efficiency, as well as good to excellent yields.

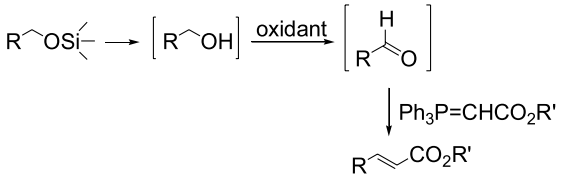
1. Introduction

One-pot methods have broadly been applied in organic synthesis. Syntheses of α,β-unsaturated esters using one-pot methodologies have been attracted attentions due to their widely potential applications in organic chemistry. For instance, one-pot oxidative olefination of alcohol using active manganese dioxide as an oxidant in the presence of Wittig reagents has been studied extensively (Scheme 1).[1–4] In those procedures, the resulting aldehydes by the oxidation of alcohols can be trapped in situ immediately by Wittig reagents to afford the corresponding olefins. Exploration of other one-pot transformations of various substrates to α,β-unsaturated esters still keeps attractive today. In principle, all the precursors, which can be converted to the aldehydes, are able to apply in the methods to generate α,β-unsaturated esters in one pot.



Scheme 1.

In this paper, we report a new one-pot transformation of silyl ethers to α,β-unsaturated esters (Scheme 2). In our initial plan, deprotection of silyl ethers, oxidation of the resulting alcohols and subsequent Wittig reaction to trap the in situ generated aldehydes were combined into a one-step operation. Such a transformation is particularly advantageous because it avoids the isolations of intermediate alcohols and aldehydes, reduces the volatility and toxicity,



Scheme 2.

and evades liability to oligomerisation, facile hydration, acerial oxidation, polymerization[5] or isomerization.[6]

2. Results and discussion

Initially, the reactions were performed under the conditions similar to the reported cases using active manganese dioxide.[1–4] However, no reactions occurred when the silyl ethers were treated under the same conditions. Obviously, active manganese dioxide is not able to remove silyl ether protecting groups in the first step. To accomplish this one-pot transformation, it is crucial to choose an appropriate reagent, which can deprotect silyl ethers and immediately oxidize the resulting alcohols to the corresponding aldehydes. Many reagents are potentially suitable to meet these requirements in the literature.[7] The oxidants that can oxidatively deprotect silyl ethers would be preferred to this transformation. However, these oxidants may encounter the difficulties due to their sensitivities to the Wittig reagents under strong acidic and strong oxidative conditions. With these considerations, Dess–Martin periodinane (DMP), a mild oxidant used for the deprotection–oxidation reaction of silyl ethers,[8] was examined for this purpose.

To our delight, Dess–Martin periodinane was proved to be

Keywords: Silyl ether; Unsaturated ester; Wittig reaction; Dess–Martin periodinane; One-pot method.
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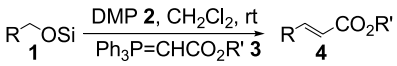
efficient in the procedure without any additives. Treatment of a mixture of silyl ethers **1** and ylide **3** in dichloromethane with DMP **2** at room temperature afforded α,β-unsaturated esters **4**, which were predominantly *trans*-isomers as expected (Scheme 3). The results were summarized in Table 1.



Scheme 3.

As shown in Table 1, the one-pot sequential deprotection–oxidation–Wittig reaction of more active silyl ethers, such as arylic, vinylic and alkynylic silyl ethers, generated α,β-unsaturated esters in 84–94% yields (entries 1–4 in Table 1). The *trans*-vinylic silyl ether was converted to 4-*trans*, 2-*trans*-unsaturated ester (entry 3 in Table 1); while the *cis*-vinylic silyl ether gave 4-*cis*, 2-*trans*-unsaturated ester under the same conditions (entry 4 in Table 1). This indicated the configuration of the *cis*-vinylic silyl ether was remained without any isomerization. However, it was found by us that the stepwise deprotection–oxidation of the *cis*-allylic silyl ether and followed by Wittig reaction predominately gave the (4*E*,2*E*)-isomer under the same conditions. This was easily explained by rapid isomerization of the resulted *cis*-enals.[6] Extension of the methodology to disilyl ethers derived from (*Z*)-1,4-buten-diol and 1,4-butynyl-diol was also successful, affording the corresponding double and symmetrical adducts (entries 5 and 6 in Table 1). Pre-existing *Z*-alkene geometry of silyl ether derived from (2*Z*)-1,4-buten-diol was preserved into its product as compared with the case using (2*Z*)-1,4-buten-diol as the substrate.[2a,4d]

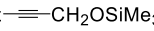
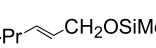
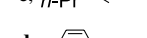
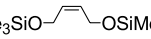
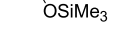
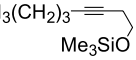
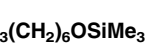
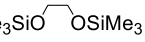
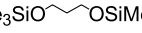
Unactivated silyl ethers, such as alkylic examples, were also proved to be successful (entries 7–9 in Table 1). The examined deprotection–oxidation–Wittig reactions of Me_3Si ethers of 1,2- and 1,3-diols both gave the expected products (entries 10 and 11 in Table 1). In contrast, the sequential oxidation–Wittig reactions of 1,2- and 1,3-diols were reported to give the cleavage products.[2a,9]

Both of THP and $^tBuMe_2Si$ were examined as protection groups of hydroxyls to replace Me_3Si group. The cases with $^tBuMe_2Si$ ethers underwent the same reaction as those with TMS ethers (entry 12 in Table 1); however, the derivatives protected with THP could not proceed the same reaction (entries 12 and 13 in Table 1).

Further investigations showed that the arylic, vinylic, alkynylic and alkylic TMS and/or TBDMS ethers, etc., could be deprotected using 1 equiv of acetic acid, however, the derivatives with THP group could not deprotected under the same conditions.

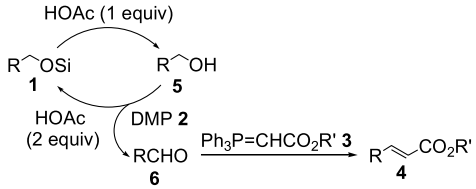
High-valent iodine-mediated cleavage of the oxygen–silyl linkage has been reported. For example, silyl protecting groups can be cleaved by sodium periodate[10] and *o*-iodoxybenzoic acid (IBX).[11] The former reaction went to completion when $NaIO_4$ was used in 1.1–2.5 mol ratio. The latter reaction was performed when IBX was used in 0.5–1.5 mol ratio. It is noteworthy that these reactions are not catalytic. Accordingly, the reaction would require

Table 1. DMP-mediated one-pot oxidative olefination of silyl ethers

Entry	Silyl ether **1**	Product **4**	Reaction time, yield, (selectivity)[a]
1	**a**, **$PhCH_2OSiMe_3$**	**a**, 	20 h, 94%, (*E*:*Z*=20:1)
2	**b**, 	**b**, 	2.5 d, 87%, (*E*:*Z*=9:1)
3	**c**, 	**c**,	2.5 d, 90%, (2*E*,4*E*:2*Z*,4*E*=10.5:1)
4	**d**, 	**d**,	3 d, 84%, (2*E*,4*Z*:2*Z*,4*Z*=8:1)
5	**e**, 	**e**,	3 d, 65%, (2*E*,4*Z*,6*E*:2*Z*,4*Z*,6*E*=3.6:1)
6	**f**,	**f**,	2 d, 78%, (2*E*,6*E*:2*Z*,6*E*=5:1)
7	**g**, 	**g**,	3 d, 48%, (2*E*,5*E*:2*Z*,5*E*=4:1)
8	**h**, 	**h**,	75 h, 60%, (*E*:*Z*=5.5:1)
9	**i**, **$CH_3(CH_2)_6OSiMe_3$**	**i**, 	3 d, 70%, (*E*:*Z*=4.5:1)
10	**j**, 	**j**,	3 d, 60%, (2*E*,4*E*:2*Z*,4*E*=5:1)
11	**k**,	**k**,	3 d, 40%, (2*E*,5*E*:2*Z*,5*E*=3.3:1)
12	**l**, 	**l**,	3 d, 62%, (*E*:*Z*=7:1)
13	**m**, 	**m**,	3 d, 65%, (*E*:*Z*=6:1)

[a] The ratios were determined by ^1H NMR.

2 equiv of DMP, at least 1.5 equiv to carry out this one-pot transformation. However, the experiments showed that only 1 equiv of DMP was enough to finish the above sequential reactions. This suggested that the desilylation process was probably not mediated by DMP except the starting stage. A reasonable explanation was that Dess–Martin periodinane (DMP) **2** or trace amount of acetic acid in available commercial source started the deprotection of silyl ethers **1** to form the corresponding alcohols **5**. The resulting alcohols **5** could be oxidized by Dess–Martin periodinane **2** to generate the corresponding aldehydes **6** and 2 equiv of acetic acid.[12] The aldehydes **6** were trapped immediately in situ with Wittig reagent **3** to give the α,β-unsaturated esters **4** (Scheme 4). With those newly produced acetic acid, the cycle of deprotection of silyl ethers **1** maintained. Therefore, the reaction did not require additional DMP for desilylation once it started.



Scheme 4.

The generation rates of aldehydes **6** may be controlled by deprotection of silyl ethers **1**. The resulting aldehydes **6** were trapped before they were isomerized and/or decomposed. Therefore, the pre-existing *Z*-alkene geometry was retained (entry 5 in Table 1). In addition, the hydroxyl groups protected with THP remained as the protected form in the products because the corresponding deprotections could not occur under such conditions (entries 12 and 13 in Table 1). The actual mechanism is still unclear.

In summary, a new one-pot oxidative olefination of silyl ethers using DMP was investigated for the first time. This protocol proved to be a useful and efficient method to directly convert the silyl ethers to corresponding α,β-unsaturated esters, and presented a significant expansion of the exiting methods.[2–4] The geometry of olefins retained during the reaction and the problems like oxidative cleavage of diols were not observed.[2a,9] Potential uses of this methodology in the multi-step synthesis of complex compounds and natural products are under investigation in our laboratory.

3. Experimental

IR spectra were recorded on a Nicolet 370 FT-IR. ^{1}H NMR spectra were performed on Varian YH 300 in $CDCl_3$ solution using tetramethylsilane as an internal standard. Dichloromethane was distilled before use from calcium hydride. Other solvents were distilled prior to use. Organic extracts were concentrated using a rotary evaporator at below 50 °C. Melting points were uncorrected. Silyl ethers,[13] Wittig reagents[14] and Dess–Martin periodinane (DMP)[12] were prepared according to the known procedures. In addition, DMP was obtained from commercial source.

3.1. General procedure

Silyl ether **1d** (0.317 g, 2 mmol) and methyl triphenylphosphoranylideneacetate (0.868 g, 2.6 mmol) were dissolved in anhydrous CH_2Cl_2 (30 mL). Dess–Martin periodinane (1.70 g, 4 mmol) was added in 3–5 portions over 16–24 h to the reaction mixture. After stirring for 64 h at room temperature, Et_2O (30 mL) and saturated aqueous $NaHCO_3$ (20 mL) were added. After stirring for another 10 min, the mixture was filtered; the organic layer was separated and concentrated under reduced pressure. The residue was purified by chromatography on silica gel by eluting with 15:1 petroleum ether–Et_2O to give methyl (2*E*,4*Z*)-2,4-heptadienoate **4d** (0.235 g, 84%) as a colourless oil.[4d] δ_H ($CDCl_3$, 300 MHz) 0.83 (t, J=7.1 Hz, 3H), 2.09–2.19 (m, 2H), 3.73 (s, 3H), 5.77 (d, J=15.6 Hz, 1H), 6.03–6.16 (m, 2H), 7.21–7.30 (m, 1H). ν_{max} (KBr) 2953, 2924, 2854, 1719, 1666, 1638, 1463, 1377, 1274, 1178 cm^{-1}.

3.1.1. Ethyl (2*E*)-3-phenylpropenoic acid 4a. A colourless oil[3] was obtained in 94% yield. δ_H ($CDCl_3$, 300 MHz) 1.34 (t, J=7.2 Hz, 3H), 4.27 (q, J=7.2 Hz, 2H), 6.44 (d, J=15.9 Hz, 1H), 7.32–7.60 (m, 5H), 7.69 (d, J=15.9 Hz, 1H). ν_{max} (KBr) 3029, 2925, 2854, 1716, 1663, 1578, 1496, 1449, 1367, 1270, 1175, 1040 cm^{-1}.

3.1.2. Methyl (2*E*)-2-hepten-4-ynoate 4b. A colourless oil[15] was obtained in 87% yield. δ_H ($CDCl_3$, 300 MHz) 0.86 (t, J=7.3 Hz, 3H), 2.39 (dq, J=7.3, 2.1 Hz, 2H), 3.76 (s, 3H), 6.15 (d, J=15.9 Hz, 1H), 6.77 (dt, J=15.9, 2.1 Hz, 1H). ν_{max} (KBr) 2953, 2924, 2854, 2217, 1730, 1666, 1625, 1462, 1377, 1274, 1159, 962, 700 cm^{-1}.

3.1.3. Methyl (2*E*,4*E*)-2,4-octadienoate 4c. A colourless oil[16] was obtained in 90% yield. δ_H ($CDCl_3$, 300 MHz) 0.92 (t, J=7.2 Hz, 3H), 1.40–1.52 (m, 2H), 2.12–2.18 (m, 2H), 3.74 (s, 3H), 5.79 (d, J=15.6 Hz, 1H), 6.12–6.23 (m, 2H), 7.23–7.31 (m, 1H). ν_{max} (KBr) 2953, 2925, 2854, 1725, 1665, 1646, 1462, 1377, 1275, 1141, 999, 701 cm^{-1}.

3.1.4. Dimethyl (2*E*,4*Z*,6*E*)-2,4,6-octatrienedioate 4e. White crystals[4d] were obtained in 65% yield, mp 112–116 °C. δ_H ($CDCl_3$, 300 MHz) 3.79 (s, 6H), 6.02 (d, J=15.3 Hz, 2H), 6.35–6.45 (m, 2H), 7.77–7.85 (m, 2H). ν_{max} (KBr) 2919, 2850, 1708, 1624, 1464, 1367, 1318, 1270, 1164, 1025, 982, 727 cm^{-1}.

3.1.5. Dimethyl (2*E*,6*E*)-2,6-octadien-4-ynedioate 4f. White crystals[4d] were obtained in 78% yield, mp 106–110 °C. δ_H ($CDCl_3$, 300 MHz) 3.76 (s, 6H), 6.29 (dd, J=16.8, 2.0 Hz, 2H), 6.87 (dd, J=16.8, 2.0 Hz, 2 Hz). ν_{max} (KBr) 2924, 2853, 2200, 1715, 1610, 1467, 1317, 1273, 1167, 978 cm^{-1}.

3.1.6. Methyl (2*E*,5*Z*)-2,5-octadienoate 4g. Yellow crystals[4d] were obtained in 48% yield, mp 86–90 °C. δ_H ($CDCl_3$, 300 MHz) 1.07 (t, J=7.5 Hz, 3H), 1.89–2.02 (m, 2H), 2.61–2.68 (m, 2H), 3.79 (s, 3H), 6.25 (d, J=15.0 Hz, 1H), 6.46 (d, J=15.0 Hz, 1H), 7.18–7.34 (m, 2H). ν_{max} (KBr) 2922, 2853, 1704, 1600, 1463, 1377, 1283, 1159, 973, 722 cm^{-1}.

3.1.7. Ethyl (2*E*)-2-decen-5-ynoate 4h. A colourless oil[17]

was obtained in 60% yield. δ_H ($CDCl_3$, 300 MHz) 0.96 (t, $J=7.3$ Hz, 3H), 1.09–1.14 (m, 4H), 1.29 (t, $J=7.2$ Hz, 3H), 2.33 (t, $J=7.5$ Hz, 2H), 4.03–4.13 (m, 2H), 4.20 (q, $J=7.2$ Hz, 2H), 5.82 (d, $J=15.6$ Hz, 1H), 6.97 (dt, $J=15.6$, 7.1 Hz, 1H). ν_{max} (KBr) 2927, 2855, 2350, 1726, 1662, 1462, 1377, 1275, 1176, 941, 702 cm^{-1}.

3.1.8. Methyl (2*E*)-2-nonenoate 4i. A colourless oil[18] was obtained in 70% yield. δ_H ($CDCl_3$, 300 MHz) 0.88 (t, $J=7.1$ Hz, 3H), 1.29–1.45 (m, 8H), 2.16–2.23 (m, 2H), 3.73 (s, 3H), 5.82 (d, $J=15.9$ Hz, 1H), 6.98 (dt, $J=15.9$, 7.2 Hz, 1H). ν_{max} (KBr) 2955, 2928, 2857, 1724, 1656, 1600, 1466, 1379, 1266, 1169, 978 cm^{-1}.

3.1.9. Diethyl (2*E*,4*E*)-2,4-hexadienoate 4j. White crystals were obtained in 60% yield, mp 57–59 °C (lit.[2a] 57–59 °C). δ_H ($CDCl_3$, 300 MHz) 1.30 (t, $J=7.1$ Hz, 6H), 4.23 (q, $J=7.1$ Hz, 4H), 6.21 (dd, $J=11.6$, 3.0 Hz, 2H), 7.33 (dd, $J=11.6$, 3.0 Hz, 2H). ν_{max} (KBr) 2924, 2853, 1670, 1609, 1462, 1246, 1160, 1032, 863, 728 cm^{-1}.

3.1.10. Diethyl (2*E*,5*E*)-2,5-heptadienedioate 4k. A yellow oil[19] was obtained in 40% yield. δ_H ($CDCl_3$, 300 MHz) 1.29 (t, $J=7.2$ Hz, 6H), 2.44–2.50 (m, 2H), 4.18 (q, $J=7.2$ Hz, 4H), 5.92 (d, $J=15.8$ Hz, 2H), 6.97 (dt, $J=15.8$, 7.2 Hz, 2H). ν_{max} (KBr) 2981, 2937, 1721, 1655, 1467, 1369, 1271, 1167, 1046, 979, 711 cm^{-1}.

3.1.11. Ethyl (2*E*)-4-[(tetrahydro-2H-pyran-2-yl)oxy]-2-butenoate 4l or 4m. A yellow oil[20] was obtained in 62 and 65% yields, respectively. δ_H ($CDCl_3$, 300 MHz) 1.29 (t, $J=7.2$ Hz, 3H), 1.50–1.83 (m, 6H), 2.48–2.54 (m, 2H), 3.46–3.53 (m, 2H), 3.81–3.88 (m, 2H), 4.20 (q, $J=7.2$ Hz, 2H), 4.59 (t, $J=3.8$ Hz, 1H), 5.90 (d, $J=15.8$ Hz, 1H), 6.99 (dt, $J=15.8$, 7.0 Hz, 1H). ν_{max} (KBr) 2925, 2855, 1725, 1655, 1464, 1367, 1298, 1262, 1176, 1036, 980, 870 cm^{-1}.

Acknowledgements

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