Stereoselective synthesis of enynones *via* base-catalyzed isomerization of 1,5-disubstituted-2,4-pentadiynyl silyl ethers or their alcohol derivatives†

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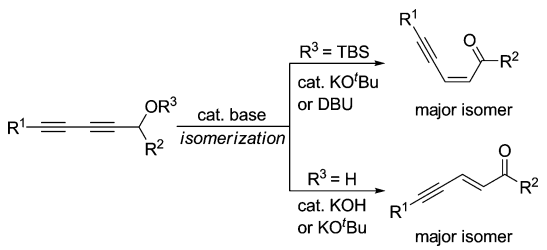
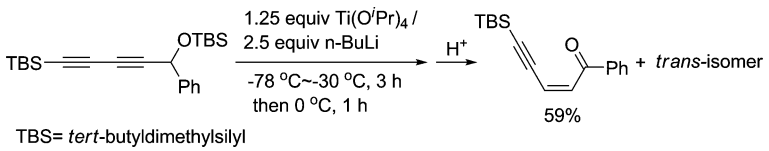
1,5-Disubstituted-2,4-pentadiynyl silyl ethers undergo smooth desilylative isomerization to afford *cis*-enynones as major products with moderate stereoselectivities in the presence of a catalytic amount of KO^{t}Bu or DBU. While the isomerization reactions of their alcohol derivatives catalyzed by KOH, KO^{t}Bu or NaH take place efficiently to produce *trans*-enynones with high stereoselectivities. These reactions provide convenient and practical routes for the synthesis of enynones with a wide range of substitution groups.

cis- and *trans*-Enynones are important building blocks in organic synthesis, *e.g.*, in conjugated addition with organocuprates,[1] phosphine[2a,b] or acid/base[2c] mediated furan synthesis, metal-catalyzed furan formations *via* (2-furyl)carbene complexes,[3] or as substrate precursors in [3,3]-sigmatropic rearrangement,[4] as an intermediacy in IBX-induced cascade oxidation/cyclization of enynols to 2-acyl furans,[5] in total synthesis of natural products[6] and so on. Therefore, efficient procedures leading to these substrates, especially with good levels of stereocontrol, are highly desirable. The synthetic methods for *cis*-selective enynones are achieved mainly by Sonogashira coupling reactions as key steps,[5,7] for example, coupling of the terminal alkynes with (*Z*)-3-iodo-propenoates followed by reduction/Grignard addition/oxidation,[5] or with 3-chloro-*cis*-2-propen-1-one with low overall yields.[8] *trans*-Enynones can be prepared by the reaction of ynals with Wittig reagents,[2a,b] however, a large amount of phosphine oxide is produced as waste which is hard to reduce. Recently, we have developed a convenient method for the selective titanation of 1,3-butadiynes using Ti(O^{i}Pr)$_4$/n-BuLi reagent.[9] During our further investigation of the coordination behavior of 2,4-pentadiynyl silyl ethers with this low valent titanium reagent, we found that under the reaction conditions shown in Scheme 1, (*Z*)-enynone could be isolated in 59% yield, while analysis of the crude reaction mixture revealed that a mixture of (*Z*)- and (*E*)-isomers existed in a ratio of 88 : 12 as determined by ^{1}H NMR. Although the real reaction mechanism was not clear yet, we wondered whether enynones might be constructed stereoselectively in a metal-free process by using a base as catalyst. As already known, isomerization of propargyl alcohols or its silyl ethers to either *trans*- or *cis*- chalcone derivatives in the presence of various bases have been reported. For example, Yoshizawa[10] reported that (*Z*)-chalcone could be stereoselectively synthesized from siloxypropynes *via* siloxyallenes using KO^{t}Bu. Zimmerman isolated the siloxyallenes and found that the kinetic protonation during the allenolate formation with fluoride salt resulted in a general preference for the formation of the (*Z*)-chalcone.[11] Müller[12] and others[13] reported that the isomerization of propargylic alcohols to (*E*)-chalcones occurred under triethylamine,[12] triton B[13a] or potassium hydroxide.[13b–d] These methods for (*E*)-chalcones usually required one or more equivalents of base except in the case of triton B. Transition metals such as Pd,[14] Ru,[15] Rh[16] and Ir[17] have also been found to induce the redox isomerization of propargylic alcohols to enones or enals.[18] However, there is no report for the corresponding reactions of pentadiynoic substrates, to the best of our knowledge. Herein we'd like to report the base-catalyzed stereoselective synthesis of both the *Z* and the *E* isomers of enynones *via* the isomerization of 1,5-disubstituted-2,4-pentadiynyl silyl ethers or their alcohol derivatives (Scheme 2).



Scheme 2

We started our investigation with TBS-substituted pentadiynoic ether **1a** (Table 1), which was conveniently prepared in a one-pot procedure through iodination/Brook rearrangement of α-alkynyloxatitanacyclopentenes developed by us.[9a] A wide range of reaction conditions were screened and some of the results are shown in Table 1. We found that addition of 0.3 equiv KO^{t}Bu to a solution of **1a** in THF at −78 °C resulted in a gradual color change to dark blue. The resulting solution was stirred at the same



Scheme 1

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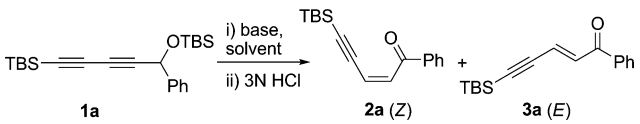
Table 1 Optimization studies for the isomerization of 2,4-pentadiynyl silyl ethers

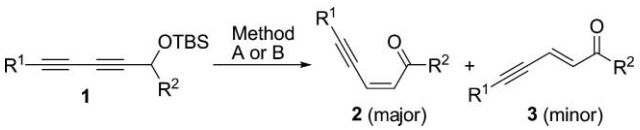


1a **2a** (*Z*) **3a** (*E*)

Entry	Base	Equiv	Solvent	Temp.	Time	Yield (%) of **2a**[a]	*Z*/*E* ratio[b]
1	KO^{t}Bu	0.3	THF	–78 °C	25 min	70 (17)	78/22
2	KO^{t}Bu	0.3	toluene	rt	12 h	—[c]	
3	KO^{t}Bu	0.3	DCM	rt	12 h	—[c]	
4	KO^{t}Bu	0.1	THF	–78 °C	1 h	54[d]	66/34
5	DBU	0.15	THF	0 °C	4 h	70 (19)	74/26
6	DBU	0.05	THF	0 °C	11 h	55	77/23
7	NaH	1.2	THF	50 °C	6 h	—[c]	
8	n-BuLi	0.1	THF	rt	7 h	—[c]	
9	KOH	0.1	THF	0 °C	5 h	messy	
10	NaOH	0.1	THF	rt	1.5 h	messy	
11	DMAP	0.1	THF	50 °C	8 h	NR[e]	

[a] Isolated yield of the pure *cis* isomer of **2a**, the isolated yields of the *trans* isomer **3a** are shown in parentheses. [b] Determined by ^{1}H NMR of the crude mixture. [c] Most of the **1a** remained. [d] NMR yield. [e] No reaction.

Table 2 KO^{t}Bu or DBU promoted isomerization of 1,5-disubstituted-2,4-pentadiynyl silyl ethers



1 **2** (major) **3** (minor)

Entry	R^1	R^2	Method[a]	Yield of **2** (%)[b]		Yield of **3** (%)[b]		**2**/**3**[c]
1	TBS	Ph (**1a**)	A	70	**2a**	17	**3a**	78/22
2	TBS	Ph (**1a**)	B	70	**2a**	19	**3a**	74/26
3	TBS	*p*-ClC$_6$H$_4$ (**1b**)	A	66	**2b**	18	**3b**	76/24
4	TBS	*p*-ClC$_6$H$_4$ (**1b**)	B	70	**2b**	17	**3b**	77/23
5	TBS	*p*-MeOC$_6$H$_4$ (**1c**)	A	56	**2c**	18	**3c**	79/21
6	TBS	*p*-MeOC$_6$H$_4$ (**1c**)	B[d]	43	**2c**	39[e]	**3c**	51/49
7	TBS	2-thienyl (**1d**)	A	63	**2d**	17	**3d**	75/25
8	TBS	2-furyl (**1e**)	A	70	**2e**	17	**3e**	81/19
9	TBS	*trans*-C$_6$H$_5$CH=CH (**1f**)	A	46	**2f**	23	**3f**	66/34
10	TBDPS	Ph (**1g**)	A	61	**2g**	20	**3g**	78/22
11	TMS	Ph (**1h**)	A	67	**2h**	15	**3h**	81/19
12	TMS	Ph (**1h**)	B	68	**2h**	31[e]	**3h**	76/24
13	Bu	Ph (**1i**)	A	63	**2i**	27	**3i**	72/28
14	Ph	Ph (**1j**)	B	44	**2j**	34	**3j**	54/46
15	TBS	n-C$_3$H$_7$ (**1k**)	A	—[f]				

[a] Method A: 30 mol% KO^{t}Bu, in THF, –78 °C, 0.25–4 h. Method B: 15 mol% DBU, in THF, 0 °C, 40 min–5 h. [b] Isolated yield. [c] Determined by ^{1}H NMR of the crude mixture. [d] 2.0 equiv of DBU was used, reaction time was 10 h. [e] Containing small amount of impurity. [f] No reaction.

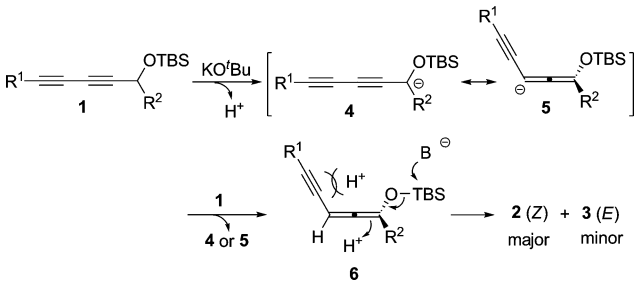
temperature for 25 min, and it was observed that the silyl ether was consumed completely. After quenching the mixture by 3 N HCl at –78 °C, *cis*-enynone **2a** was isolated in 70% yield, together with 17% of the *trans*-isomer of **3a**. The *cis*/*trans* ratio was 78/22 as indicated by ^{1}H NMR of the crude reaction mixture (Table 1, entry 1). The results showed that the isomerization of the silyl ether **1** was *cis*-selective. It should be noted that quenching the reaction with H_2O or $NaHCO_3$ resulted in a complex mixture. Reactions in toluene or DCM only led to low conversions (entries 2–3). Decreasing the catalyst loading to 0.1 equiv resulted in lower yield and stereoselectivity (entry 4). As for base catalyst, DBU is also effective for the isomerization at 0 °C, leading to similar yields and stereoselectivities as that of KO^{t}Bu, although with a longer reaction time (4–11 h) (entries 5 and 6). Other bases, such as NaH, BuLi, KOH, NaOH or DMAP did not afford good results (Table 1, entries 7–11).

We chose the reaction conditions shown in Table 1, entry 1 (method A) or entry 5 (method B) to examine the scope of this reaction. The method is applicable to a wide range of suitably substituted 2,4-pentadiynyl silyl ethers, and the corresponding enynones were formed in good to high overall yields as illustrated in Table 2. In most cases, (*Z*)-enynone **2** was obtained as a major product, which could be separated from *trans*-isomers by column chromatography. We first investigated the electronic effects of the arene substituent of R^2 at C-1. It was found that an electron-withdrawing group (-Cl) or an electron-donating group (-OMe) did not give a significant differences in the yields or selectivity under the catalysis of KO^{t}Bu, furnishing the corresponding

(*Z*)-enynones **2b** and **2c** in 66% and 56% yields, respectively (entries 3, 5). However, DBU was not as efficient as KO^{t}Bu when **1c** bearing an electron-donating group (-OMe) was used (entry 6). In this case, 2.0 equiv of DBU and a longer reaction time (10 h) was needed to achieve the higher yield. A thienyl or furyl group of R^2 was also compatible with this isomerization to generate the desired (*Z*)-**2d** and (*Z*)-**2e** in 63–70% yields (entries 7–8). When R^2 is a cinnamyl group, the corresponding **2f** was obtained in 46% yield with lower stereoselectivity (entry 9). We then investigated the effect of the R^1 group at the alkyne terminus for this isomerization. Butadiyne **1g** bearing a sterically hindered TBDPS (*tert*-butyldiphenylsilyl) group afforded the desired (*Z*)-enynone **2g** smoothly in 61% yield, however, the stereoselectivity was not improved (entry 10), indicating that the TBDPS group is too remote from the reactive site to influence the stereochemical course. Similar results were achieved when using **1h** with a TMS group (entries 11–12). Alkyl substituted diyne **1i** also provided excellent conversion with a *Z*/*E* ratio of 72 : 28 (entry 13). However, the presence of a phenyl group on R^1 resulted in a 54 : 46 mixture of *Z*/*E* isomers (entry 14). No reaction occurred even at refluxing temperature when R^2 is an alkyl group such as n-propyl group (entry 15), due to the low acidity of pentadiynoic proton, in which the proton abstraction is difficult to proceed.

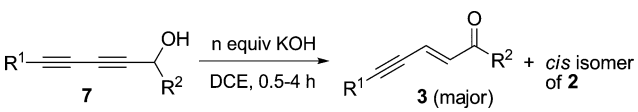
We propose the following mechanism for this reaction[10,11] (Scheme 3). Deprotonation of α-H in **1** by base affords anion **4**, which can be described as an allenic anion **5**. Protonation of **5** either by remaining **1** or *t*-BuOH generated in the first step furnishes linear allenic enolate **6**. Protonation occurs preferentially from the less hindered side of **6**, that means, *trans* to the larger alkynyl group, leading to the thermodynamically less stable (*Z*)-isomer **2**.

We next proceeded to investigate the *trans*-selective formation of enynones from penta-2,4-diyn-1-ol **7**. After much effort, we were delighted to find that the best results were achieved by using KOH as a base in a solvent of DCE. As shown in Table 3, entry 1, the desired *trans*-enynone **3a** was obtained in 87% yield with 96 : 4 ratio of *E*/*Z* isomer using 15 mol% KOH at 30 °C (it was noted that if the temperature was below 20 °C, the reaction could not complete). The reaction proceeded also very well using 10 mol% KO^{t}Bu, to generate **3a** in 83% yield with high stereoselectivity (entry 2). NaH could induce the isomerization, however, with a lower yield of **3a** (entry 3). With the optimal conditions in hand, we investigated the scope of this reaction. The reaction was found to be quite general and proceeded cleanly in most cases to give the *trans*-enynones **3** in good yields with excellent selectivity (Table 3). Substrates bearing aryl and heteroaryl groups at the propargylic position were all compatible under the reaction conditions, furnishing **3a–3e** in 57–87% yields (entries 1–7). However, a vinyl group at C-1 resulted in a lower stereoselectivity (entry 8). A sterically hindered naphthyl group at C-1 did not affect the efficiency of the isomerization, and the corresponding product **3p** was obtained in 76% yield with 95/5 selectivity (entry 9). In the case of butyl-substituted **7i**, a satisfactory result was obtained by increasing the amount of KOH to 0.8 equiv (entry 10). The reaction was also efficient with aryl (R^1) substituted substrates **7j–7o** to afford the similar results as that obtained from TBS-substituted ones (entries 11–16). These



Scheme 3

Table 3 Stereoselective synthesis of *trans*-enynones



Entry	R^1	R^2	Equiv of KOH	Temp.	Product	Yield of **3** (%)[a]	**3**/**2**[b]
1	TBS	Ph (**7a**)	0.15	30 °C	**3a**	87 (4)	96/4
2	TBS	Ph (**7a**)	0.1[c]	rt	**3a**	83	97/3
3	TBS	Ph (**7a**)	0.1[d]	0 °C	**3a**	70	99/1
4	TBS	*p*-ClC_6H_4 (**7b**)	0.15	30 °C	**3b**	79 (5)	95/5
5	TBS	*p*-$MeOC_6H_4$ (**7c**)	0.3	50 °C	**3c**	57	94/6
6	TBS	2-thienyl (**7d**)	0.3	30 °C	**3d**	84	97/3
7	TBS	2-furyl (**7e**)	0.3	30 °C	**3e**	57	94/6
8	TBS	*trans*-$C_6H_5CH{=}CH$ (**7f**)	0.3	30 °C	**3f**	40 (18)	68/32
9	TBS	1-naphthyl (**7g**)	0.3	50 °C	**3p**	76	95/5
10	Bu	Ph (**7i**)	0.8	50 °C	**3i**	63	96/4
11	Ph	Ph (**7j**)	0.1	rt	**3j**	77	96/4
12	Ph	*p*-ClC_6H_4 (**7k**)	0.1	rt	**3k**	77	95/5
13	Ph	*p*-$MeOC_6H_4$ (**7l**)	0.3	50 °C	**3l**	66	93/7
14	Ph	*trans*-$C_6H_5CH{=}CH$ (**7m**)	0.1	30 °C	**3m**	47[e](11)	70/30
15	Ph	2-thienyl (**7n**)	0.1	30 °C	**3n**	68	92/8
16	Ph	2-furyl (**7o**)	0.3	30 °C	**3o**	66	89/11

[a] Isolated yield of the pure isomer **3**. The isolated yields of the *cis* isomer **2** are shown in the parentheses. [b] Determined by ^{1}H NMR of the crude mixture. [c] KO^{t}Bu was used instead of KOH, rt, 40 min. [d] NaH was used instead of KOH, in THF, 0 °C, 15 min. [e] Isomeric purity: 97 : 3.

reactions likely proceed through tautomerization of an allenol intermediate,[12a,13a] which leads to a thermodynamically stable *trans* product **3**.

In conclusion, we have developed an efficient and metal-free process for the stereoselective synthesis of *cis*- or *trans*-enynones *via* base-catalyzed isomerization of 2,4-pentadiynyl silyl ethers or their alcohol derivatives. These reactions provide convenient and practical routes for enynones with a wide range of substitution groups. The resulting enynone derivatives are attractive substrates for further synthetic manipulations.

Experimental section

Typical procedure for the selective formation of *cis*-enynones from 1,5-disubstituted-2,4-pentadiynyl silyl ethers catalyzed by KO^{t}Bu (Method A)

To a stirred solution of *tert*-butyl(5-(*tert*-butyldimethylsilyl)-1-phenylpenta-2,4- diynyloxy)-dimethylsilane **1a** (0.3 mmol, 115 mg) in THF (3 mL) was added KO^{t}Bu powder (30 mol%, 0.09 mmol, 10 mg) at −78 °C under argon. After stirring for 25 min at the same temperature, the mixture was quenched at −78 °C with 3 N HCl (*ca.* 0.5 mL). At this stage the color of the solution changed from dark blue to pale yellow, then the suspension was warmed up to room temperature and stirred for several minutes (during this process, more 3 N HCl (*ca.* 5 mL) was added to the solution). The mixture was extracted with EtOAc, and the combined organic extracts were washed with brine, dried over $MgSO_4$. The solvent was evaporated *in vacuo* and the residue was purified by flash chromatography on silica gel (eluent: petroleum ether/dichloromethane = 3 : 1) to afford *cis*-enynones **2a** and *trans* isomer **3a** in 70% and 17% yields, respectively.

Typical procedure for the selective formation of *cis*-enynones from 1,5-disubstituted-2,4-pentadiynyl silyl ethers catalyzed by DBU (Method B)

To a solution of **1a** (0.4 mmol, 154 mg) in THF (4 mL) at 0 °C was added DBU (15 mol%, 0.06 mmol, 9.0 μL, in some cases, DBU was used as a 0.15 M solution in THF). After stirring for 4 h at 0 °C, the reaction mixture was quenched with 3 N HCl at 0 °C and extracted with EtOAc. The combined organic extracts were washed with brine, dried over $MgSO_4$. The solvent was evaporated *in vacuo* and the residue was purified by flash chromatography on silica gel (eluent: petroleum ether/dichloromethane = 3 : 1) to afford *cis*-enynones **2a** and *trans* isomer **3a** in 70% and 19% yields, respectively.

Typical procedure for the selective formation of *trans*-enynones from penta-2,4-diyn-1-ol catalyzed by KOH

To a stirred solution of KOH (15 mol%, 0.06 mmol, 3.4 mg) in DCE (4 mL) at 30 °C was added 5-(*tert*-butyldimethylsilyl)-1-phenylpenta-2,4-diyn-1-ol **7a** (0.4 mmol, 108 mg) under argon (KOH was weighed in a glove box due to its hygroscopic property). After stirring for 1 h at the same temperature, the reaction mixture was quenched with 3 N HCl and extracted with EtOAc (for the cases of **3j–3o**, the reactions were quenched by saturated NH_4Cl solution). The combined organic extracts were washed with brine, and then dried over $MgSO_4$. The solvent was evaporated *in vacuo* and the residue was purified by flash chromatography on silica gel (eluent: petroleum ether/dichloromethane = 3 : 1) to afford *trans*-enynones **3a** in 87% yield.

(*Z*)-5-(*tert*-Butyldimethylsilyl)-1-phenylpent-2-en-4-yn-1-one (2a)

Pale yellow solid. mp 43-44 °C. ^{1}H NMR ($CDCl_3$, Me_4Si, 400 MHz) δ 0.05 (s, 6H), 0.88 (s, 9H), 6.21 (d, J = 11.6 Hz, 1H), 6.93 (d, J = 12.0 Hz, 1H), 7.43–7.48 (m, 2H), 7.53–7.58 (m, 1H), 7.93–7.96 (m, 2H); ^{13}C NMR ($CDCl_3$, Me_4Si, 100 MHz) δ −5.0, 16.5, 26.0, 102.0, 105.8, 120.2, 128.5, 128.8, 133.0, 134.9, 137.4, 190.6. IR (neat) 3062, 3029, 2954, 2929, 2857, 2147, 1666, 1598, 1581, 1250, 1231, 839, 824, 776, 749, 691 cm^{-1}. HRMS (EI) for $C_{17}H_{22}OSi$ [M]$^+$: calcd 270.1440, found 270.1436.

(*E*)-5-(*tert*-Butyldimethylsilyl)-1-phenylpent-2-en-4-yn-1-one (3a)

Pale yellow oil. ^{1}H NMR ($CDCl_3$, Me_4Si, 400 MHz) δ 0.18 (s, 6H), 0.98 (s, 9H), 6.88 (d, J = 15.6 Hz, 1H), 7.36 (d, J = 16.0 Hz, 1H), 7.44–7.48 (m, 2H), 7.54–7.58 (m, 1H), 7.93–7.96 (m, 2H); ^{13}C NMR ($CDCl_3$, Me_4Si, 100 MHz) δ −4.9, 16.6, 26.0, 103.2, 104.5, 124.8, 128.5, 128.7, 133.2, 134.1, 137.0, 188.8. IR (neat) 3063, 2954, 2930, 2857, 2119, 1663, 1599, 1586, 1282, 1209, 1005, 846, 824, 776 cm^{-1}. HRMS (EI) for $C_{17}H_{22}OSi$ [M]$^+$: calcd 270.1440, found 270.1442.

Acknowledgements

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