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CARBONYL ADDITION REACTION BY MEANS OF β-SILYL- AND β-STANNYLPHOSPHOROUS YLIDES: DIASTEREOSELECTIVE E-PROPENYLATION OF α-CHIRAL ALDEHYDES

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Abstract: E-Propenylation of aldehydes using β-silyl- or β-stannyl-phosphorous ylides is devised, and extended to the diastereoselective reaction of α-methyl and α-alkoxy aldehydes.

We have recently reported that the β-silylphosphorous ylides **1a** and **1b** provide vinyl and isopropenyl alcohols with high 1,2-asymmetric induction, respectively, in the reaction of α-chiral aldehydes.[1] In this paper we describe diastereoselective E-propenylation of α-chiral aldehydes using β-silyl- or β-stannylphosphorous ylides **3**.

The conventional method[2] preparing the ylides **1a** and **1b**, that includes alkylation of phosphoranes **2a** and **2b** with iodomethylsilanes and subsequent deprotonation of the resulting β-silylalkyltriarylphosphonium iodide (Eq. 1), could not apply to the generation of ylides **3** which have an additional methyl group at the β-position of the phosphorane, because **2a** has low reactivity toward α-haloethylsilanes. Now, it was found that the ylides **3** could be obtained by addition of appropriate silyl or stannyl lithiums **4** to 1-propenyl-triarylphosphonium bromide **5** (Eq. 2).[3]

$$Ar_3P{=}CHR \xrightarrow[\text{(ii) n-BuLi or LDA}]{\text{(i) } ICH_2SiR^1R^2R^3} Ar_3P{=}C(R)CH_2SiR^1R^2R^3 \qquad \textbf{Eq. 1}$$

2a : R = H **1a** : R = H
2b : R = CH_3 **1b** : R = CH_3

$$Ar_3\overset{+}{P}CH{=}CHCH_3\ Br^- \xrightarrow{LiSiR^1R^2R^3\ \textbf{4}\ (Sn)} Ar_3P{=}CH(CH_3)CHSiR^1R^2R^3\ (Sn) \qquad \textbf{Eq. 2}$$

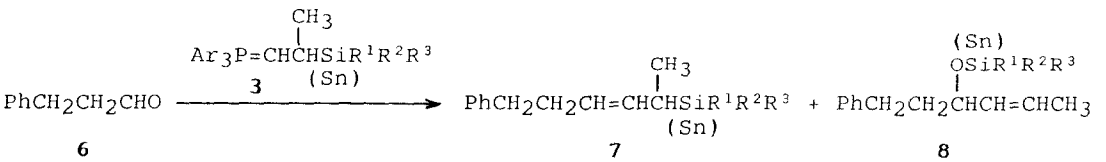
5a : Ar = Ph **3**
5b : Ar = 4-MeOPh

Although trimethylsilyl lithium, prepared from hexamethyldisilane and methyl lithium in HMPA,[4] did not add to 1-propenyltriphenylphosphonium bromide (**5a**), dimethylphenylsilyl lithium,[5] diphenylmethylsilyl lithium,[5] and tributyl-stannyl lithium[6] added to **5** to provide the corresponding β-silyl and β-stannyl ylides **3**.[7] The results in the reaction of **3** with 3-phenylpropionaldehyde (**6**) are summerized in Table I. With the exception of entry 5, the formation of allylsilane or allylstannane is negligible, in contrast to the previous cases in which a substantial amount of allylsilanes formed in the reaction of

Table I. E-Propenylation of 3-Phenylpropionaldehyde (**6**) with β-Silyl and β-Stannylphosphorous Ylides **3**[a]

entry	ylide **3**			products				
		Ar	(Sn)$SiR^1R^2R^3$	**7** yield (%)		**8** yield (%)		E : Z[b]
1	(**3a**)	Ph	$SiMe_3$	(**7a**)	0[c]	(**8a**)	0[c]	--
2	(**3b**)	Ph	$SiPhMe_2$	(**7b**)	< 1	(**8b**)	58	40 : 1
3	(**3c**)	4-MeOPh	$SiPhMe_2$	(**7b**)	< 1	(**8b**)	38	20 : 1
4	(**3d**)	Ph	$SiPh_2Me$	(**7c**)	< 1	(**8c**)	77	40 : 1
5[d]	(**3e**)	Ph	$Sn(n\text{-}Bu)_3$	(**7d**)	9	(**8d**)[e]	74	20 : 1
6[d]	(**3f**)	4-MeOPh	$Sn(n\text{-}Bu)_3$	(**7d**)	< 1	(**8d**)[e]	50	20 : 1

(a) Unless otherwise mentioned, reactions were carried out in THF at -78 °C by using ylides prepared from 1.7 equiv of **4** and 2.0 equiv of **5**.
(b) The rarios were determined by the analysis of ^1H NMR (400 MHz).[11]
(c) Ylide **3a** could not be formed (see text).
(d) This reaction was conducted by using a ylide prepared from 1.2 equiv of **4** and 1.5 equiv of **5**.
(e) Isolated as destannylated alcohol.



2-silylethylidenetriphenylphosphorane (**1a**) or 2-silylisopropylidenetriphenylphosphorane (**1b**) with aldehydes.[1] The reactivities of **4** to the phosphonium salt **5b** are decreased by electron-donating 4-methoxyphenyl groups on the phosphorous atom of **5b**, resulting lower yield of **8** (entries 2 vs 3, and 5 vs 6). Better yield of **8** is secured with **3d** rather than with **3b**. The addition of stannyl lithium to **5a** is more efficient, a smaller excess being enough for complete consumption of the aldehyde. Notably the reaction was selective with respects to the geometry of the olefinic bond formed, especially high E-selectivities were found in entries 2 and 4. Tentative explanation for this selectivity is

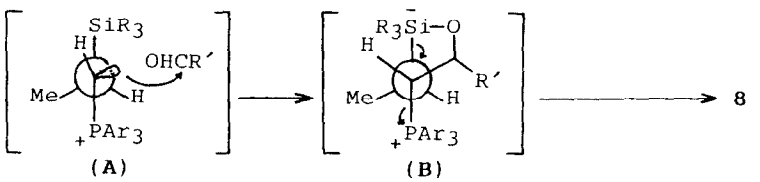
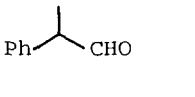
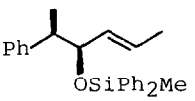
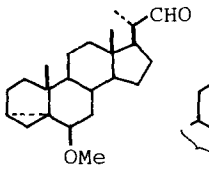
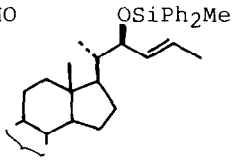
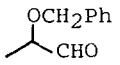
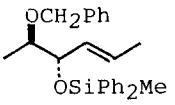
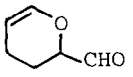
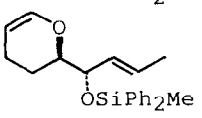


Figure 1

as follows. Suppose that E-propenyl products **8** would form from the five-coordinated silyl intermediate (**B**) by the trans elimination of phosphine as depicted in Figure 1, the aldehyde might approach to the sterically less

Table II. Diastereoselective E-Propenylation of α-Chiral Aldehydes with β-Silylphosphorous Ylide 3d[a]

entry	aldehyde	products[b]	E : Z	erythro:threo[c]	yield(%)
1		 **9**	30 : 1	15 : 1	79
2	**10** 	 **11**	>50 : 1	>50 : 1	60
3[d]		 **12**	30 : 1	10 : 1	45[e]
4		 **13**	>50 : 1	16 : 1	81

(a) A typical experimental procedure: A THF solution (5.8 ml) of diphenylmethylsilyl lithium[5] (1.5 mmol) was added to a suspension of 1-propenyltriphenylphosphonium bromide[3] **5a** (1.7 mmol) in ether (15 ml) at -78 °C and stirred for 20 min. To the resulting orange-yellow solution was added an ether solution (1 ml) of 2-phenylpropanal (1.0 mmol) at -78 °C. Extractive workup followed by treatment with methyl iodide to remove triphenylphosphine and purification by silica gel chromatography provided **9** in 79 % yield.
(b) The ratios were determined by the analysis of ^{1}H NMR (400 MHz).[11] >50 : 1 means that the minor isomer was not detectable.
(c) Erythro/threo are used as defined by Noyori and co-workers.[12]
(d) β-Stannyl ylide **3e** instead of **3d** gave propenylation products exclusively in 80 % yield with the selectivities E/Z = 25 and erythro/threo = 5.5.
(e) The moderate yield is due to the partial enolization of the aldehyde.

congested face of the ylide in the conformation (**A**) in which the silyl and phosphorous groups are antiperiplanally orientated.[8] Eventually **3d** and **3e** are turn out to be the reagent of choice for the E-selective propenylation.

This reaction can be extended to the diastereoface selective E-propenylation of α-chiral aldehydes. The results using the ylide **3d** are shown in Table II. With α-methyl aldehydes, high Cram-selectivities were observed, specially, single isomer (erythro-E) was obtained in the reaction of a steroidal aldehyde **10**[9] (entries 1 and 2). Moreover, with α-alkoxy aldehydes, **3d** provided erythro isomers selectively (entries 3 and 4). The diastereoselectivities observed in these reactions were, however, slightly lower than those reported previously.[1]

The method described in this paper is useful for the synthesis of natural products under acyclic stereocontrol, since further stereoselective transformations of the propenyl group are possible to this type of molecule.[10] Further studies along this line are in progress.

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11. ^{1}H NMR ($CDCl_3$): desilylated alcohol of E-**8**; δ 1.55 (1H, brs), 1.72 (3H, ddd, J=6.5, 1.6, 1.0 Hz), 1.70∿1.95 (2H, m), 2.70 (2H, m), 4.08 (1H, td, J=7.0, 6.5 Hz), 5.53 (1H, ddq, J=15.0, 6.5, 1.6 Hz), 5.68 (1H, dqd, J=15.0, 6.5, 1.0 Hz): E-erythro-**9**; δ 0.49 (3H, s), 1.29 (3H, d, J=7.1 Hz), 1.47 (3H, d, J=6.1 Hz), 2.85 (1H, qd, J=7.1, 5.5 Hz), 4.19 (1H, dd, J=7.2, 5.5 Hz), 5.23 (1H, dq, J=15.4, 6.1 Hz), 5.32 (1H, dd, J=15.4, 7.2 Hz), 7.1∿7.5 (15H, m): E-erythro-**11**; δ 0.42∿2.00 (22H, m), 0.61 (3H, s), 0.66 (3H, s), 0.97 (3H, d, J=6.0 Hz), 1.01 (3H, s), 1.59 (3H, d, J=6.0 Hz), 2.77 (1H, t, J=3.0 Hz), 3.32 (3H, s), 4.17 (1H, d, J=6.0 Hz), 5.41 (1H, dqd, J=15.0, 6.0, 0.5 Hz), 5.52 (1H, ddd, J=15.0, 6.0, 1.0 Hz), 7.32∿7.62 (10H, m): desilylated alcohol of E-erythro-**12**; δ 1.13 (3H, d, J=6.8 Hz), 1.71 (3H, ddd, J=7.0, 1.8, 1.0 Hz), 2.24 (1H, brs) 3.56 (1H, qd, J=6.8, 3.8 Hz), 4.15 (1H, brdd, J=7.5, 3.8 Hz), 4.52 (1H, d, J=12.5 Hz), 4.62 (1H, d, J=12.5 Hz), 5.48 (1H, ddq, J=16.0, 7.5, 1.8 Hz), 5.72 (1H, dqd, J=16.0, 7.0, 1.0 Hz), 7.35 (5H, m). E-threo isomer; δ 3.39 (1H, dq, J=8.0, 6.8 Hz), 3.88 (1H, dd, J=8.0, 7.8 Hz): desilylated alcohol of E-erythro-**13**; δ 1.73 (3H, brd, J=6.5 Hz), 1.6∿2.1 (4H, m), 2.2 (1H, brs), 3.80 (1H, ddd, J=11.0, 3.8, 2.0 Hz), 4.19 (1H, brdd, J=6.8, 3.8 Hz), 4.69 (1H, m), 5.54 (1H, ddq, J=15.5 6.8, 1.5 Hz), 5.78 (1H, dqd, J=15.5, 6.5, 1.0 Hz), 6.39 (1H, d, J=6.0 Hz).
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