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New and Highly (*E*)-Selective Synthesis of Terminal 1,3-Diene via Three-Carbon Elongation of Aldehyde

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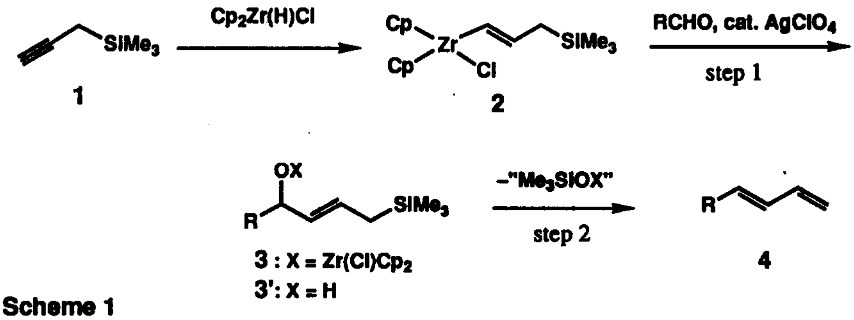
Abstract: A new synthetic method of 1,3-diene by three-carbon elongation of aldehyde is described. 3-Trimethylsilyl-1-propenylzirconocene chloride (**2**), generated from 3-trimethylsilyl-1-propyne (**1**) and $Cp_2Zr(H)Cl$, reacts with aldehyde in the presence of catalytic $AgClO_4$ and subsequent one-pot 1,4-elimination affords 1,3-dienes in high yields with excellent (*E*)-selectivities.

In this communication, we wish to describe a facile and highly (*E*)-selective method for the synthesis of terminal 1,3-dienes directly by three-carbon elongation of aldehydes (eq 1).

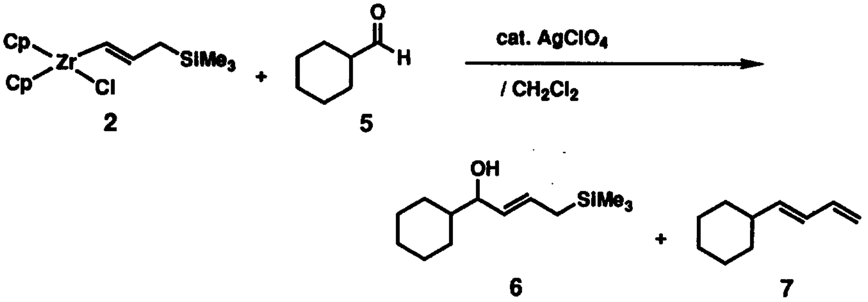
(1)

In the preceding paper,[1] we reported that a catalytic amount of $AgClO_4$ facilitates the Grignard-type addition of alkenyl- or alkylzirconocene chloride to aldehyde. We envisaged that this finding could be utilized for 1,3-diene synthesis provided that the following reaction scheme worked well (Scheme 1). The alkenylzirconocene chloride **2**, generated from 3-trimethylsilyl-1-propyne (**1**)[2] and $Cp_2Zr(H)Cl$,[3] would add to aldehyde in the presence of catalytic $AgClO_4$ to give the intermediary adduct **3** (step 1). Quenching at this stage would give allylic alcohol **3'**. Subsequent 1,4-elimination of "Me_3SiOX" would give 1,3-diene **4**,[4] which corresponds to the vinylogous Peterson olefination (step 2).[5]



Scheme 1

With this plan in mind, we treated **1** with $Cp_2Zr(H)Cl$ for 10 min to generate **2**. To the resulting solution was added aldehyde **5** followed by 5 mol% of $AgClO_4$. After 20 min, allylic alcohol **6** was isolated in 76% yield along with a small amount of diene **7** (4% yield). Acid treatment of **6** (cat. H_2SO_4 / CH_2Cl_2, room temp, 5 min) led to the formation of 1,3-diene **7** in 81% yield with excellent (*E*)-selectivity (*E*/*Z* = >99/1; capillary GC, OV-1).

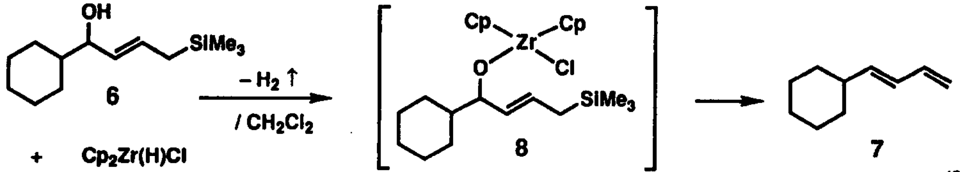


(2)

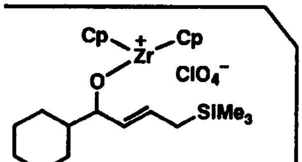
	6	7
rt, 20 min	76%	4%
rt, 20 min then reflux, 4 h	—	73%

Furthermore, this two-step conversion can be effected in one pot without isolating the allylic alcohol 6. Thus, after the addition reaction of **2** to **5** had completed as above, the reaction mixture was gently refluxed. TLC-Monitoring revealed the gradual conversion of the adduct **6** to the diene **7**, which was complete after 4 h. By this simple one-pot procedure, 1,3-diene **7** was obtained in 73% yield (eq 2).

In order to gain insight into the reaction mechanism, zirconocene alkoxide **8** was prepared from alcohol **6** and $Cp_2Zr(H)Cl$, where quantitative H_2 gas evolution was observed (eq 3). Contrary to our expectation, subsequent refluxing for 4 h (Cf. eq 2) led to no elimination and the starting alcohol **6** was recoverd in 97%. Clean elimination occurred, however, upon addition of a catalytic amount of $AgClO_4$ (5 mol%) at this stage, and 1,3-diene **7** was obtained in 78% yield after refluxing for 4 h. Thus, the presence of the perchlorate ion is essential also at this step, which, we surmised, may serve to generate a cationic zirconocene species as **9** to facilitate the departure of "$Cp_2Zr=O$".⁶⁾ The chain carrier of the cationic species may be Me_3SiClO_4, and indeed, $AgClO_4$ could be replaced by Me_3SiClO_4 to effect an even faster 1,3-diene formation.⁷⁾



(3)

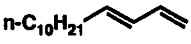
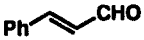
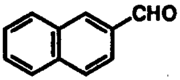
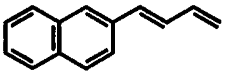
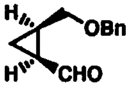
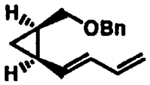
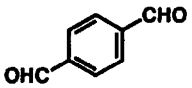
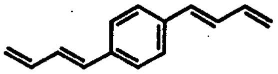
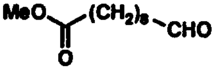
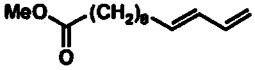


9

reflux, 4 h	trace
5 mol% $AgClO_4$ reflux, 4 h	78%
5 mol% Me_3SiClO_4 reflux, 2 h	76%

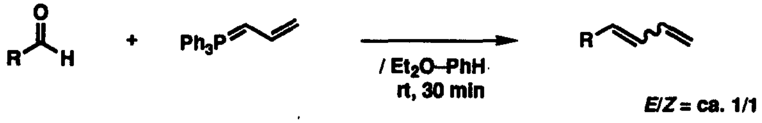
Table 1 shows the results of this reaction with some other aldehydes, which clearly shows the broad synthetic utility of this reaction. All reactions proceeded smoothly to give corresponding terminal 1,3-dienes in high yield with excellent (*E*)-selectivity.[8] In the reaction with aromatic aldehydes, the 1,4-elimination step was even more facile, which did not require any heating (runs 2, 3, 5). TLC-Monitoring showed no, if any, indication of accumulation of the intermediary alcohol during the course of the reaction. *trans*-Cinnamaldehyde gave (*E,E*)-triene **11** (run 2). The aldehyde having a cyclopropane ring was converted into **13** without event (run 4). Terephthalaldehyde was converted to bis-1,3-diene **14** with execellent (*E*)-selectivity (run 5). The reaction proceeded smoothly also in the case of an aldehyde having an ester function to afford **15** (run 6).

Table 1. Reaction of **2** with some aldehydes.[9]

Run	Aldehyde	Conditions	1,3-Diene	Yield / % a)	*E/Z* b)
1	$n\text{-}C_{10}H_{21}CHO$	rt, 1 h; then reflux, 1 h	 **10**	82	97/3
2		rt, 30 min	 **11**	90	96/4
3		rt, 30 min	 **12**	87	96/4
4		rt, 20 min	 **13**	78c)	98/2
5		rt, 20 min	 **14**	84	>99/1
6		rt, 50 min; then reflux, 1 h	 **15**	80	98/2

a) Yields refer to isolated, purified products.
b) Determined by ^1H NMR (400 MHz) analysis.
c) Starting aldehyde was recovered in 11% yield.

The present protocol is notable for its excellent (*E*)-selectivity. For comparison, the same conversion was carried out by utilizing the Wittig reagent,$^{10)}$ which led to stereo-random mixture (*E*/*Z* = ca. 1/1) of 1,3-diene in low yield (eq 4). We applied this reaction to all the aldehydes shown in Table 1 to prepare the authentic *E*/*Z*-mixture of dienes **10–15**.



(4)

In conclusion, a new and facile synthetic method of 1,3-diene is described, which relies on three-carbon elongation of aldehyde. According to this procedure, terminal 1,3-dienes are easily obtained with exellent (*E*)-selectivity in high yield.

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References and Notes:

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8. Typical procedure is as follows: To a suspension of $Cp_2Zr(H)Cl$ (234 mg, 0.907 mmol) in CH_2Cl_2 (3.0 mL) was added 3-trimethylsilyl-1-propyne (**1**) (106 mg, 0.944 mmol), and the mixture was stirred at room temperature for 10 min. To this solution was sequentially added 2-naphthaldehyde (118 mg, 0.756 mmol) in CH_2Cl_2 (1.0 mL) and then $AgClO_4$ (8 mg, 39 μmol, 5 mol%) and the solution was stirred for further 30 min. After the reaction mixture was poured into saturated $NaHCO_3$ aqueous solution and extractive workup (EtOAc) followed purification on preparative TLC (hexane/EtOAc = 90/10) gave 1,3-diene **12** (119 mg, 87%). ^{1}H NMR analysis showed that the *E*/*Z* selectivity was 96/4.
9. All new compounds were fully characterized by ^{1}H-, ^{13}C NMR, IR, and HRMS.
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