Pergamon

Tetrahedron Letters 39 (1998) 7885–7888

TETRAHEDRON LETTERS

Stereoselective Synthesis of Cyclopentanols by Lewis Acid-Mediated [3+2] Annulation of Allyldiisopropylphenylsilane with α,β-Unsaturated Diesters

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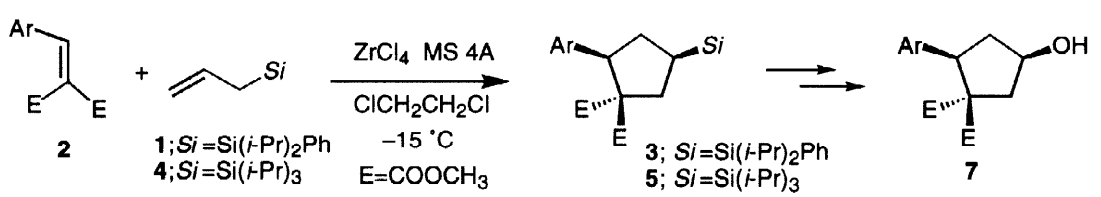
Received 24 June 1998; revised 10 August 1998; accepted 17 August 1998

Abstract

$ZrCl_4$-mediated annulation of allyldiisopropylphenylsilane with α,β-unsaturated diesters and subsequent oxidative cleavage of the carbon-silicon bond furnished cyclopentanols highly stereoselectively.

Keywords: Annulation; Cyclobutanes; Cyclopentanes; Silicon and compounds

The development of efficient methods for constructing carbocycles continues to be an important goal of synthetic organic chemistry. Lewis acid-promoted [3+2] as well as [2+2] annulation of allylsilane constitute attractive strategy[1] for the stereoselective synthesis of both 5-membered[2,3] and 4-membered silyl-substituted ring compounds.[4,5] Use of allylsilane bearing a sterically demanding silyl group suppressed the Hosomi-Sakurai reaction,[6] thereby promoting the formation of the cycloadducts in high yields. As part of our continuing effort to explore annulation reactions using allylsilane,[3e,3f,5a,5c] we have elucidated, in a previous paper,[7] that allyldiisopropylphenylsilane (**1**) is particularly useful as a counterpart for the [3+2] annulation and, furthermore, the diisopropylphenylsilyl group is highly susceptible to the oxidative cleavage.[8,9] We wish to report herein novel stereoselective formation of silyl-substituted cyclopentanes (**3** and **5**) by zirconium(IV) chloride-mediated [3+2] annulation of allylsilanes (**1** and **4**) with α,β-unsaturated diesters (**2**) and confirmed that the diisopropylphenylsilyl group could be oxidative cleaved smoothly to afford cyclopentanols (**7**) highly stereoselectively.



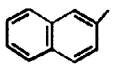
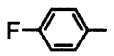
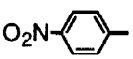
0040-4039/98/$ - see front matter
PII: S0040-4039(98)01748-1

Table 1. Effect of the Lewis Acid

Entry	Lewis Acid	Reaction time	Yield of **3a**/%
1	$ZrCl_4$	2 h	42[a]
2	$ZrCl_4$	2.5 h	68
3	$HfCl_4$	2 h	37
4	$SnCl_4$	4.5 h	33
5	$TiCl_4$	24 h	trace

a) Reaction was carried out without molecular sieves 4A.

Table 2. [3+2] Cycloannulation of Allylsilanes

Entry	SM[a]	Ar	Si=Si(*i*-Pr)$_2$Ph Yield of **3**/%	Si=Si(*i*-Pr)$_3$ Yield of **5**/%
1	**2a**		68	70
2	**2b**		56	70
3	**2c**		56	64
4	**2d**		54	61

a) Starting material.

At the outset, treatment of allyldiisopropylphenylsilane (**1**) with dimethyl benzylidenemalonate (**2a**) in the presence of zirconium(IV) chloride (1.0 equiv) in 1,2-dichloroethane at −15 °C for 2.5 h furnished a silyl-substituted cyclopentane (**3a**) in 42% yield as a single diastereomer judged by 400 MHz ^{1}H NMR (Table 2, Entry 1). Addition of MS 4A increased the yield of **3a** to 68% yield.[10,11] The relative stereochemistry of **3a** was unambiguously determined by multiple ^{1}H NMR NOE experiments. Other Lewis acids were less effective for the annulation (Entries 3-5). The annulation with allyltriisopropylsilane (**4**) yielded the cycloadduct (**5a**) in 70% yield. The reactivity of **1** turned out to be comparable to that of **4**, which is generally the most reactive for the annulation;[2e] hence **1** is superior to other allylsilanes. For example, yield of the cycloadduct with **2a** using allylsilanes bearing other silyl groups are as follows: Si(*t*-Bu)Ph$_2$ = 44%, SiMe$_2$(*t*-Bu) = 24%, SiPh$_3$ = trace.

The present $ZrCl_4$-promoted annulation with several β-aryl-substituted α,β-unsaturated diesters took place smoothly to afford tetra-substituted cyclopentanes in moderate to good yields and the results are shown in Table 2. Stereoselectivity of the annulation is fairly high (>96: 4) as determined by 400 MHz ^{1}H NMR.

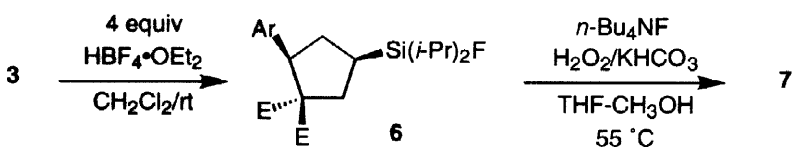


Table 3. Oxidative Cleavage of the Carbon-Silicon Bond

Entry	SM[a]	Time	Yield of **6**/%	Time	Yield of **7**/%
1	**3a**	1 d	95	4 h	83
2	**3b**	1 d	86	4 h	73
3	**3c**	3 d	90	6 h	80
4	**3d**	5 d	94	10 h	81

a) Starting material.

Transformation of the silyl group of **3** into a hydroxy moiety was successfully achieved in 2 steps.[7] Treatment of **3** with HBF$_4$•OEt$_2$ for 1-5 d gave **6** and subsequent HOOH oxidation in the presence of fluoride for 4-6 h afforded cyclopentanols (**7**) stereoselectively in good yields. (Table 3)

Although Knölker already reported titanium(IV) chloride-promoted [2+2] annulation of allylsilane with α,β-unsaturated esters leading to cyclobutanes,[4b] the sole cycloadducts obtained with **1** and **2** were

cyclopentanes, [3+2] cycloadducts. We speculated that if the annulation could be performed at lower temperatures, a [2+2] cycloadduct might be formed. Thus, β-unsubstituted α,β-unsaturated diesters (**8**)[12] were employed as substrates (Table 4). As expected, annulation took place smoothly at −78 °C to afford cyclobutanes (**9**) exclusively in high yields (Entries 1 and 3). In striking contrast, the reaction course changed dramatically at −10 °C to afford a [3+2] cycloadducts (**10**) exclusively (Entries 2 and 4). Furthermore, treatment of **9a** with zirconium(IV) chloride (1.0 equiv) at −10 °C for 30 min gave rise to **10a** in 80% yield. This result clearly implies that cyclobutanes (**9**) are kinetic products while cyclopentanes (**10**) are thermodynamic products.[13] It is probable that the cyclopentanes (**3**) were obtained via initial formation of the cyclobutane followed by ring enlargement to the cyclopentane.

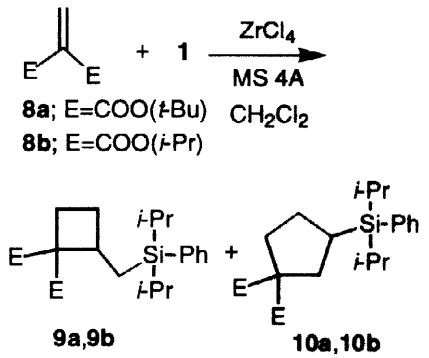
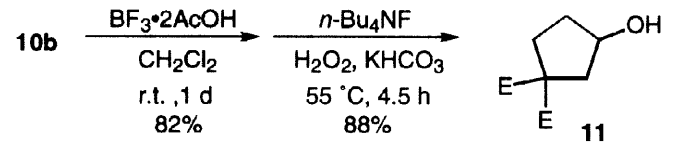


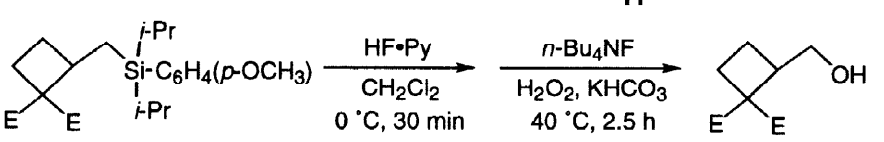
Table 4. Temperature effect

Entry	E	Temp./°C	Yield of **9**/%	Yield of **10**/%
1	COO(*t*-Bu)	−78	100	0
2	COO(*t*-Bu)	−10	0	95
3	COO(*i*-Pr)	−78	62	0
4	COO(*i*-Pr)	−10	0	75

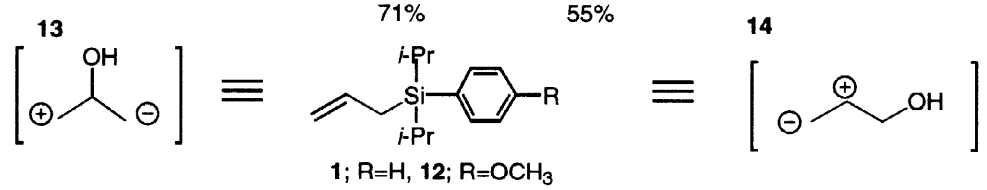
Finally, oxidative cleavage of the silyl group thus obtained was studied. Transformation of the silyl group of **10b** took place smoothly under the identical conditions used above to afford a cyclopentanol (**11**) in a high yield (Scheme 1). Unfortunately, all of our attempts for the protodesilylation of **9b** failed due to the decomposition of the cyclobutane ring. Treatment of a cyclobutane (**13**), which was obtained by $ZrCl_4$-promoted annulation of allyldiisopropyl-(4-methoxyphenyl)silane (**12**) with **8b** in 70%, with HF•Py at 0 °C followed by oxidation afforded a hydroxymethylcyclobutane (**14**) in a good yield (Scheme 2).



Scheme 1



Scheme 2



1; R=H, **12**; R=OCH_3

In summary, we have developed a novel [3+2] annulation reaction leading to cyclopentanols. The usefulness of **1** and **12** as synthetic equivalents of 2-hydroxy-1,3-dipole and 2-hydroxymethyl-1,2-dipole has been demonstrated.

Acknowledgments: Financial support from Mitsubishi Petrochemical Foundation for the Promotion of Science and a grant for academic research by Abe Yoshishige Memorial Fund for Education are greatly appreciated.

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[10] A typical experimental procedure for the preparation of **3a** is described (entry 2, Table 1). To a suspension of **1** (142 mg, 0.61 mmol), **2a** (102 mg, 0.47 mmol), and powdered molecular sieves 4A (200 mg) in 1,2-dichloroethane (2.8 ml) was added zirconium(IV) chloride (109 mg, 0.47 mmol) at –15 °C. After being stirred at that temperature for 2.5 h, the reaction mixture was quenched by addition of aqueous triethylamine solution. The aqueous layer was extracted with ethyl acetate and the combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, and concentrated to dryness. Purification of the crude mixture by thin layer chromatography (SiO_2, hexane: ethyl acetate = 4:1, v/v) gave **3a** (145 mg, 68%).

[11] Data for selected compounds follow: **3a**; ^{1}H-NMR (400 MHz, $CDCl_3$) δ= 7.78-7.56 (2H, m), 7.40-7.35 (3H, m), 7.10-7.05 (5H, m), 4.08 (1H, dd, J= 10.8, 6.9 Hz), 3.75 (3H, s), 3.05 (3H, s), 2.78 (1H, dd, J=13.7, 13.7 Hz), 2.36 (1H, ddd, J=13.7, 7.1, 1.6 Hz), 2.28 (1H, dddd, J=12.8, 6.9, 6.9, 1.6 Hz), 2.06 (1H, ddd, J=12.8, 12.8, 10.8 Hz), 1.58 (1H, dddd, J= 13.7, 12.8, 7.1, 6.9 Hz), 1.48-1.38 (2H, m, C<u>H</u>$(CH_3)_2$), 1.13-1.10 (12H, m, CH(C<u>H</u>$_3)_2$ x 2); ^{13}C-NMR (100 MHz, $CDCl_3$) δ=173.32 (CO), 171.08 (CO), 140.75, 135.17, 134.26, 128.91, 128.55, 127.84, 126.69, 66.56 (C), 52.73 (CH_3), 52.69 (CH_3), 51.72 (CH), 38.19 (CH_2), 36.00 (CH_2), 22.28 (CH), 18.70 (CH_3), 18.60 (CH_3), 11.42 (CH), and 11.35(CH).
7a; ^{1}H-NMR (400 MHz, $CDCl_3$) δ= 7.35-7.20 (5H, m), 4.39 (1H, dddd, J=8.4, 7.6, 5.9, 4.4 Hz), 4.05 (1H, dd, J=11.0, 8.4 Hz), 3.72 (3H, s), 3.32 (1H, bs, OH), 3.23 (3H, s), 2.62 (1H, dd, J= 14.6, 4.4 Hz), 2.59 (1H, ddd, J= 13.7, 8.4, 8.4 Hz), 2.37 (1H, dd, J= 14.6, 7.6 Hz), 2.16 (1H, ddd, J= 13.7, 11.0, 5.9 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$) δ=172.30 (CO), 171.82 (CO), 139.14, 128.58, 127.97, 127.17, 70.94 (CH), 64.72 (C), 52.67 (CH_3), 52.26 (CH_3), 49.56 (CH), 44.17 (CH_2), and 41.43 (CH_2).

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[13] Similar behavior on the change of reaction course by the temperature has been observed; see Ref. 2g, 2j, and 4b.

[14] After submission of this manuscript, Knölker reported that *t*-$BuPh_2Si$ and $(i\text{-}Pr)_2PhSi$ groups are susceptible to the oxidative cleavage. See: Knölker H-J, Jones PG, Wanzl G. Synlett 1998;613-616.