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Silicon Effect Favoring the Formation of a Cyclopentene *via* Palladium-Catalyzed 5-*Endo-trig* Cyclisation

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Abstract :
A silyl substituted cyclopentene was prepared from acyclic triethylsilyl pentenol derivatives *via* pallladium-catalyzed *5-endo-trig* process.

Keywords: Palladium and compounds, cyclopentenes, silicon, cyclisation.

Palladium-catalyzed cyclisations have been the subject of intensive studies since the first works of Tsuji and Trost. One can assume that nearly all rings are available by this methodology.[1] In our continous effort studying the reactivity of variously silylated allylic compounds,[2] we want to report here the preparation of silyl-substituted cyclopentenes and vinylcyclopropanes. To our knowledge, palladium catalyst usually favour 3-*exo-trig* process and disfavour 5-*endo-trig* cyclisation.[3] In some conjugated systems, vinylcyclopentenes are obtained as the main product.[4] Goré et al. have reported a fully detailled study on the reactivity of allenes, with halogenated alkenes in the presence of Pd(II) salts. Depending on the substitution of the vinyl or aryl group, they selectively obtained cyclopentenes or vinylcyclopropanes.[5] In a different approach, Hiroi prepared cyclopentenes from cyclopropyl-sulfones or -sulfoxides.[6]

It has been reported that, in palladium-catalyzed allylic substitutions, silyl groups directed attack of the nucleophile distal from his position in the π-allyl cationic complexe.[7] Another advantage is that, in proper conditions, silicon could be removed or used for further functionalization. In this short communication, we demonstrate that, in palladium-catalysed reactions, silicon at a correct position will favor 5-*endo-trig* cyclisation versus 3-*exo-trig*. For this study, starting materials were prepared by standard protocols from the commercially cheap 1,4-butyne diol.[2] We first examined the reaction of the simpliest allylic acetate **1** bearing a dimethylmalonate group in β relative to the silicon (entry 1, table 1). After 4 hours at reflux, the expected cyclopentene **2** was isolated in 74% yield.[8] As expected, the corresponding regioisomer **3** gave the vinyl cyclopropane **4** (entry 2). Finally, we used keto-ester **5**. It could reacts either in hetero- or carbo-cyclisation. Dihydrofuran derivative **6** was obtained in 69% yield, confirming the preference, when choice is, for 5-*exo-trig* versus 5-*endo-trig* cyclisation.

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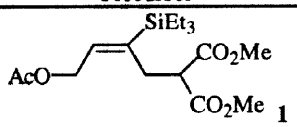
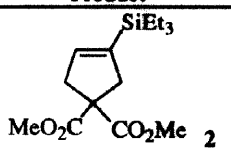
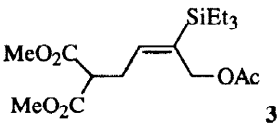
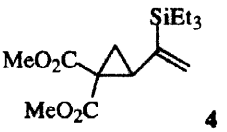
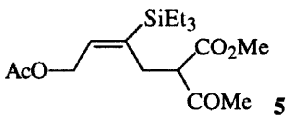
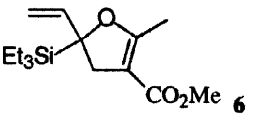
Table 1 : Cyclisations catalyzed by Pd(0).

Entry	Precursor	t (h) ; T(°C)[a]	Product	Yield (%)[b]
1	 1	4 ; 60	 2	74 (94)
2	 3	12 ; rt	 4	50 (80)
3	 5	3 ; 60	 6	69

a) NaH (1.1 equiv), 5 mol% $Pd(PPh_3)_4$ prepared *in situ* b) non optimized yields after purification and yields based on recovered starting material.

In conclusion, we have demonstrated that silyl group, at a proper position can drive palladium-catalyzed cyclisations to the 5-*endo-trig* process. Balance has to be found between the size and the basicity of the internal nucleophile. We are currently studying the scope and the limitation of this reaction and work is underway to extend this process toward an enantioselective version.

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8. All new compounds have been fully characterized. Typical procedure for cyclisation :
The materials were dried by flame before reaction and kept under Argon. To a suspension of NaH (0.123 g, 1.1.equiv) in dry THF (10 mL), is added at 0°C, the silylated malonic acetate **1** (1.0 g, 2.8 mmol). After 30 min., a preformed solution of $Pd(OAc)_2$ (5 mol%), PPh_3 (20 mol%) in THF (12 mL) was added. The mixture was warmed at reflux and evolution followed by TLC. After 4h, a saturated solution of aqueous NH_4Cl (20 mL) was added. The solution was extracted with ether (2x25 mL), the organic layer washed with brine (2x50 mL) and dried over $MgSO_4$. Evaporation of the solvent under reduced pressure followed by flash chromatography (PE:9.5/EA:0.5) yielded to 0.62 g (74%) of the expected cyclopentene **2**.
Anal. calcd. for $C_{15}H_{25}O_4Si$: C, 60.37 ; H, 8.78. Found : C, 60.41 ; H, 8.90.
^1H NMR (400 MHz, $CDCl_3$) : δ : 5.85 (t, J = 2 Hz, 1H) ; 4.72 (s, 6H) ; 3.11 (d, J = 2 Hz, 2H) ; 3.06 (d, J = 2 Hz, 2H); 0.94 (t, J = 8 Hz, 9H) ; 0.61 (q, J = 8 Hz, 6H).
^{13}C NMR (50 MHz, $CDCl_3$) δ : 172.9, 140.0, 138.0, 60.2, 52.8, 45.1, 43.3, 7.4, 3.1.
IR (neat) 2940, 2900, 1740, 1600, 1450, 1250, 1150, 730 cm^{-1}.