

Reactions of dicarbanion equivalents generated from complexation of 1,3-dienes on Ti(II) moiety

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Received 24 August 2006; revised 14 September 2006; accepted 18 September 2006

Available online 6 October 2006

Abstract—Conjugated dienes are able to react as 1,2- or 1,4-dicarbanions by coordination on Ti(II) moiety. These two possibilities are exemplified in this letter with isoprene, myrcene and several aldehydes to give 1,4- and 1,6-diols. When allowed to react with esters at room temperature, the titanium–diene complexes lead to cyclopentenol derivatives. Surprisingly, when this reaction is performed at lower temperature (−40 °C), allylic ketones are formed with high regio and diastereoselectivities.

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A wide variety of beautiful organic syntheses result from Kulinkovich's method.¹ It involves the generation of alkene–titanium reagents through an exchange of ligands of the in situ formed (η^2 -ethylene) or (η^2 -propene)Ti(O^{*i*}Pr)₂ complex, and their use as dicarbanion source with various electrophilic substrates. In this field, only few works are relevant to the employment of conjugated dienes. de Meijere and co-workers have observed that they behave as 1,2-dicarbanions due to the vinyltitanacyclopropane intermediates **A** and **C** whereas Sato and co-workers mentioned a titanacyclopentene **B** with 1,4-dicarbanionic properties (Fig. 1).^{2,3} Formation of the same five-membered intermediate was recently proposed by Goeke et al. when Ti(O^{*i*}Pr)₄ is treated with 2 equiv of butenylmagnesium chloride.⁴

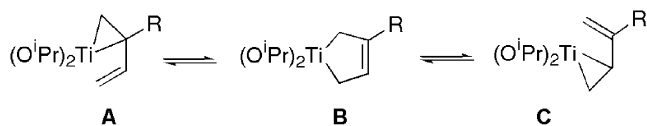


Figure 1. Conjugated diene–titanium complexes A–C.

As a continuation of our efforts on organic synthesis mediated by titanium derivatives,⁵ we have investigated

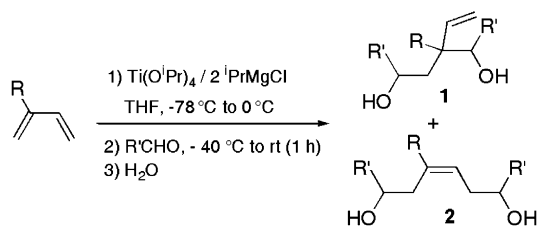
the reactivity of two dienes, isoprene and myrcene, towards aldehydes and esters according to the Kulinkovich methodology; we wish to report here our main results.

Benzaldehyde has been condensed first at low temperature (−40 °C) on the isoprene complex generated in situ by the ligand exchange method.⁶ After warming the solution to room temperature, the reaction mixture was stirred during 1 h and quenched with water. Usual treatment offered the two diols **1a** and **2a** in 1/2 ratio (Table 1, entry 1). Thus, while Goeke et al. reported that the butadiene complex leads exclusively to hex-3-ene-1,6-diol,⁴ the analogue isoprene complex behaves both as a 1,2- and 1,4-dicarbanion. This difference suggests that methyl substitution at the diene ligand gives rise to higher nucleophilicity of the substituted double bond allowing the diene to display its 1,2-dicarbanion properties. On the other hand, switching benzaldehyde to bulkier aldehydes such as isobutyraldehyde and pivalaldehyde led exclusively to 1,6-diols (**2b** and **2c**, Table 1, entries 2 and 3). We suggest that the absence of 1,2-condensation adduct in both the last cases may be due to steric factors. A similar regioselectivity was observed with myrcene. Thus, while the coupling with acetaldehyde and propanal led to a mixture of 1,4- and 1,6-diols, the reaction with isobutyraldehyde afforded exclusively the 1,6-diol **2f** (Table 1, entries 4 and 5 vs 6).

Remarkably, each diol has been isolated as a single diastereoisomer. Thus, this coupling which creates two

Keywords: Titanium; Diene; Diol; Cyclopentenol; Allylic ketone.

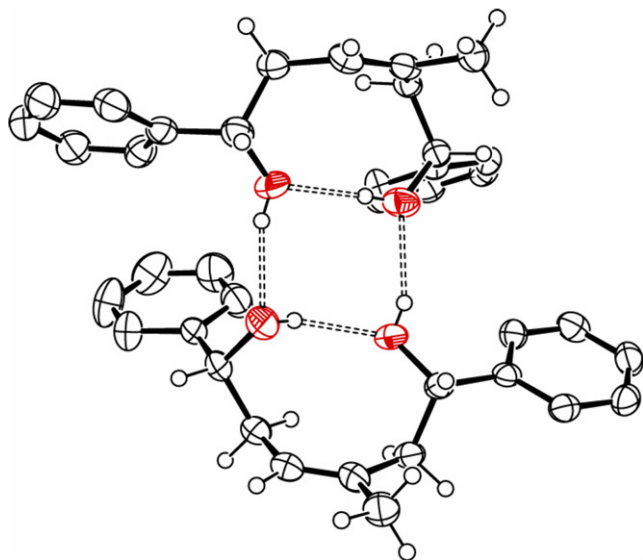
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Table 1. Synthesis of 1,4-diols **1** and 1,6-diols **2** from aldehydes and 1,3-dienes assisted with titanium complex

Entry	R	R'	1 Yield (%)	2 Yield (%)
1	Me	Ph	11 (1a) ^a	23 (2a) ^a
2	Me	^t Pr	—	38 (2b) ^a
3	Me	^t Bu	—	18 (2c) ^a
4	(CH ₂) ₂ CH=CM ₂	Me	17 (1d) ^a	51 (2d) ^a
5	(CH ₂) ₂ CH=CM ₂	Et	15 (1e) ^a	36 (2e) ^a
6	(CH ₂) ₂ CH=CM ₂	^t Pr	—	69 (2f) ^a

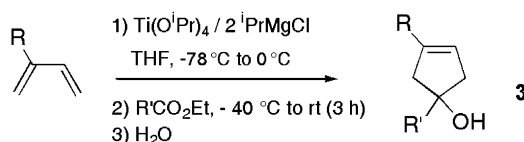
^a Product isolated as a single diastereoisomer.

or three chiral centres proceeds with a complete diastereoselectivity. Suitable crystals for X-ray diffraction have been obtained by slow evaporation of a CH₂Cl₂/pentane solution of **2a**.⁷ The ORTEP view represented in Figure 2 shows that both enantiomers of the pseudo-*meso* diastereoisomer **2a** crystallise in the unit cell with a square shape hydrogen bonds network. In addition, the geometry of the double bond can be attributed to be *Z* which is in accordance with the literature.⁴

**Figure 2.** ORTEP view of the racemate of the pseudo-*meso* diastereoisomer **2a**.

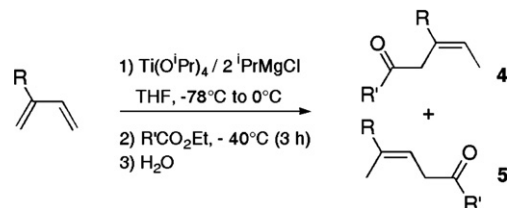
To extend the scope of this reaction, we applied the same procedure with esters. Thus, esters were added at $-40\text{ }^{\circ}\text{C}$ to the preformed titanium isoprene complex. Then, the solution was allowed to stir at room temperature during 3 h and quenched with water.⁸ Usual treatment afforded the cyclopentenol **3** in moderate to good yields (Table 2, entries 1–4).⁹ When employing myrcene instead of isoprene the reaction proceeds smoothly leading to the corresponding cyclopentenols in higher yields

(55–70% yields, Table 2, entries 5–8). It can be noticed that this reaction is only slightly affected by the bulkiness of the esters.

Table 2. Synthesis of cyclopentenols **3** from esters and 1,3-dienes assisted with titanium complex

Entry	R	R'	Yield (%)
1	Me	Me	30 (3a)
2	Me	Et	45 (3b)
3	Me	Ph	45 (3c)
4	Me	Bn	60 (3d)
5	(CH ₂) ₂ CH=CM ₂	Me	70 (3e)
6	(CH ₂) ₂ CH=CM ₂	Et	60 (3f)
7	(CH ₂) ₂ CH=CM ₂	^t Pr	65 (3g)
8	(CH ₂) ₂ CH=CM ₂	^t Bu	55 (3h)

At this point, it should be mentioned that cyclopentenols are always accompanied by a small amount of allylic ketones whose structures are represented in Table 3. Surprisingly, we noticed that when the temperature of the reaction mixture was carefully maintained below $-40\text{ }^{\circ}\text{C}$, the allylic ketones **4** and **5** can be formed selectively in moderate to good yields (Table 3).¹⁰ At this temperature, the ester insertion appears to be regio and stereoselective since the carbonyl products are obtained as a single isomer. Esters generally react with the most substituted double bond leading after hydrolytic workup to the head *cis*-allylic ketones (**4a–f**, Table 3, entries 1–6). The regioselectivity of this reaction can be reversed through the use of the bulky ethyl-2,2-dimethylpropionate (**5g**, Table 3, entry 7). Of significant importance is also the fact that no trace of 1,2-adduct (homoallylic ketones) or double insertion product

Table 3. Synthesis of allylic ketones **4** and **5** from esters and 1,3-dienes assisted with titanium complex

Entry	R	R'	4 Yield (%)	5 Yield (%)
1	Me	^t Pr	48 (4a)	—
2	(CH ₂) ₂ CH=CM ₂	H	22 (4b)	—
3	(CH ₂) ₂ CH=CM ₂	Me	54 (4c)	—
4	(CH ₂) ₂ CH=CM ₂	Et	57 (4d)	—
5	(CH ₂) ₂ CH=CM ₂	Bn	58 (4e)	—
6	(CH ₂) ₂ CH=CM ₂	^t Pr	35 (4f)	—
7	(CH ₂) ₂ CH=CM ₂	^t Bu	—	35 (5g)

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