

SYNTHESIS OF HOMOALLYL ALCOHOLS BY THE REACTION OF  $\pi$ -ALLYL-DICYCLOPENTADIENYL TITANIUM(III) WITH CARBONYL COMPOUNDS

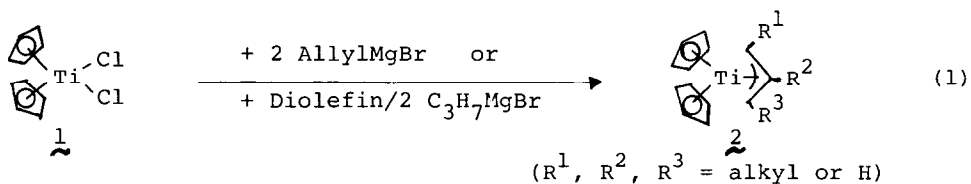
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Summary: Reaction of  $\pi$ -allyldicyclopentadienyltitanium(III) complexes, preformed or formed in situ, with aldehydes or ketones proceeds with regioselectivity, high stereoselectivity and chemospecificity, affording, under mild conditions, the corresponding homoallyl alcohols after hydrolysis in excellent yields.

$\pi$ -Allylnickel and palladium complexes are finding increasing acceptance for use as reagents or intermediates in organic synthesis because of their ready availability, unusual reactivity patterns and high specificity<sup>1</sup>. In addition, the  $\pi$ -allylcobalt complex  $\eta^3\text{-C}_3\text{H}_5\text{Co[P(OMe)}_3\text{]}_3$  has been shown to be an extremely effective homogeneous catalyst for hydrogenation of aromatic hydrocarbons<sup>2</sup>. However, to the best of our knowledge, no other  $\pi$ -allyltransition metal complexes have been used in organic synthesis.

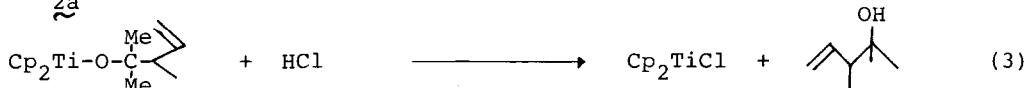
The  $\pi$ -allyltitanium complexes of the type  $(\eta^5\text{-C}_5\text{H}_5)_2\text{Ti}(\eta^3\text{-allyl})$  (2) are readily obtained by reaction of  $(\eta^5\text{-C}_5\text{H}_5)_2\text{TiCl}_2$  (1) either with allyl Grignard reagents<sup>3</sup> or with an alkyl Grignard reagent and diolefins<sup>4</sup> (eq. 1). Therefore, if 2 showed interesting reactivity, it could become a useful reagent or intermediate in organic synthesis.



We report here that 2 can be utilized in the title reaction.

When acetone was added to a purple ether solution of  $(\eta^5\text{-C}_5\text{H}_5)_2\text{Ti}(\eta^3\text{-C}_4\text{H}_7)$  (2a)<sup>4</sup>

at room temperature under argon, reaction occurred spontaneously and the color of the solution changed to brown. Quenching the reaction mixture with 4N-HCl followed by oxidation with air afforded 2,3-dimethyl-4-penten-2-ol and 1 in 92 and 90% yields, respectively. These results strongly suggested that the reaction proceeds via the pathway as shown in eqs. 2, 3 and 4, because it is known that  $(\eta^5\text{-C}_5\text{H}_5)_2\text{TiCl}$  can be readily oxidized to 1 by oxygen in the presence of HCl.<sup>3</sup>



Similarly, 2a reacted with benzaldehyde to give 2-methyl-1-phenyl-3-buten-1-ol and 1 in excellent yields.

Not only the high reactivity of 2a towards ketones and aldehydes<sup>5</sup> but also the recoverability of 1 in good yield after the reaction suggests considerable synthetic potential. In addition, it was observed that the addition reactions proceed similarly by use of 2a formed in situ from 1, propylmagnesium bromide and butadiene. As the  $\pi$ -allyltitanium complexes are quite air sensitive, the in situ method is preferable for synthetic purposes.

The results of the reaction between 2 (generally prepared in situ) and carbonyl compounds are summarized in Table 1, which shows that the reaction has wide applicability.

A representative (in situ) procedure is as follows:  $\text{C}_3\text{H}_7\text{MgBr}$  (16.6 ml of a 1.0 M solution in ether, 16.6 mmol) was added under argon to a stirred solution of 1 (2.1 g, 8.4 mmol) and butadiene (0.86 g, 15.9 mmol) or isoprene (0.60 g, 8.8 mmol) in ether (40 ml). After 30 min at 20°C<sup>8</sup>, 0.9 to 1.0 equiv. of an aldehyde or ketone was added by a syringe, and the solution was stirred for 1 h at room temperature. The reaction mixture was quenched with 4N-HCl (40 ml), stirred for 30 min under argon, and with stirring air was passed through the resulting two layers of ether (pale red color) and water (green<sup>9</sup>) for 15 min. During this operation the green color faded out and 1.7 g of red crystals of 1 precipitated, and were isolated by filtration. The ether layer was separated and the aqueous layer (pale red) was extracted with ether. The combined ether layers were dried over  $\text{MgSO}_4$  and then the solvent was removed under reduced pressure to afford a mixture of 1 and an oil. Pentane (30 ml) was added to the mixture and 1 (0.1 g) was separated by filtration. Chromatography of the pentane solution on silica gel (by ether) afforded the product as an oil.

Table 1  
REACTION OF  $\pi$ -ALLYLTITANIUM COMPLEXES WITH CARBONYL COMPOUNDS

Rn.	Titanium complex	Carbonyl compound	Product	Yield <sup>a,b</sup> %	$\underline{1}$ Recovered %
1	1-Methylallyl <sup>c</sup>	Acetone		88 (92)	86 (90)
2		Methyl vinyl ketone		91	92
3		Benzaldehyde		93	91
4		Propionaldehyde		84	91
5	1,2-Dimethylallyl <sup>c</sup>	Cyclohexanone		95 (98)	86 (85)
6		Acrolein		90	87
7		Chloroacetone		95	94
8		Levulinic acid methyl ester		94	89
9	1-Ethylallyl <sup>d</sup>	Acetone		83 (86)	92 (90)

<sup>a</sup>Isolated yield, based on the carbonyl compound. <sup>b</sup>Yields obtained by the in situ procedure; yields obtained by using the isolated titanium complex in parentheses. <sup>c</sup>Prepared from  $\underline{1}$ , diene and  $C_3H_7MgBr$ . <sup>d</sup>Prepared from  $\underline{1}$  and 1-ethylallylmagnesium bromide. Isolated in 60% yield, mp. 90.5-91.0°C.

<sup>e</sup>The compound is a 65:35 mixture of diastereoisomers. <sup>f</sup>95:5 mixture of threo and erythro isomers, determined by  $^1H$  NMR.<sup>6</sup> <sup>g</sup>93:7 mixture of threo and erythro isomers, determined by GLC (PEG).<sup>7</sup> <sup>h</sup>Ratio of diastereoisomers was not determined. <sup>i</sup>90:10 mixture of diastereoisomers.

A striking feature of the reaction is the regiospecificity and high stereoselectivity and chemospecificity.

As is seen from the table, the more substituted  $\gamma$  carbon of the allyl group becomes attached to the carbonyl carbon. With  $\alpha,\beta$ -unsaturated aldehydes and ketones, the allyl unit adds exclusively in 1,2-fashion.

The threo diastereomer was obtained predominantly from 2a and benzaldehyde<sup>10</sup> (run 3) or propionaldehyde (run 4), which is seen as excluding the participation of a free radical intermediate.

Functional groups other than aldehydes and ketones are unreactive or react sluggishly. Thus, the allyl unit was selectively introduced at the aldehyde or ketone carbon of compounds containing either an ester (run 8) or halogen group (run 7).

Further work is underway to establish the scope of the present reaction and to explore the reactivity of the  $\pi$ -allyltitanium complex towards other substrates.

#### References and Notes

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