

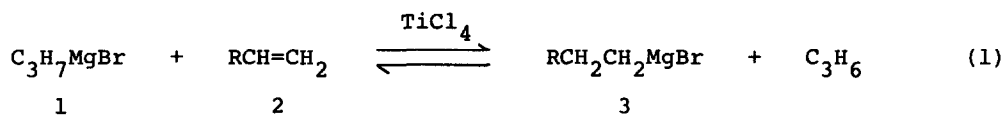
**Cp₂TiCl₂-CATALYZED GRIGNARD EXCHANGE REACTIONS WITH 1,3-DIENES
OR STYRENES. PREPARATION OF ALLYLIC AND α -ARYLETHYL GRIGNARD
REAGENTS BY A CONVENIENT AND QUANTITATIVE METHOD**

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The addition of a catalytic amount of Cp₂TiCl₂ to an ether solution of propylmagnesium bromide and 1,3-dienes brings about an exchange reaction forming allylic Grignard reagents. Styrene also undergoes the exchange reaction under the same conditions affording α -phenethylmagnesium bromide.

Finkbeiner and Cooper have reported that when propylmagnesium bromide (1) and 1-olefins (2) are refluxed in ether with a catalytic amount of TiCl₄, a reversible exchange takes place and Grignard reagent (3) is obtained as shown in eq 1.¹ They also reported that though styrene undergoes exchange under the same conditions, the reaction with 1,3-dienes is complex and only small yields of the corresponding mono-Grignard reagents are obtained.



We have now found that Cp₂TiCl₂ catalyzes the exchange of 1,3-dienes with Grignard reagent to give allylic Grignard reagents in excellent yields, and that Cp₂TiCl₂ is a more effective catalyst than TiCl₄ for exchange with styrene.
Exchange reaction of 1,3-dienes.

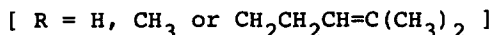
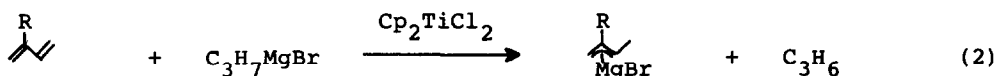
The present reaction, as represented by the example of isoprene and propylmagnesium bromide, is a strikingly convenient method for preparation of allylic

Grignard reagents.

A catalytic amount of Cp_2TiCl_2 (0.2 mmol) was added to a mixture of $\text{C}_3\text{H}_7\text{MgBr}$ (20 mmol) and isoprene (22 mmol) in 20 ml of ether contained in a 100 ml Schlenk flask fitted with a condenser, and the reaction mixture was then stirred for 3 h at 25°C under argon. In one experiment, the reaction mixture was hydrolyzed by dilute HCl and gas chromatographic analysis of the hydrolysis product indicated the formation of 2-methyl-1-butene (76%) and 2-methyl-2-butene (21%), whereas no 3-methyl-1-butene and 2-methylbutane were detected. In another experiment, the reaction product was treated with acetone at room temperature for 2 h to afford 2,3,4-trimethyl-4-penten-2-ol in 95% yield, while 2-methyl-2-pentanol, the reaction product expected from propylmagnesium bromide and acetone, was not detected [see Table 1]. These results strongly indicate the selective and almost quantitative production of 1,2-dimethylallylmagnesium bromide from isoprene and that the reaction is nonreversible² as shown in eq 2.

Similarly, butadiene exchanges with $\text{C}_3\text{H}_7\text{MgBr}$ to give the allylic Grignard reagent which shows reactivity indistinguishable to that of the Grignard reagent obtained from Mg and crotyl or 2-methylallyl bromide. In this case, however, the rate was slower than that for isoprene. Thus, treatment with acetone after 20 h reaction of $\text{C}_3\text{H}_7\text{MgBr}$ with an excess of butadiene gave a 79% yield of 2,3-dimethyl-4-penten-2-ol with 19% of 2-methyl-2-pentanol.

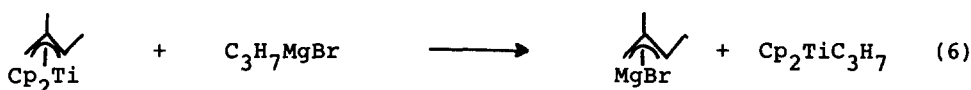
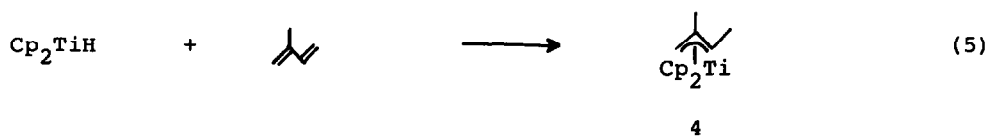
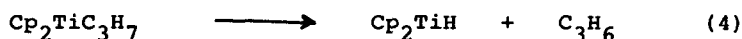
Myrcene also underwent exchange with $\text{C}_3\text{H}_7\text{MgBr}$ completely in 3 h at 25°C affording the allylic Grignard reagent with the structure shown in eq 2.



We are now investigating the exchange reactions of various dienes to clarify the scope and limitations of the present reaction. Results obtained so far have revealed that 1,2-dienes did not give allylic Grignard reagents.

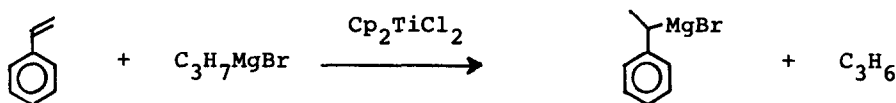
It has been reported that π -allyltitanium(III) compound, **4**, is obtained in high yield by reaction of $\text{C}_3\text{H}_7\text{MgBr}$ (2 mol) with Cp_2TiCl_2 (1 mol) in the presence of isoprene, and that the reaction proceeds via intermediate Cp_2TiH .³ Thus the selective production of methylallyl Grignard reagent in the present reaction may be explained by the formation of intermediate **4** followed by titanium-magnesium exchange as shown in eqs 3-6. The finding that 1,2-dienes did not give allylic Grignard reagents is rationalized by the observation that no allylic titanium compounds were obtained from the

reaction of Cp_2TiCl_2 and $\text{C}_3\text{H}_7\text{MgBr}$ in the presence of 1,2-dienes.³



Exchange reaction with styrene

Cp_2TiCl_2 also showed far higher catalytic activity than TiCl_4 for exchange with styrene. After 5 h reaction of styrene and 1.1 equivalents of $\text{C}_3\text{H}_7\text{MgBr}$ in the presence of a catalytic amount of Cp_2TiCl_2 at 30°C , unreacted styrene was not detectable by GLC analysis, and an 80% yield of α -phenethyl alcohol was isolated on air oxidation of the Grignard reagent (Table 1). Using TiCl_4 as catalyst, it was reported that a 40% yield of α -phenethyl alcohol was obtained on air oxidation after 20 h reaction of styrene and $\text{C}_3\text{H}_7\text{MgBr}$ at the ether reflux temperature.¹



π -Benzyltitanium compounds may be intermediates in this reaction, and investigation to clarify the mechanism of this reaction on these lines and of applications to various styrene derivatives is now in progress.

TABLE 1

Reactions of Grignard Reagents Prepared by Exchange of
1,3-Dienes or Styrene with Propylmagnesium bromide

Olefin	Reagent	Product (Yield, %) ^a
Butadiene	H ₂ O	1-Butene, trans-2-Butene, cis-2-Butene (53) (13) (15)
	(CH ₃) ₂ CO	2,3-Dimethyl-4-penten-2-ol (79) ^b
Isoprene	H ₂ O	2-Methyl-1-butene (76), 2-Methyl-2-butene (21)
	(CH ₃) ₂ CO	2,3,4-Trimethyl-4-penten-2-ol (95)
Myrcene	H ₂ O	2-Methyl-6-methylen-2-octene (88) 2,6-Dimethyl-2,6-octadiene (8)
Styrene	H ₂ O	Ethylbenzene (98)
	O ₂	α-Phenethyl alcohol (80) ^c

^aGLC analysis, based on propylmagnesium bromide (for butadiene and isoprene) or olefin (myrcene and styrene). ^bOther product is 2-methyl-2-pentanol, yield based on reacted propylmagnesium bromide is 98%. ^cIsolated yield.

References and Note

1. H.L. Finkbeiner and G.D. Cooper, *J. Org. Chem.*, **27**, 3395 (1962).
2. Nonreversibility was confirmed by the fact that no exchange reaction was observed when allylmagnesium bromide was treated with 1-olefin in the presence of Cp₂TiCl₂.
3. H.A. Martin and F. Jellinek, *J. Organometal. Chem.*, **12**, 149 (1968).

(Received in Japan 8 October 1979)