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Hydroalumination of Alkynes with LiAlH₄ in the Presence of Cp₂TiCl₂

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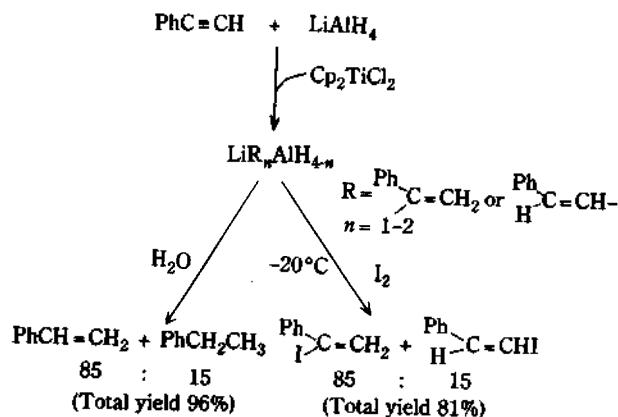
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The lithium alkenylhydroaluminates, which are produced by the catalytic hydroalumination of alkynes with the Cp₂TiCl₂-LiAlH₄ reagent system, give corresponding iodoalkenes on iodination and alkenes on hydrolysis.

The titanium complex, which is product by the reaction of Cp₂TiCl₂ with LiAlH₄, efficiently promotes the catalytic hydroalumination and isomerization of alkenes.^{1,2} NaBH₄ is also utilized as a reagent for the hydroboration of alkenes and alkynes in the presence of catalytic amounts of Cp₂TiCl₂.³ Investigations have also proved that organoaluminum compounds act as unique nucleophiles and can be employed as useful reagents in organic synthesis.⁴ It was reported that the alcohols through the hydroalumination of alkenes by use of the TiCl₄-LiAlH₄⁵ or Cp₂TiCl₂-LiAlH₄⁶ are prepared. In this communication, it is briefly discussed that the catalytic hydroalumination of alkynes in the presence of Cp₂TiCl₂, and the efficiency of the reaction was evaluated by converting the resulting alkenylaluminates to the corresponding iodoalkenes on iodination and alkenes on hydrolysis.

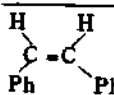
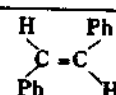
The hydroalumination of alkynes was carried out by a similar manner as described previously,³ using Cp₂TiCl₂ (1.0 mmol), LiAlH₄ (20.0 mmol), and phenylethyne (20.0 mmol) in THF (30 ml). The resulting mixture was stirred for 5 h at 25°C under argon. The reaction mixture was added to I₂ (40.0 mmol) in THF (30ml) under argon at -20°C. The mixture was stirred for 1 h at room temperature, and then extract-

ed with diethyl ether. The etheral extract was washed with a 10% NaHSO₃ solution, and dried (Na₂SO₄). Evaporation of the etheral extract gave the residue. The GLC analysis of the residue indicated that the reaction mixture contained α-iodostyrene, β-iodostyrene, and phenylethane. Also, the hydroalumination of diphenylethyne was carried out by the method described above. The mixture was treated with H₂O, and extracted with diethyl ether. The organic layer was dried (Na₂SO₄), the solvent was removed by means of a rotary evaporator. The products were obtained by column chro-



Scheme

Table 1. Hydroalumination of Diphenylethyne^a

PhC≡CPh	Molar ratio		Time (h)	Yield of Products (%) ^b			Recovered of PhC≡CPh (%)
	LiAlH ₄	Cp ₂ TiCl ₂				PhCH ₂ CH ₂ Ph	
20	20	0	5	0	5	0	91
20	20	0	28	14	38	0	45
20 ^c	20	0	28	26	54	0	trace
20	20	1	5	54	34	8	trace
20 ^d	20	20	24	24	19	36	0

^aThe reaction was carried out at 25°C. ^bThe yield was determined by GLC and based on diphenylethyne used. ^cThe experiment was refluxed at 65°C. ^dSmall amounts of unidentified products were detected.

matography with hexane and benzene, and purified GLC. The results are illustrated in Scheme and Table 1, respectively.

As shown in Scheme, phenylethyne is metalated preferentially at the α -position so that quenching the reaction mixture with I_2 , α -iodostyrene and β -iodostyrene were produced in 85:15 ratio.

The results in Table 1 show that the catalytic hydroalumination of alkynes is promoted by use of catalytic amounts of Cp_2TiCl_2 to the corresponding alkenes on hydrolysis or alkenyl iodides on iodination in excellent yields. The formation of *cis*- and *trans*-1,2-diphenylethenes in the ratio of 61:39 suggests that the hydroalumination of diphenylethyne with $LiAlH_4$ catalyzed Cp_2TiCl_2 takes preferentially place in *cis* addition rather than *trans* addition.⁷ The formation of the hydrogenated product, 1,2-diphenylethane, is also observed. The result suggests that small amount of dialuminates may be produced during the reaction. However, the detailed mechanism of this reaction is not clear at present, experiments

remain in a lot of parts.

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A Short Synthesis of (Z)-13-Eicosen-10-one, the Component of the Peach Fruit Moth Pheromone

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(Z)-13-Eicosen-10-one(1), a principal component of the sex pheromone of the peach fruit moth, *Carposina niponensis* Walsingham is the most serious pests on apple, peach in Korea¹ and Japan.² In 1977, Y. Tamaki *et al*² identified (Z)-13-eicosen-10-one (1) (Figure 1) and (Z)-12-nonadecen-9-one in the ratio of 20:1 as the major components of the female sex pheromone of the peach fruit moth. (Z)-13-Eicosen-10-one (1) alone exerts a similar pheromone activity.³

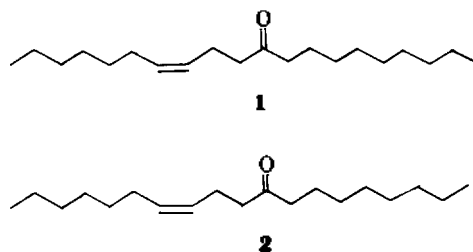
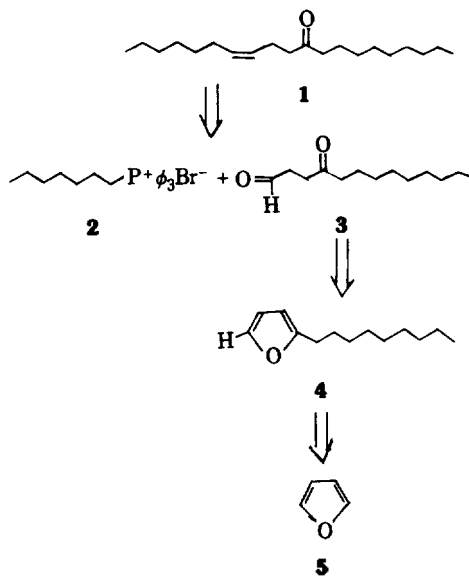


Figure 1

Since the peach fruit moths are hardly attracted by light traps, survey of the trend of their outbreak in the field is difficult.⁴ Pheromone vials containing 1-3mg of (Z)-13-eicosen-10-one(1) adhered to rubber or plastic capsule resulted in a good forecasting outbreaks of this insect.⁵

Several synthesis of (Z)-13-eicosen-10-one(1) have been



Scheme 1. Retrosynthetic Analysis of 1

reported in the literature.⁶ A search for more efficient and convenient methods for the synthesis of (Z)-13-eicosen-10-one(1) is still very worthwhile. Here we wish to report a short synthesis of (Z)-13-eicosen-10-one(1) from furan, which is