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HYDROMETALLATION

IV *. HYDROALUMINATION OF ALKYNES BY $HAl(NR_2)_2$ COMPOUNDS CATALYZED BY Cp_2TiCl_2

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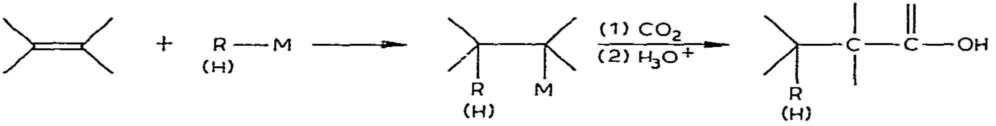
Summary

Bis(dialkylamino)alanes react with alkynes in the presence of a catalytic amount of Cp_2TiCl_2 in benzene solvent to produce hydroalumination products in high yield Two terminal and five internal alkynes were studied and the addition was found to take place in a *cis* manner The reaction is stereospecific and provides a convenient and economical route to alkenylaluminum compounds

Introduction

Considerable interest in recent years has been directed toward the development of carbometallation and hydrometallation reactions involving alkenes and alkynes. The reasons for this interest are clear, first, alkenes and alkynes are very fundamental and economic building blocks and, secondly, carbometallation and hydrometallation provide routes to form carbon—metal bonds which can then be easily functionalized (eqs 1 and 2) to form numerous classes of compounds.

Carbometallation reactions have evolved significantly in just the last few years due to the efforts of numerous workers, however,



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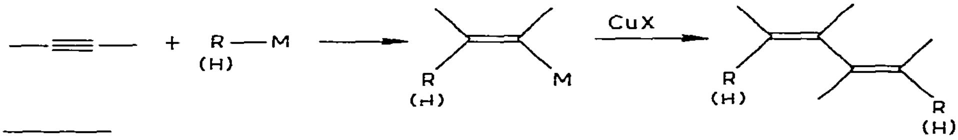

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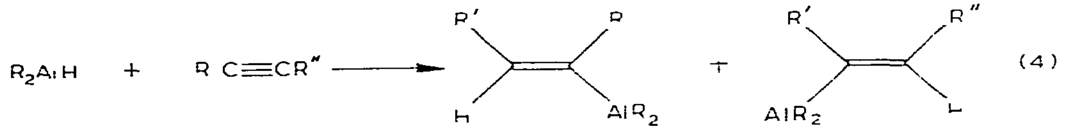
[*] For part III see ref 8

[**] Dedicated to Professor H Normant on the occasion of his 72nd birthday on June 25th 1979

hydrometallation reactions have been much less developed The work of Brown [1] in the development of hydroboration as a synthetic tool in organic chemistry stands alone in terms of the degree of development of the method and in terms of its utility However, the product of hydroboration (R_3B) contains a C—B bond which is relatively unreactive compared to C—Mg or C—Al bonds In addition, diborane is quite expensive thus providing sufficient impetus to develop other hydrometallation reactions, particularly those that can form more active C—M bonds and whose metal hydride reagent is not expensive

The first reports of the addition of Al—H bonds to alkynes was by Wilke [2] It was shown that both substitution (eq 3) and addition (eq 4) can take place

$$R_2AlH + R'C\equiv CH \longrightarrow R'C\equiv CAlR_2 + H_2 \qquad (3)$$



depending on the exact conditions of the reactions Further development in this area concerned the mechanism and regioselectivity of the hydroalumination of alkynes and was due to the excellent work of Eisch and coworkers [3] These workers, in a series of studies, were able to provide considerable understanding of the detailed nature of hydroalumination with respect to the nature of the R_2AlH compound, the alkyne, solvent, temperature, etc

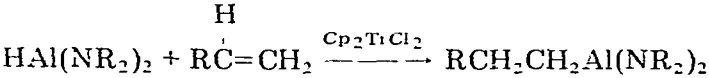
Although hydroalumination of alkynes by R_2AlH compounds is a reasonably convenient and effective reaction, nevertheless, a serious shortcoming exists in the use of vinylalanes ($R_2AlC{=}C\lt$) in organic synthesis Because dialkyl- or diaryl-vinylalanes are the products of this reaction, an ambiguous product is formed when the reaction is allowed to take place with an organic substrate since both the saturated R group and the vinyl of the vinylalane can react.

More recently, Schwartz and coworkers have developed a hydrometallation reaction involving the addition of $Cp_2Zn(H)Cl$ to alkenes and alkynes [4] The reaction proceeds well with terminal alkenes using stoichiometric amounts of the hydride. In addition, Sato and coworkers [5] have effected the reduction of alkenes and alkynes with $LiAlH_4$ in the presence of transition metal halides Although one might assume that hydrometallation products are produced as intermediates, deuterolysis of the reaction mixture shows that only $TiCl_4$ and $TiCl_3$ catalysts produce a deuterium incorporated product.

Sometime ago we reported the direct synthesis of dialkylaminoalanes by the reaction of aluminum, hydrogen and secondary amines [6] (eq 5) The bis-

$$Al + H_2 + 2\,R_2NH \xrightarrow[140^\circ C\ \ 2000\ psi]{Benzene} HAl(NR_2)_2 + \tfrac{3}{4}\,H_2 \qquad (5)$$

(dialkylamino)alanes are produced in nearly quantitative yield and in a high state of purity. The benzene solutions are filtered from excess aluminum and the resulting solutions are used directly in reactions with alkenes and alkynes We communicated earlier [7] that bis(dialkylamino)alanes add to olefins and alkynes in the presence of catalytic amounts of Cp_2TiCl_2 in benzene solution in



$$HAl(NR_2)_2 + R\overset{H}{C}{=}CH_2 \xrightarrow{Cp_2TiCl_2} RCH_2CH_2Al(NR_2)_2 \qquad (6)$$

high yield Bis(dialkylamino)alanes are reasonably inexpensive hydrides compared to diborane and the resulting C—Al compounds should be more reactive than the corresponding C—B compounds produced in hydroboration We have reported recently the details of $HAl(NR_2)_2$ hydroalumination of alkenes [8] and now we wish to report our latest results in hydroalumination of alkynes to form alkenylalanes

Experimental

Apparatus

All reactions were performed under nitrogen or argon at the bench using Schlenk tube techniques or in a glove box equipped with a recirculating system to remove oxygen and solvent vapors [9] Calibrated syringes equipped with stainless steel needles were used to transfer reagents All glassware and syringes were heated in an oven and cooled under a flow of nitrogen or argon All inorganic and organic compounds including internal standards for GLC were prepared by weighing the reagent in a tared volumetric flask and diluting with the appropriate solvent.

All melting points are corrected and all boiling points are uncorrected Proton NMR were obtained using a Varian 60 MHz model A60 and T60 or a JEOL 100 MHz Fourier Transform spectrometer Model PFT-100 All Chemical shift values are expressed in ppm (δ values) relative to Me_4Si as the internal standard All mass spectra were obtained using a Hitachi RMU-7 or Varian Model M-66 mass spectrometer GLPC analyses were obtained using an F and M Model 700 or 720 gas chromatograph IR spectra were obtained using a Perkin—Elmer Model 621 or 256 IR spectrometer High pressure reactions were carried out using an autoclave rated to 15000 psi obtained from the Superpressure Division of American Instrument Co of Silver Springs, Maryland

Analytical

Gas analyses were carried out by hydrolyzing samples with 0 1 *M* HCl on a standard vacuum line equipped with a Toepler pump [10]. Aluminum was determined by adding excess standard EDTA solution to hydrolyzed samples and then back titrating with standard zinc acetate solution at pH 4 using dithizone as an indicator Amines were analyzed by injecting hydrolyzed samples with an internal standard on the gas chromatograph Carbon, hydrogen analyses were carried out by Atlantic Microlab, Inc , Atlanta, Georgia

Analysis of all products, arising from the quenching of reactions of hydrides with alkynes, with H_2O, D_2O, I_2 and CO_2 were identified by GLC and/or NMR Some products were isolated by preparative GLC and compared to authentic samples obtained commercially or synthesized by known methods All NMR spectra were obtained in $CDCl_3$ or benzene-d_6 using Me_4Si as the internal standard

Materials

Solvents Fisher reagent grade benzene and hexane were stirred over concentrated H_2SO_4, washed with Na_2CO_3, then distilled water, dried over anhydrous $MgSO_4$ and then distilled from $NaAlH_4$ under nitrogen. The catalyst Cp_2TiCl_2 was obtained from Alfa Inorganics.

Alkynes 1-Hexyne (b.p. 70—71°C), 2-hexyne (b.p. 83—84°C), 4-octyne (b.p. 132—133°C), 1-phenyl-1-propyne (b.p. 185—186°C), diphenylethyne (b.p. 170°C at 19 mmHg) and 1-octyne (b.p. 124—125 C) were obtained from Chemical Samples Company or Aldrich Chemical Co. and distilled and stored over 4A molecular sieves.

1-Trimethylsilyl-1-octyne Into a 250 ml three-necked, round bottomed flask fitted with a teflon-coated magnetic stirring bar, rubber serum cap and a pressure-equalizing addition funnel was placed 14.8 ml (160 g, 100 mmol) of 1-octyne in 80 ml of freshly distilled hexane. The stirred mixture was cooled with an ice water bath and 50 ml of 2.03 *M* n-butyllithium in hexane added slowly. The reaction mixture was allowed to warm to room temperature and stirred for an additional 3 h. The resulting white slurry was cooled again using an ice water bath and 13 ml (11.1 g, 112 mmol) of trimethylchlorosilane (distilled from quinoline) was added slowly over a period of 0.5 h. The mixture was allowed to warm to room temperature, and 50 ml of water added slowly. The hexane layer was separated and washed twice with water, dried over anhydrous Na_2SO_4 and the solvent was removed under vacuum. The crude product was distilled and gave 15.1 g (0.083 mol, 83% yield) of 1-trimethylsilyl-1-octyne, b.p. 45—59°C at 1.0—1.2 mmHg. The IR, NMR and mass spectrum agreed with that reported earlier [11]. Anal. Found: C, 72.23; H, 12.13. $C_{11}H_{22}Si$ calcd.: C, 72.44; H, 12.16%.

General reactions of alkynes with $HAl(N\text{-}i\text{-}Pr_2)_2$

A 10 × 18 mm test tube with a Teflon-coated magnetic stirring bar was flamed and cooled under a flow of argon or nitrogen. A saturated solution of Cp_2TiCl_2 in benzene (0.02 *M*) was prepared (the solutions had to be made fresh each day). One or two ml of benzene was introduced into the reaction vessel and then the alkyne was added. The mixture was stirred for 2 to 3 minutes before the reagent was added. Then the reaction mixture was stirred at room temperature or at a higher temperature, depending upon the reactant, for up to 40 h in some cases. In general, the reactions involving internal alkynes were complete in 20 minutes. The reactions were quenched by various means (see below, General Quenching Techniques) and worked up by the regular method (addition of water, extraction with diethyl ether or hexane and drying over $MgSO_4$). Most products were separated by GLC using a 6 ft. 10% Apiezon L 60—80 column with a helium flow rate of 45 ml/min: 2-hexyne, 1-octyne and 1-hexyne (70°C, flow rate 45 ml/min), 1-trimethylsilyl-1-octyne (100°C, flow rate 45 ml/min); 1-phenylpropyne (125°C, flow rate 60 ml/min). The yield was calculated by using a suitable hydrocarbon internal standard for each case ($n\text{-}C_{12}H_{26}$, $n\text{-}C_{14}H_{30}$ or $n\text{-}C_{16}H_{34}$) and the products were identified by comparing the retention times of authentic samples with the products under similar conditions and/or by coinjection of products and authentic samples obtained commercially or synthesized by known methods.

Yields of *cis*-stilbene (δ 6 60 vinyl H), *trans*-stilbene (δ 6 10, vinyl H) and 1 2-diphenylethane (δ 2 92 benzyl H) were determined by NMR integration and based on total phenyl protons However, the ratio of *cis*-stilbene to *trans*-stilbene was also checked by TLC

General quenching techniques

Quenching with H_2O After the desired reaction time for the catalytic hydrometallation reaction described above, the reaction was quenched with water or a saturated solution of ammonium chloride to produce the protonated species The amount of recovered starting material and products were determined by the methods described above

Quenching with D_2O The same procedure used for quenching with H_2O was followed The amount of recovered starting material and products were determined by GLC methods and conditions described above Each product was collected from the gas chromatograph and submitted for mass spectral analysis. The corrected percent of deuterium incorporation for the product was calculated by comparing the mass spectrum of the protonated species with the mass spectrum of the deuterated species and by subtracting the contributions of naturally occuring isotopic components from each molecular ion peak This procedure was followed for all unsaturated substrates observed under these reaction conditions

The regioselectivity of reactions was monitored by the use of NMR for 1-phenyl-1-propyne and 1-trimethylsilyl-1-octyne For 1-phenyl-1-propyne, 95% of the product, *cis*-1-phenylpropene, was deuterated with 90% of the deuterium located on the number 1 carbon as indicated by a quartet of triplets at 5 78 ppm, *J* 7 Hz (1 H) and a doublet at 1 89 ppm, *J* 7 Hz (3 H) The other isomer showed a singlet at 1 89 ppm and a multiplet at 6 36—6 54 ppm It was identified as *trans*-1-phenyl-1-propene

The products from the reduction of 1-trimethylsilyl-1-octyne were prepared independently *cis*-Trimethylsilyl-1-octene was prepared by the hydrogenation of 1-trimethylsilyl-1-octyne with 5% Pd/C in 95% ethanol and monitored until the desired amount of hydrogen was absorbed The *cis*-isomer was collected and purified via GLC under the aforementioned conditions The *trans*-isomer was also detected by GLC The *cis*-isomer when coinjected under GLC conditions with the product of the hydroalumination reaction, showed a trace characteristic of only the *cis*-isomer The *trans*-isomer obtained from the hydrogenation reaction had an identical retention time as the minor product from the hydroalumination reaction

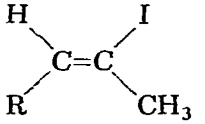
The following data were obtained for *cis*-1-trimethylsilyl-1-octene· IR(neat, film) 2960s, 2940s, 2860m, 1600m, 1470m, 1260s, 850s(br), NMR (CCl_4, TMS) 9 H singlet at 0 14 ppm, 11 H multiplet at 0.74—2 66 ppm, 2 H quartet at 2 15 ppm, *J* 8 Hz, 1 H doublet at 5 49 ppm, *J* 13 0 Hz, 1 H doublet of triplets at 6 33 ppm, *J* 14 Hz and 7 Hz; mass spectrum, *m/e* (rel intensity) 184 (M^+, 2) 170(13), 169(70), 141(4), 125(4), 114(23), 109(13), 99(26), 73(100), 67(9), 59(91), 44(21), 41(14).

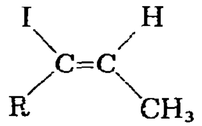
Anal Found C, 71 54, H, 13 14. $C_{11}H_{24}Si$ calcd C, 71 65, H, 13 12%

The NMR spectrum of the *trans*-isomer matched the spectrum reported in the literature [12]· NMR (CCl_4, TMS) 9 H singlet at 0 16 ppm, 11 H multiplet at 0 9—1 6 ppm, 2 H multiplet at 2 1 ppm, 1 H doublet at 5 6 ppm J = 18 Hz 1 H doublet of triplets at 6 0 ppm, J = 18 Hz and 6 Hz

When 1-trimethylsilyl-1-octyne was allowed to react under the catalyzed hydrometallation conditions described above, 87% of the product, *cis*-1-trimethylsilyl-1-octyne, was deuterated and approximately 90% of the deuterium was located on carbon number 2, as indicated by the following NMR ($CDCl_3$ TMS) 9 H singlet at 0 14 ppm, 11 H muliplet at 0 80—1 56 ppm, 2 H broad singlet at 2 14 ppm, 1 H singlet at 5.49 ppm The other isomer (*trans*-1-trimethylsilyl-1-octene) had no deuterium incorporation but showed a triplet at 6 33 ppm which corresponded to the expected splitting pattern of the non-deuterated *trans*-isomer

Quenching with I_2 A known concentration of iodine in benzene was prepared and a stoichiometric amount was added to the catalytic hydroalumination reaction after the desired time. This mixture was stirred at room temperature for 1 h. Afterwards, water was added, followed by a saturated sodium thiosulfate solution. The organic layer was separated and dried over sodium sulfate and analyzed by GLC or NMR This procedure was followed for 2-hexyne. The iodoalkenes were identified by NMR in the following way When the catalytic hydroalumination reactions of internal alkynes were quenched with D_2O, the products were the *cis*-alkenes which were confirmed by coinjection of authentic samples on the gas chromatograph From Zweifel's [13] work, it is known that hydroaluminated compounds quenched with iodine maintain their regiochemistry. Therefore, the iodoalkene obtained from the quenching with I_2 of the reaction involving 2-hexyne was 2- and 3-iodo-*cis*-2-hexene. NMR was used to distinguish between the two isomers





(CH_3 singlet at 2 36 ppm) (CH_3 doublet at 1.63 ppm *J* 7 Hz)

Anal. Found. C, 34.51; H, 5 25 Calcd. for mixture of $C_6H_{11}I$ C, 34 30, H, 5.28%.

Quenching with carbonyl compounds After the desired catalytic hydroalumination reaction had taken place, a stoichiometric amount of desired carbonyl compound (acetone and benzaldehyde) was added, followed by additional stirring for 10 h while maintaining the desired temperature with an oil bath The reaction mixtures then were worked up by addition of water. The organic layer was then separated, dried over $MgSO_4$, filtered and analyzed by NMR techniques.

One of the products arising from the quenching of the reaction product involving octyne with acetone is the reduction product, isopropanol. Isopropanol was determined by observation of the methyl group attached to the carbinol carbon (doublet at 1 2 ppm) Acetone was determined by observation of the methyl groups attached to the carbonyl carbon (2 05 ppm). 4-Octyne was identified by the triplet corresponding to the methyl group at 0 98 ppm 4-Octyne also was determined by GLC analysis The addition products were determined by NMR observation of the methyl groups which appeared as singlets at 1.22 ppm and by comparing these spectra with those obtained from the reaction of the corresponding octyl Grignard reagent with acetone. The integrity of the octenyl addition compound was established by the methyl singlet at 1.22 ppm and the appearance of a multiplet at 5.5—6.3 ppm.

For the products arising from the quenching of the reaction product from octyne with benzaldehyde benzaldehyde was determined by the singlet associated with the aldehydic proton at 9.94 ppm, the reduction product, benzyl alcohol, was determined by the singlet at 4.58 ppm, and the addition product from 4-octyne was determined by the appearance of the vinyl multiplet at 5.5—6.3 ppm and also by GLC, mass spectral and IR analyses.

When $HAl(N\text{-}i\text{-}Pr_2)_2$ was allowed to react with 4-octyne in the presence of 2 mol % of Cp_2TiCl_2 and then allowed to react with benzaldehyde, the major product was diisopropylbenzylamine. The following data were obtained for the product n_D^{25} 1.5300, NMR ($CDCl_3$, TMS) 12 H doublet at 1.01 ppm, J 5 Hz, 2 H multiplet at 2.66—3.34 ppm, 2 H singlet at 3.63 ppm, 5 H multiplet at 7.10—7.40 ppm, mass spectrum, m/e (rel intensity) 191 (M^+, 8), 176(56), 134(5), 132(3), 114(2), 106(6), 105(6), 91(100), 84(2), 77(6), 65(6), 51(3), 43(5), 42(4), 41(5), 39(3), IR(neat, film) 3090w, 3070w, 3030m, 2970s, 2940m, 2880w, 1605m, 1495m, 1470m, 1455m, 1385s, 1375s, 1210s 1385s, 1375s, 1210s, 1180s, 1155m, 1140m, 1120m, 1075w, 1050s, 1025s.

Anal. Found C, 81.49, H, 11.00. $C_{13}H_{21}N$ calcd. C, 81.61, H, 11.07%.

Results and discussion

The reactions of various alkynes with $HAl(N\text{-}i\text{-}Pr_2)_2$ and 5 mol % Cp_2TiCl_2 in benzene at room temperature under an argon atmosphere were studied and the results are tabulated in Table 1. In the case of internal alkynes (2-hexyne, 2-octyne, 1-phenyl-1-propyne and diphenylethyne), a small amount (5, 10, 3 and 0%, respectively) of the corresponding alkane was observed. (The alkane product could be minimized by allowing the reaction to be conducted at 0°C in 80/20 mixture of benzene/THF for 2 h.) However, the major products are *cis*-2-hexene (94%), *cis*-2-octene (90%), *cis*-1-phenyl-1-propene (96%) and *cis*-stilbene (96%), with only 1—4% of the *trans*-isomer observed. All the products were confirmed by matching the infrared spectra of identical samples obtained by the hydrogenation (Pd/C and hydrogen) of the starting materials or samples obtained from the Aldrich Chemical Company. When the reaction mixtures were quenched with D_2O, 96—97% of the *cis*-alkenes formed (Table 1) contained deuterium according to mass spectral analysis. When the reaction with 2-hexyne was quenched with iodine, the NMR spectrum showed a 53/47 ratio of 2-iodo-*cis*-2-hexene to 3-iodo-*cis*-2-hexene. This result is expected on steric as well as electronic grounds since there is little difference between methyl and propyl groups sterically or electronically. Equation 7 can be used to describe

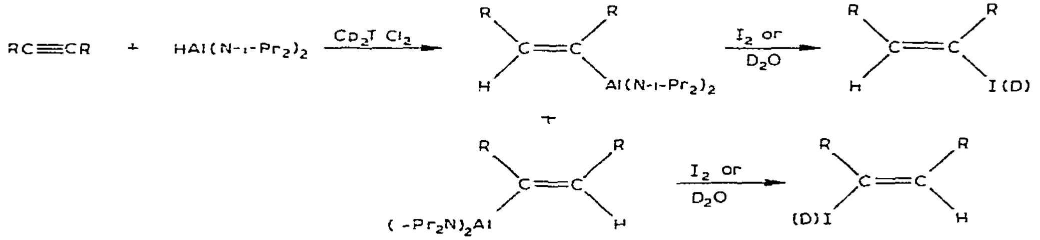


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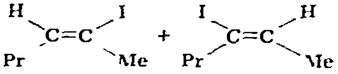
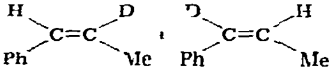
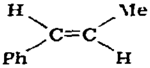
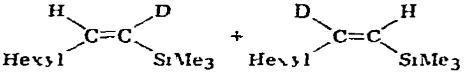
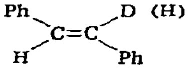
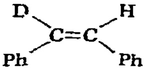
TABLE 1

REACTIONS OF ALKYNES WITH HAl(N-i-Pr$_2$)$_2$ IN 1/1 RATIO IN THE PRESENCE OF 5 MOL% Cp$_2$TiCl$_2$ IN BENZENE [a]

Alkyne	Work up	Products [b]	Yield (%)
1-Octyne [c]	D_2O	Octane-d_0 + Octane-d_1 + Octane-d_2 + Octane-d_3 45 22 18 15	54
		1-Octene-d_0 + 1-Octene-d_1 22 78	46
1-Hexyne [c]	D_2O	Hexane-d_0 + Hexane-d_1 + Hexane-d_2 + Hexane-d_3 41 23 19 17	49
		1-Hexene-d_0 + 1-Hexene-d_1 18 82	51
2-Octyne	D_2O	Octane-d_0	10
		cis-2-Octene-d_0 + *cis*-2-Octene-d_1 3 97	90
		trans-2-Octene	Trace
2-Hexyne	D_2O	Hexane	5
		cis-2-Hexene-d_0 + *cis*-2-Hexene-d_1 4 96	94
		trans-2-Hexene	1
	I_2	 53 47	82 82
PhC≡CCH$_3$	D_2O	1-Phenylpropane	3
		 10 90	95
			1
Hexyl-C≡CSiMe$_3$ [d]	D_2O	Hexyl-CH$_2$CH$_2$SiMe$_3$	5
		 10 90	87
PhC≡CPh	D_2O		4
			95

[a] All reactions carried out in benzene at room temperature for 1 h and quenched with D_2O or a benzene solution of iodine [b] Yields were determined by GLC and are based on alkyne and/or octane as the internal standard. The relative ratios of isomers were determined by NMR using benzhydrol as the internal standard. [c] Reaction carried out at 0°C for 8 h [d] Reaction carried out at 45°C for 12 h

the results of the reactions of HAl(N-i-Pr$_2$)$_2$ with internal alkynes in benzene.

A separate study was conducted in order to determine the product composition from 0 to 100% reaction. In this connection, a representative internal alkyne, 2-hexyne, was allowed to react with HAl(N-i-Pr$_2$)$_2$ in the presence of 10 mol % Cp$_2$TiCl$_2$ in benzene. The results are summarized in Table 2. When the reaction was carried out at room temperature for 16 h, only 52% deuterium

TABLE 2

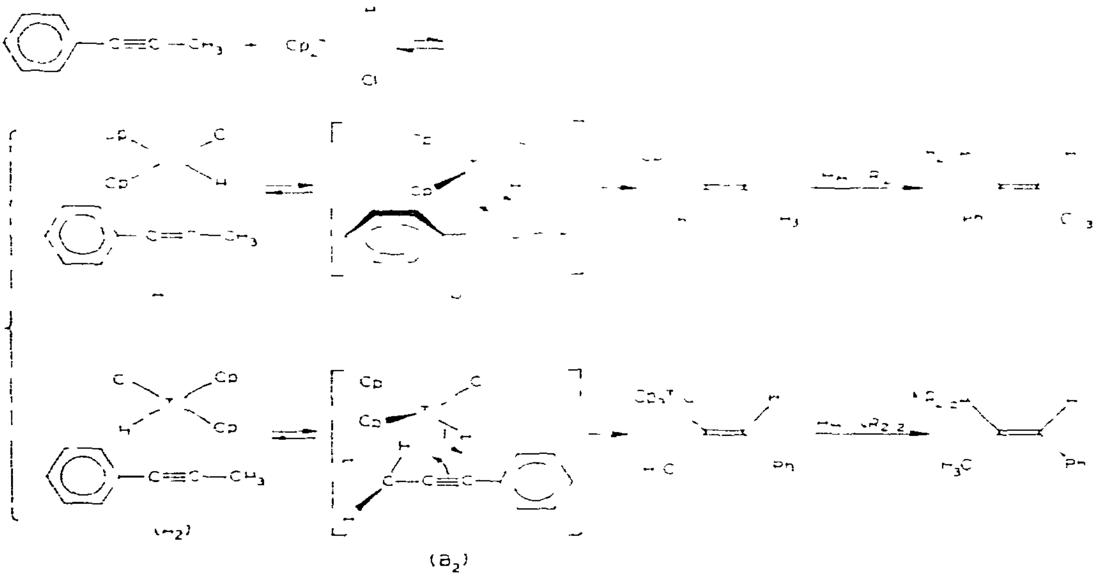
REACTIONS OF 2-HEXYNE WITH HAl(N-i-Pr_2)$_2$ AND Cp_2TiCl_2 IN 1.0/1.02/0.1 MOL RATIO[a]

Time (h)	2-Hexyne recovered (%)	Hydrolysis products		*trans*-2-hexene (%)	D incorporation in *cis* product (%)
		Hexane (%)	*cis*-2-hexene (%)		
0.7	80	7	17	—	—
1	75	8	20	—	95
2	65	8	30	trace	96
4	53	8	39	trace	95
8	30	8	62	trace	95
16	17	10	73	2	91
16[c]	0	23	47	26	52

[a] Reactions were carried out in benzene at 0°C under an argon atmosphere. [b] Yield was determined by GLC using octane as the internal standard and normalized (%) 2-hexyne + (%) hexane + (%) *cis* 2-hexene = 100%. [c] The temperature was allowed to increase to room temperature.

incorporation of the product was observed, however, when the reaction was carried out at 0°C, 91% deuterium incorporation was observed, once again indicating formation of the intermediate *cis*-2-hexenylaluminum compound in high yield.

These results indicate the the intermediate alkenyltitanium compound is not stable at room temperature under hydrometallation conditions and subsequently undergoes decomposition The decomposition produced H_2, which in the presence of catalyst hydrogenates the alkyne to the alkene, which in turn can be hydrogenated to the alkane This suggestion accounts for the low deuterium content of the product following work-up procedures A separate experiment showed that hydrogen is indeed produced when HAl(N-i-Pr_2)$_2$ is added to Cp_2TiCl_2 at room temperature Hydrogen was also produced when diisobutyloctenylaluminum in benzene was added to 5 mol % of Cp_2TiCl_2 The amount of alkane produced in this reaction was reasonably constant throughout the reaction at 0° C, indicating that the alkane is formed in the initial stages of the reaction by hydrogenation If the alkene or alkane produced at 0° C was a result of homolytic cleavage of the alkenyl- or alkyl-titanium intermediate followed by hydrogen atom abstraction from the solvent, one would expect that the amount of alkane would increase as the reaction proceeds However, this was not the case Therefore, it is more likely that the alkyne was hydrogenated in the presence of H_2 and catalyst at the beginning of the reaction. Also, a significant amount of *trans*-olefin was formed when the temperature was increased from 0 to 25° C, indicating homolytic cleavage of the intermediate *cis*-alkenyltitanium compound with resultant loss of stereochemistry of the formed radical If the alkyne was added after the catalyst and alane were allowed to react for a few minutes under a slight vacuum, the amount of alkane produced decreased to less than 3%, however, the amount of alkene also decreased to 45% with 94% deuterium incorporation It would seem from this result that the actual hydrometallation of the alkyne by the transition metal hydride ($Cp_2Ti(H)Cl$) is rapid and that the slow step involves transmetallation of the alkenyltitanium compound and that the alkenes and alkanes formed at



Scheme 1 Proposed mechanism for the catalytic hydrometallation of 1-phenyl-1-propyne

0° C are produced by hydrogenation of the alkenyltitanium compounds

When 1-phenyl-1-propyne was allowed to react under normal hydrometallation conditions (Table 1), 95% *cis*-1-phenyl-1-propene, 3% 1-phenylpropane and 1% *trans*-1-phenyl-1-propene were produced upon quenching with water The *cis*-alkene produced in this manner matches the NMR, IR, mass spectrum and refractive index of *cis*-1-phenyl-1-propene obtained from the catalytic hydrogenation of 1-phenyl-1-propyne. When the catalytic hydrometallation reaction was quenched with D_2O, the product contained 97% deuterium according to mass spectral analysis The NMR spectrum showed a 10/90 ratio of 2-deuterio-*cis*-1-phenyl-1-propene to 1-deuterio-*cis*-1-phenyl-1-propene However, Eisch [14] reported that quenching the product from the reaction of diisobutylaluminum hydride and 1-phenyl-1-propyne at 50° C with D_2O produced an 80/20 ratio of the 2-deuterio-*cis*-1-phenyl-1-propene to 1-deuterio-*cis*-1-phenyl-1-propene, indicating that attack occurred at the least hindered carbon in a ratio of 4 to 1 The reverse regiochemistry observed for the hydrometallation reaction products reported herein indicates, according to Scheme 1, that the formation of the titanocene hydridochloride-alkyne complex A_1 determines the regiochemistry of the products Complex A_1 is less hindered than complex A_2, because the cyclopentadienyl and phenyl groups can adopt a staggered arrangement (B_1), however, the cyclopentadienyl and methyl groups in complex A_2 cannot do so as readily (B_2). In addition, it is possible that there is some interaction between unfilled orbitals of titanium and π electrons of the phenyl ring that would help stabilize transition state (B_1). For these reasons complex A_1 is favored over complex A_2.

Following the transition metal hydride addition step, the transmetallation step involving $HAl(N\text{-}i\text{-}Pr_2)_2$ should proceed simply to exchange aluminum for titanium on the same carbon holding the titanium and therefore this step would have no effect on the regioselectivity of the reaction

When a representative terminal alkyne (e g 1-octyne) was allowed to react with $HAl(N\text{-}i\text{-}Pr_2)_2$ in the presence of Cp_2TiCl_2 in benzene an approximately 50/50 mixture of alkane/alkene was observed When the reaction mixture was quenched with D_2O the alkene showed a relatively high percentage of deuterium incorporation (78%) however, the octane showed deuterium only to extent of 55% According to mass spectral analysis of the reaction product, four octanes [octane-d_0 (45%), octane-d_1 (22%), octane-d_2 (18%) and octane-d_3 (15%)] were produced These observations are accounted for by Scheme 2

SCHEME 2

$$\text{Hexyl-C}{\equiv}\text{CH} + \text{HAl(NR}_2)_2 \xrightarrow{\text{cat}} \text{Hexyl-C}{\equiv}\text{CAl(NR}_2)_2 + \text{H}_2$$

$$\text{(I)} \qquad\qquad\qquad\qquad \text{(II)}$$

$$\text{II} + \text{HAl(NR}_2)_2 \xrightarrow{\text{cat}} \text{Hexyl-CH}{=}\text{C[Al(NR}_2)_2]_2$$

$$\text{(III)}$$

$$\text{III} + \text{HAl(NR}_2)_2 \xrightarrow{\text{cat}} \text{Hexyl-CH}_2\text{C[Al(NR}_2)_2]_3$$

$$\text{(IV)}$$

$$\text{I} + 2\,\text{H}_2 \xrightarrow[\text{(2) D}_2\text{O}]{\text{(1) cat}} \text{Hexyl-CH}_2\text{CH}_3$$

$$\text{II} + 2\,\text{H}_2 \xrightarrow[\text{(2) D}_2\text{O}]{\text{(1) cat}} \text{Hexyl-CH}_2\text{CH}_2\text{D}$$

$$\text{III} + \text{H}_2 \xrightarrow[\text{(2) D}_2\text{O}]{\text{(1) cat}} \text{Hexyl-CH}_2\text{CHD}_2$$

$$\text{IV} + \text{D}_2\text{O} \rightarrow \text{Hexyl-CH}_2\text{CD}_3$$

$$\text{II} + \text{D}_2\text{O} \rightarrow \text{Hexyl-C}{\equiv}\text{CD}$$

The deuterium incorporation exhibited in the octane products indicates that metallation or deprotonation of the acetylenic hydrogen occurs with subsequent addition of H—Al across the multiple bond [14] Since hydrogen is present due to catalyst decomposition, hydrogenation reactions are possible, thereby accounting for the formation of alkanes Lowering or raising the reaction temperature, increasing the reagent/alkyne ratio or increasing the amount of catalyst had little effect on the product ratios

In order to circumvent the problem of producing a wide variety of products from terminal alkynes as in the above example, 1-trimethylsilyl-1-octyne was prepared (eq 6 and 7) When this alkyne was allowed to react under the usual

$$\text{CH}_3(\text{CH}_2)_5\text{C}{\equiv}\text{CH} + n\text{-BuLi} \xrightarrow{\text{hexane}} \text{CH}_3(\text{CH}_2)_5\text{C}{\equiv}\text{CLi} + \text{Butane}\uparrow \qquad (6)$$

$$\text{CH}_3(\text{CH}_2)_5\text{C}{\equiv}\text{CLi} + \text{ClSiMe}_3 \xrightarrow{\text{hexane}} \text{CH}_3(\text{CH}_2)_5\text{C}{\equiv}\text{CSiMe}_3 + \text{LiCl}\downarrow \qquad (7)$$

catalytic hydrometallation conditions, only 5% of the totally saturated compound (octane-d_0) and the *trans*-alkene were produced with the *cis*-alkene being the predominant product (87%). The *cis*-alkene product on hydrolysis produced a product whose NMR, IR and mass spectrum matched those obtained for the product from the Pd/C hydrogenation of 1-trimethylsilyl-1-octyne When the hydrometallation reaction product was quenched with D_2O 80% of the product contained deuterium according to mass spectral analysis NMR analysis of the products showed that approximately 90% (Table 1) of the deuterated compound was the *cis*-1-trimethylsilyl-2-deuterio-1-octene This result is somewhat surprising in that one would expect, on the basis of previous studies [14], that the aluminum would be adjacent to the more electronegative silicon atom However, as discussed earlier in Scheme 1, the regiochemistry of the product is determined by formation of the intermediate alkynyltitanium compound. The bulky trimethylsilyl group hinders the approach of the titanium catalyst and therefore 90% of the newly formed titanium compound has the titanium located in the 2-position Interestingly, a similar result was obtained when $HAl(NEt_2)_2$ was used as the reagent

Clearly, the reaction of $HAl(NR_2)_2$ compounds (which are economically attractive hydrometallation reagents) with alkynes in the presence of a catalytic amount of Cp_2TiCl_2 in benzene produces alkenylalanes in high yield and predictable stereochemistry. Because of the importance of alkenylalanes as synthetic intermediates, this reaction should be of potential interest to synthetic organic chemists.

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