

In accord with this interpretation, the major keto acetate product obtained from the reaction of methyl isopropyl ketone with octene-1 [$C_6H_{13}CH(OAc)CH_2CH_2COCH(CH_3)_2$] derived from the primary α -keto radical rather than the more stable tertiary keto radical.

The selective oxidation of organic free radicals provides novel approaches to organic synthesis. Further examples will be presented in a forthcoming publication.

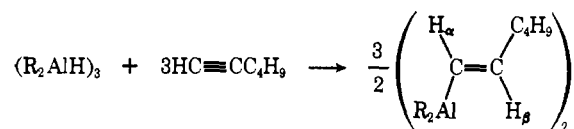
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Mixed Alkenyl-Hydride-Bridged Alkylaluminum Dimers. Intermediates in the Monohydroalumination of Alkynes¹

Sir:

The monohydroalumination of alkynes with dialkylaluminum hydrides proceeds *via* a cis addition of Al-H to the triple bond to afford dialkylalkenylalanes of predictable stereochemistry.² It has been established



that these dialkylalkenylalanes form stable vinyl-bridged dimers which do not dissociate when heated below 100°. We now wish to present evidence for the formation of mixed alkenyl-hydride-bridged alane dimers, a new class of dimeric organoaluminum compounds, as stable intermediates during the monohydroalumination of various alkynes. This evidence was obtained by following the changes in the vinyl proton region of the 60-MHz nmr spectra of the reaction mixtures during the course of the hydroalumination reactions.

To a solution of 1-hexyne in *n*-hexane was added at 25° an equimolar amount of diisobutylaluminum hydride.⁴ A portion of the reaction mixture was placed into an nmr tube. After 47% reaction the nmr spectrum (Figure 1a) exhibited primarily two separate doublets of triplets centered at δ 7.55 and 5.49 ppm, resulting from the β - and α -alkenyl protons, respectively. As the reaction progressed, the β -proton resonances changed to what appeared to be a doublet of quartets, whereas two sets of doublets of triplets were observed in the α -proton region (Figure 1b). Finally, when all of the available hydride was utilized the spectrum of the resultant diisobutyl(*trans*-1-hexen-1-yl)alane exhibited doublets of triplets both at δ 7.42 and 5.75

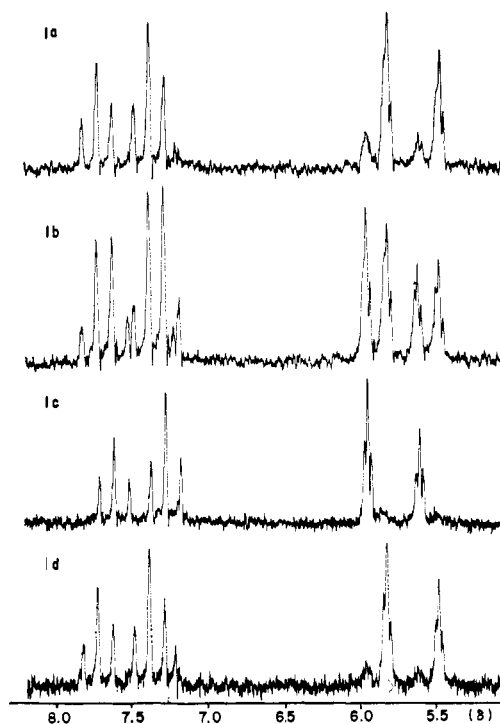
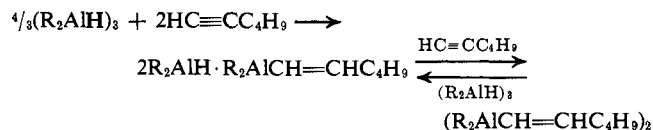


Figure 1. Vinyl proton region of the nmr spectrum of solutions of diisobutylaluminum hydride and 1-hexyne at 25°: (a) 47% reaction (15 min), (b) 67% reaction (45 min), (c) after complete reaction (25 hr), (d) sample used in (c) with 1.5 equiv of diisobutylaluminum hydride added.

ppm, attributed to the β - and α -alkenyl protons, respectively (Figure 1c). It is apparent that the spectrum of Figure 1b results from superposition of the resonance signals observed in the spectra of Figures 1a and 1c. Moreover, it is important to note here that the spectrum in Figure 1a can be replicated by adding an excess of diisobutylaluminum hydride to diisobutyl(*trans*-1-hexen-1-yl)alane. It should also be noted that exchange of vinyl and of hydride bridging groups is slow on the nmr time scale. Separate signals, rather than time averaged signals, are observed for the vinyl groups of complexes I and II. When excess diisobutylaluminum hydride is added to complex II, two types of hydride resonance signals are observed.

The observed changes in the nmr spectra with increasing reaction time are compatible with the formation of a complex between the alkenylalane and excess diisobutylaluminum hydride.⁵ Further reaction of the complex with remaining alkyne affords the diisobutyl(*trans*-1-hexen-1-yl)alane dimer. Based on the nmr



data and cryoscopic molecular weight determinations,⁶ we propose structure I for the dialkylalkenylalane

(5) The spectra also reveal that the resonance signal for the hydride in the complex (δ 3.75) is downfield from that for the hydride in the diisobutylaluminum hydride (δ 2.9).

(6) Molecular weights were determined by freezing point depression measurements of 0.01–0.03 *m* solutions in benzene. Molecular weights obtained (calculated values in parentheses) were: I, 463 (448); II, 414 (366). The fact that the molecular weight of II differs from the theoretical value by more than the experimental error ($\pm 5\%$) suggests that the complex is partially dissociated.

(1) This research was supported by Grant No. GP-9398 from the National Science Foundation.

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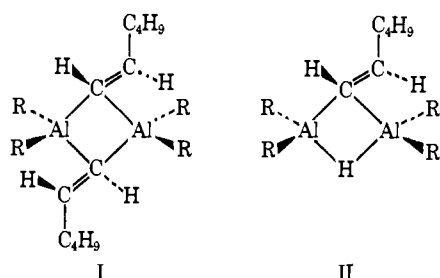
(4) Diisobutylaluminum hydride is trimeric in benzene solution: K. Ziegler, W. R. Kroll, W. Larbig, and O. W. Steudel, *Justus Liebigs Ann. Chem.*, **629**, 53 (1960); E. G. Hoffmann, *ibid.*, **629**, 104 (1960).

Table I. Nmr Data (60 MHz) for Alkenyl-Hydride^a and Dialkenyl-Bridged Alkylaluminum Dimers in *n*-Hexane

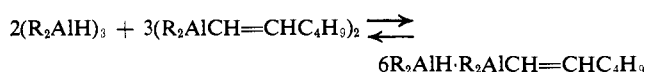
Alkenylalane derived from ^b	Proton resonance positions (δ) and coupling constants (Hz)					Hydride ^d
	α -Alkenyl		β -Alkenyl		Hydride ^d	
	Complex I ^c	Complex II ^d	Complex I ^c	Complex II ^d		
<i>n</i> -C ₄ H ₉ C≡CH	5.75 $J_{\alpha,\beta} = 20$ $J_{\alpha,\gamma} = 1$	5.49 $J_{\alpha,\beta} = 20$ $J_{\alpha,\gamma} = 1$	7.42 $J_{\beta,\gamma} = 6$	7.55 $J_{\beta,\gamma} = 6$		3.75
<i>tert</i> -C ₄ H ₉ C≡CH	5.78 $J_{\alpha,\beta} = 20$	5.58 $J_{\alpha,\beta} = 20$	7.39	7.51		3.80
C ₆ H ₅ -C≡CH ^e	6.57 $J_{\alpha,\beta} = 21$	6.28	8.12	8.10		3.92
C ₂ H ₅ C≡CC ₂ H ₅			7.14 $J_{\beta,\gamma} = 6$	7.24 $J_{\beta,\gamma} = 6$		3.74

^a No attempt has been made to isolate the mixed alkenyl-hydride-bridged dimers. ^b 1.0–1.5 *M* solutions in *n*-hexane. ^c Complex I = dialkenyl-bridged compound. ^d Complex II = mixed alkenyl-hydride-bridged compound. ^e The hydroalumination of phenylacetylene affords vinylalane, alkenylalane (*via* metalation), and styrene (by exchange reactions): J. R. Surtees, *Aust. J. Chem.*, **18**, 14 (1965); R. L. Miller, unpublished results.

dimer, and the mixed-bridged structure II for the complex between diisobutylaluminum hydride and the dialkenylaluminum.⁷



Structure I is similar to that proposed by Visser and Oliver⁹ for vinyl-bridged alkylgallium dimers. The driving force for the formation of an alkenyl bridge may be due to stabilization obtained by overlap of the double-bond π orbitals with the vacant nonbonding three-center orbital of the aluminum atom. The formation of the alkenyl-hydride-bridged species II can be accounted for in terms of a diminished steric interaction when hydride serves as a bridge between the aluminum atoms. Supporting evidence for this view stems from the observation that the more sterically hindered diisobutyl(1-ethyl-*trans*-1-buten-1-yl)alane, derived from the monohydroalumination of 3-hexyne, has a greater tendency to form the mixed-bridge complex than does diisobutyl(*trans*-1-hexen-1-yl)alane. Finally, the equilibrium constant for the formation of the mixed dimeric complex II is 4.3×10^3 in hexane



at 37°, indicating that formation of the mixed bridge compound is favored over reversal to the component species.¹⁰

(7) Additional evidence for the formation of mixed-bridged species was obtained by taking the ir spectra during the hydroalumination reaction. The intense Al-H stretching band⁸ at 1760 cm^{-1} disappeared rapidly as the hydroalumination of 1-hexyne and 3-hexyne progressed and was replaced by an intense band in the 1300–1400- cm^{-1} region. After 50% reaction, the 1760- cm^{-1} band disappeared, and the 1300–1400- cm^{-1} band reached its maximum intensity. As the reaction progressed further, the intensity of the latter band decreased.

(8) G. Schomburg and E. G. Hoffmann, *Z. Elektrochem.*, **61**, 1110 (1957).

(9) H. D. Visser and J. P. Oliver, *J. Amer. Chem. Soc.*, **90**, 3579 (1968).

(10) The equilibrium constant for the formation of II was obtained by integration of the vinyl proton region of spectra resulting from solutions of known amounts of I and diisobutylaluminum hydride. Owing to the

Investigation of the hydroalumination of other alkynes with diisobutylaluminum hydride revealed that formation of the mixed-bridge complexes is a general phenomenon. A summary of the nmr spectral properties of various alkynes resulting from the hydroalumination of various alkynes is shown in Table I.

From the results obtained in this study, it is apparent that elucidation of the mechanism of the hydroalumination reaction involving alkynes must take into account mixed-bridged alkenyl-hydride species as reactive intermediates.

small amount of dissociation of the mixed-bridged species derived from 3-hexyne, its equilibrium constant could not be determined by this method.

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The Configurational Stability of Phosphorus in Five-Membered Ring Phosphorochloridites

Sir:

Although previous nmr investigations^{1,2} have established the configurational stability of phosphorus in five-membered ring phosphite esters, analogous phosphorochloridites I allegedly undergo rapid inversion of configuration at phosphorus *via* a bimolecular chlorine exchange mechanism.² Thus, in pinacol phosphorochloridite (Ia), rapid inversion at phosphorus results in equivalence of the methyl nmr signals.² Similar studies^{3,4} of ethylene phosphorochloridite (Ib) also indicate that exchange of chlorine occurs in the neat liquid at room temperature. We wish to report our initial investigations of the nmr spectra of isobutylene phosphorochloridite (Ic), which show that the configurational lability at phosphorus in five-membered ring phosphorochloridites is solely a matter of the purity of the sample.

(1) H. Goldwhite, *Chem. Ind. (London)*, 494 (1964).

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