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A NEW ALKENYLATION REACTION OF ALDEHYDES AND KETONES USING VINYLALANES

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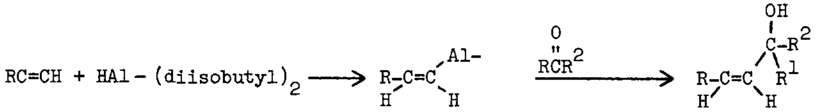
I would like to report that vinylalanes react smoothly, conveniently and rapidly with aldehydes and ketones in ether-hydrocarbon or hydrocarbon solvents at room temperature to give the corresponding allylic alcohols. The reaction proceeds stereospecifically to give the *trans* allyl alcohol as indicated by the 10.3µ out-of-plane CH bending band in the infrared and by the coupling constant (J=16 cps) of the olefinic protons in the nmr made clearly observable with the europium tetramethlheptanedionate shift reagent[1].

The vinylalanes employed were readily obtained, as previously reported, [2,4] by the addition, exclusively *cis*, of diisobutyl aluminum hydride to the appropriate acetylene.



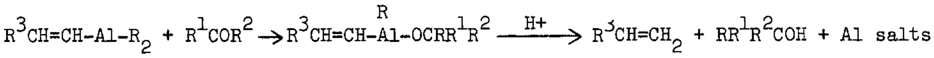
Representative examples of this new alkenylation reaction are listed in Table I.

Table 1

No.	Substrate	Acetylene used to prepare the vinyl alane	Solvent[a]	Product	% Yield[b]
1	ØCHO	1 - pentadecyne	ether	$\phi\overset{OH}{C}HCH \overset{t}{=} CH(CH_2)_{12}CH_3$[g]	*ca.* 50[c]
2	ØCHO	1 - Pentadecyne	benzene	"	*ca.* 50[c]
3	acetone	1 - hexyne	ether	$(CH_3)_2\overset{OH}{C}CH \overset{t}{=} CH(CH_2)_3CH_3$[g,3]	42[d]
4	cyclohexanone	1 - hexyne	ether	$(CH_2)_5\overset{OH}{C}CH \overset{t}{=} CH(CH_2)_3CH_3$[g]	40[d,e]
5	CH_3CH_2CHO	1 - heptyne	ether[f]	$CH_3CH_2\overset{OH}{C}HCH \overset{t}{=} CH(CH_2)_4CH_3$[g]	30[d,h]

a) Refers to solvent in which the carbonyl component was added. b) No attempts were made at optimization. c) The total product from these two reactions were investigated in some detail using thick-layer chromatography to separate the components. The overall reaction course in the two solvent was virtually identical. In addition to the desired allyl alcohol (yield calculated on the basis of unrecovered hydrocarbon) there was obtained *ca.* a 10% yield of benzyl alcohol and *ca.* a 25% recovery of a hydrocarbon mixture consisting of pentadecene along with some pentadecyne. d) After distillation. e) bp. 80-81° (0.1 mm); A 5-10% yield of (lower boiling) cyclohexanol was also obtained. f) Added during 35 min because of the magnitude of the exotherm accompanying the addition. g) Analysed satisfactorily. h) Distilled from glass wool because of bad foaming; b.p. 100-101° (*ca.* 5 mm). The ir spectra of the material before and after distillation were virtually identical; the nearly colorless liquid residue prior to distillation represented at 54% yield of product.

A competing reduction of the carbonyl function (see Table footnotes c and d) would be one factor responsible for the moderate yields of allyl alcohol obtained. Another possible factor could be a competing alkylation (isobutylation) of the carbonyl substrate by the vinyl diisobutyl alane. The recovery of pentadecene in Examples 1 and 2 of Table I (see Table footnote c) would be consistent with this proposal.



$$R^3CH{=}CH\text{-}Al\text{-}R_2 + R^1COR^2 \rightarrow R^3CH{=}CH\text{-}\overset{R}{Al}\text{-}OCRR^1R^2 \xrightarrow{H+} R^3CH{=}CH_2 + RR^1R^2COH + Al\ salts$$

Recently, Zwiefel and Steele[4] described the reaction of aluminum "ate" complexes with carbon dioxide, formaldehyde and acetaldehyde and reported that vinylalanes fail to react with carbon dioxide in ether or ether-hydrocarbon mixtures at room temperature.[5]

The simplicity of the procedure involved is illustrated with the following example.

Hexenyl diisobutyl alane is prepared[2,4] by treating a solution of 9.6 ml (7 g, 0.085 mole) of hexyne in 60 ml of n-hexane with 70 ml of 1.2M diisobutyl aluminum hydride in hexane[6] 0.084 mole) and heating the colorless solution at 50° for 2 hr. The solution is then cooled in ice-water and a solution of 6.3 ml (4.9 g, 0.085 mole) of acetone (reagent grade) in 30 ml of anhydrous ether is added dropwise during 15 min maintaining the temperature of the reaction mixture between 5-10°. The cooling bath is then removed and the solution stirred for an additional hour, allowing warming to room temperature. The reaction mixture is poured into ice-water, acidified (HCl) and extracted with ether.
Drying and evaporating the ether yields 8.2 g (68%) of nearly colorless liquid residue which is distilled from glass wool (compound foams badly) to give 5 g (42%) of 2-methyloct-3-ene-2-ol[3] as a colorless sweet smelling liquid, b.p. *ca.* 75° (*ca.* 5 mm), λmax 10.3μ. (film) (The infrared spectra of the product before and after distillation were essentially identical.)

The fact that vinylalanes are much more easily prepared than vinyl Grignard or vinyl lithium compounds recommends them highly for attempting alkenylations of aldehydes or ketones.

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3. G. Buchi and S. H. Feairhelfer, J. Org. Chem., 34,611 (1969).
4. G. Zweifel and R. B. Steele, J. Am. Chem. Soc., 89,2754 (1067).
5. a) By way of comparison, we attempted the reaction between benzaldehyde and the "ate" complex from pentadecyne according to the procedure described by these authors. The yield of allyl alcohol obtained was comparable (maximally 10% higher) to that of examples 1 and 2 of Table I.
   b) Our current findings suggest that vinyl alanates may well react directly with carbonyl compounds rather than through the intermediacy of vinyl lithium derivatives.[4]
6. Texas Alkyls Inc., Houston, Texas.