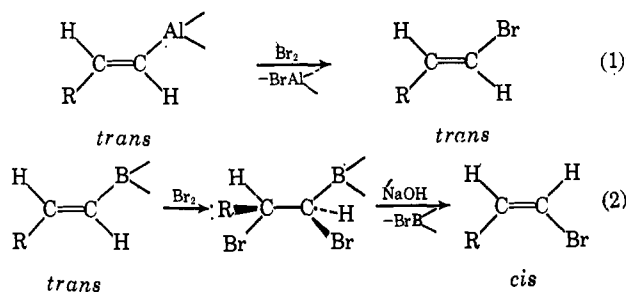


Table I. Halogenation of Vinylalanes in Tetrahydrofuran

Vinylalane derived from	Halogen ^a	Vinyl halide, <i>trans</i>	% ^{b,c} <i>cis</i>
1-Hexyne	I ₂	94	<2
	ICl	76 ^d	<2
	Br ₂	72	<2
3-Hexyne	I ₂	<2	72
	Br ₂	<2	42

^a Both bromine and iodine monochloride were dissolved in methylene chloride and then added to the vinylalane. Iodine was used in tetrahydrofuran. ^b Analysis by glpc with an internal standard. ^c The assignments for the vinyl halides are based on infrared and nmr data. ^d *trans*-1-Iodo-1-hexene.

With increasing reactivity of the halogen, there is less discrimination between cleavages at the hexenyl-aluminum and isobutyl-aluminum bonds. In these cases the vinyl halide is contaminated with the isobutyl halide. In order to maximize the yield of the vinyl halide, larger amounts of halogens should be used.



The simplicity of this procedure makes it a valuable method for synthesis of isomerically pure vinyl halides. The isobutyl groups on aluminum do not interfere with the isolation of the halides since they are converted to isobutane in the hydrolysis step. It is of special importance in that 1-iodo-1-alkenes, which cannot be prepared by the addition of hydrogen iodide to 1-alkynes in the presence of peroxides, are obtained in excellent yield from the corresponding vinylalanes. A representative procedure is given below.

To 0.10 mole of 1-hexyne in 20 ml of *n*-heptane was added 0.10 mole of diisobutylaluminum hydride while maintaining the temperature below 40°. When the initial exothermic reaction had subsided, the reaction mixture was heated for 2 hr at 50°. The heptane was then removed under reduced pressure (0.5 mm), and the residue obtained was diluted with 40 ml of tetrahydrofuran. To this vinylalane solution at -50° was added 0.10 mole of iodine in 40 ml of tetrahydrofuran. After allowing the reaction mixture to warm up to room temperature, the diisobutylalane (-Al(C₄H₉)₂) was decomposed at 20-30° by dropwise addition of 20% sulfuric acid (exothermic reaction). When the isobutane evolution had diminished, the reaction mixture was poured into ice-20% H₂SO₄. The vinyl iodide was extracted into pentane and the combined extracts were washed first with sodium thiosulfate, then with sodium bicarbonate. Distillation gave 15.52 g of *trans*-1-iodo-1-hexene (74%); bp 50-52° (3 mm), *n*_D²⁰ 1.5072. A small amount of the vinyl iodide was converted to the vinyl-lithium derivative,⁶ which was hydrolyzed with deuterium oxide. The infrared and nmr spectra of the

(6) D. Seyferth and L. G. Vaughan, *J. Am. Chem. Soc.*, **86**, 883 (1964).

olefin obtained were identical with those of an authentic sample of *trans*-1-hexene-1-*d*₁.

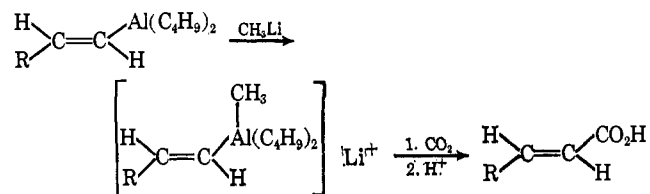
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Received March 13, 1967

A New and Convenient Method for the Preparation of Isomerically Pure α,β -Unsaturated Derivatives via Hydroalumination of Alkynes

Sir:

Relatively little attention has been directed to the utilization of organoalanes as Grignard-like reagents. Ziegler and co-workers¹ have shown that the addition of carbon dioxide to trialkylalanes at atmospheric pressure and at room temperature in hydrocarbon solvents results in the carbonation of only one carbon-aluminum bond. Similarly, we have observed that carbonation of vinylalanes in hydrocarbon solvents affords the corresponding α,β -unsaturated acids in modest yields (30-37%). Both trialkylalanes and vinylalanes, however, fail to react with carbon dioxide in ether or hydrocarbon-ether mixtures at room temperature.

We now wish to report that the *ate* complexes of vinylalanes may be utilized for Grignard-type reactions. The required vinylalanes are readily accessible via hydroalumination of alkynes with diisobutylaluminum hydride in hydrocarbon solvents.^{2,3} This involves a *cis* addition of the aluminum-hydrogen bond to the triple bond, yielding *trans*-vinylalanes from 1-alkynes and *cis*-vinylalanes from disubstituted alkynes. Treatment of the hydrocarbon solutions of vinylalanes with methyllithium in ether in a 1:1 ratio followed by carbonation gives the corresponding carboxylic acids in excellent yields. Likewise, acetaldehyde and para-



formaldehyde⁴ may be treated with the *ate* complexes at 25 and 35°, respectively, to yield α,β -unsaturated alcohols. A summary of the experimental results of these reactions is given in Table I.

Examination of the reaction mixtures by glpc revealed that the products obtained in each case were isomerically pure. Consequently, the reactions of vinylalanes with Grignard co-reagents proceed with retention of configuration. It was also noted that carbonation occurs exclusively at the vinyl-aluminum bond. The isobutyl moieties of the hydroaluminating agent are converted to isobutane in the hydrolysis step, and hence do not interfere in the isolation of the products.

(1) K. Ziegler, F. Krupp, K. Weyer, and W. Larbig, *Ann.*, **629**, 251 (1960).

(2) G. Wilke and H. Müller, *ibid.*, **629**, 222 (1960).

(3) G. Zweifel and R. B. Steele, to be published.

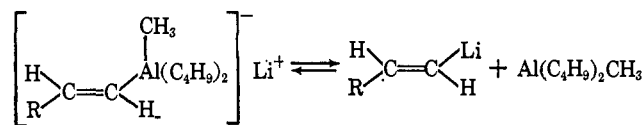
(4) It has been reported that the reaction of Grignard compounds with paraformaldehyde proceeds very slowly, whereas organolithium derivatives react at a much faster rate: A. Schaap, L. Brandsma, and J. F. Arens, *Rec. Trav. Chim.*, **84**, 1200 (1965).

Table I. Reactions of Vinylalanes with Various Reagents in Ether

Vinylalane derived from	Reagent	Product	Yield, % ^{a,b}
1-Hexyne	CO ₂	<i>trans</i> -2-Heptenoic acid	78
	HCHO ^c	<i>trans</i> -2-Hepten-1-ol	73
	CH ₃ CHO	<i>trans</i> -3-Octen-2-ol	68 ^d
Cyclohexyl-acetylene	CO ₂	<i>trans</i> -3-Cyclohexyl-2-propenoic acid	72
2-Butyne	CO ₂	<i>trans</i> -2-Methyl-2-butenic acid	76
3-Hexyne	CO ₂	<i>trans</i> -2-Ethyl-2-pentenoic acid	78

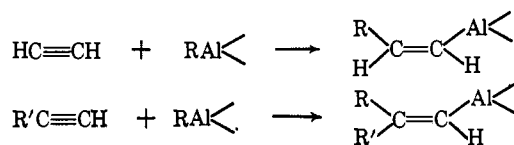
^a By isolation. ^b Yields are based on the amount of alkyne used. ^c Paraformaldehyde. ^d Yield 90% by glpc analysis.

Although the nature of the reactive organometallic intermediates has not been established, it is conceivable that the reactions proceed *via* the vinylolithium derivatives resulting from disproportionation of the vinylalanes. The configurational stability of vinylolithium



compounds in solution, a requirement in view of the high stereospecificity of the above reactions, has been demonstrated by Seyferth and co-workers.⁵ We have observed that tetraalkylalanes do not react with carbon dioxide; however, their disproportionation into alkylolithium compounds and trialkylalanes should be thermodynamically unfavorable.

The synthesis of vinylalanes is not confined to the hydroalumination reaction. Thus trialkylalanes add to acetylene under mild conditions to yield *cis*-vinylalanes, whereas addition of the aluminum-carbon bond to 1-alkynes affords the corresponding disubstituted vinylalanes.² The availability of *cis*- and *trans*-mono-



substituted vinylalanes greatly increases the versatility of the above reactions.

The simplicity of the present procedure for the conversion of alkynes into α,β -unsaturated derivatives *via* vinylalanes is illustrated by the following example.

To 0.10 mole of 1-hexyne in 20 ml of *n*-heptane was added by means of a hypodermic syringe 0.10 mole of diisobutylaluminum hydride, while maintaining the temperature below 40°. After the initial exothermic reaction had subsided, the reaction mixture was heated for 2 hr at 50°. To the vinylalane formed was added at room temperature 0.10 mole of methylolithium in ether (60 ml). The solution was cooled to -30°, then carbonated by introducing a stream of carbon dioxide while maintaining the temperature at -30 to -10°. The reaction mixture was poured slowly into an ice-concentrated hydrochloric acid mixture and the carboxylic acid produced was extracted into ether. Distil-

(5) D. Seyferth, *Record Chem. Progr. (Kresge-Hooker Sci. Lib.)*, **26**, 86 (1965).

lation gave 10.0 g of *trans*-2-heptenoic acid (78%), bp 89° (0.3 mm), n_{D}^{22} 1.4560, amide mp 124°.⁶

Acknowledgment. This work was supported by National Science Foundation Grants GP-3521 and GP-6633.

(6) P. Bruylants, *Bull. Soc. Chim. Belges*, **41**, 333 (1932), reports for *trans* amide mp 125°.

(7) National Institutes of Health Predoctoral Fellow, 1965-1966.

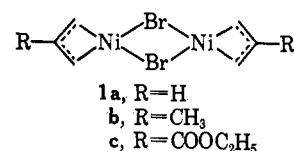
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Organonickel Compounds as Reagents for Selective Carbon-Carbon Bond Formation between Unlike Groups

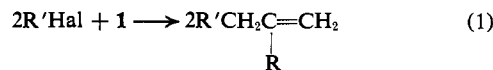
Sir:

The extension of carbon chains by the coupling of two different groups using as reagents an organic halide, RHal, and an alkyl- or arylmetal derivative, R'Met, is seldom employed in synthetic practice if alternative operations are available. This is due in part to the fact that coupling products RR and R'R' are usually formed in substantial amounts¹ and in part to the intervention of a variety of other side reactions, *e.g.*, α - or β -elimination processes. We report here a new and promising method for the *selective combination of unlike groups* at carbon using organonickel reagents.

Reaction of a variety of allylic bromides with excess nickel carbonyl in dry benzene (50°, 2-3 hr) followed by removal of solvent and recrystallization from ether at -70°² gives good yields of π -allylnickel(I) bromides, for example, **1a-c**, in 80-95% yield.^{3,4} These complexes are relatively inert toward alkyl halides in either hydro-



carbon solvents or ether-type solvents (*e.g.*, tetrahydrofuran). In more *polar, coordinating media*, *e.g.*, dimethylformamide, *N*-methylpyrrolidone, or hexamethylphosphoramide, a facile reaction occurs between the complexes **1** and a *wide variety* of halides, with iodides generally being more reactive than (and preferable to) bromides.⁵ Equation 1 summarizes the over-all reaction, and Table I presents the results ob-



(1) For example, because of fast halogen-metal exchange prior to coupling. See D. E. Applequist and D. F. O'Brien, *J. Am. Chem. Soc.*, **85**, 743 (1963).

(2) All operations with organonickel compounds have been conducted with rigorous exclusion of oxygen using an argon atmosphere either with plastic glove bag or argon-line techniques.

(3) The complex **1a**, first prepared by E. O. Fischer and G. Bürger, *Z. Naturforsch.*, **16b**, 77 (1961), was originally obtained only in ca. 10% yield; however, much higher yields are easily realized if thermal or oxidative decomposition of the complexes is avoided.

(4) These complexes can also be obtained efficiently from allylic bromides using bis(1,5-cyclooctadiene)nickel as reagent; see G. Wilke *et al.*, *Angew. Chem. Intern. Ed. Engl.*, **5**, 159 (1966). However, the synthesis from commercially available nickel carbonyl is usually more expeditious.

(5) Chlorides are less generally useful because of their much lower reactivity.