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A STEREOSELECTIVE SYNTHESIS OF DISUBSTITUTED TRANS-ALKENES BY THE REACTION OF TRANS-ALKENYLTRIALKYLALUMINATES WITH ALKYL HALIDES AND SULFONATES

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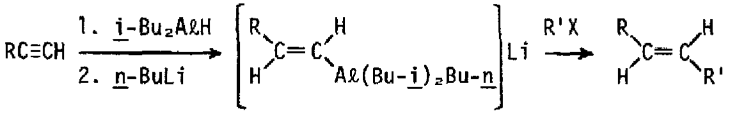
A markedly rate-enhancing effect of polar solvents, such as tetrahydrofuran (THF), has been noted recently in the coupling of aryllithiums[1] or alkenyllithiums[2] with alkyl halides. Although the latter reaction provides a stereospecific route to alkenes, the synthesis of the requisite stereo-defined alkenyllithium via lithiation of alkenyl halides which, in turn, requires the stereoselective preparation of the halides is often cumbersome. To alleviate this difficulty, the direct use of stereo-defined alkenylaluminums[3] or alkenylborons[4] readily obtainable via the respective hydrometallation in the alkenyl-alkyl coupling has been explored.[5]

We now report that trans-alkenyltrialkylaluminates (1) prepared by the reaction of alkynes with diisobutylaluminum hydride (DIBAH), followed by treatment with an equimolar amount of n-butyllithium, react with certain alkyl halides to produce the corresponding trans-alkenes ($\geq$98% trans), thereby providing a simple one-pot procedure for the stereoselective preparation of trans-alkenes.

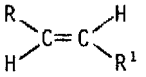


1

(1)

The stereochemistry of the products has been established by a combination of ^{1}H and ^{13}C NMR, IR ($\approx$970 cm^{-1}) and GLC. As shown in Table 1, this reaction proceeds well with more reactive halides and sulfonates, such as methyl iodide, allyl bromide, propargyl bromide, benzyl iodide and α-chloromethyl methyl ether. Primary alkyl iodides and sulfonates give the desired coupling products in somewhat lower yields.

Table 1. Stereoselective Synthesis of trans-Alkenes

Acetylene (RC≡CH)	R^1X	Reaction Conditions[a] Solvent	Time (hr)	Yield[b](%) of 
1-Heptyne	Methyl iodide	THF	24	65
1-Heptyne	n-Propyl mesylate	THF	24	44
1-Hexyne	n-Octyl mesylate	hexane	24	41
1-Hexyne	n-Octyl iodide	THF	110[c]	49
1-Hexyne	Allyl bromide	THF	3	73 (60)
tert-Butylethylene	Allyl bromide	hexane-THF	3	79 (65)
1-Hexyne	Propargyl bromide	THF	6	60[d]
1-Hexyne	Benzyl iodide	THF	18[e]	51
1-Hexyne	Benzyl bromide	THF	12[c]	46
1-Hexyne	α-Chloromethyl methyl ether	THF	1	51

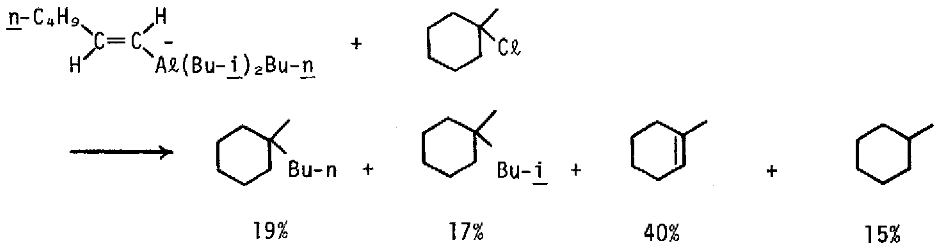
[a] Hydroalumination was carried out at 50-55° for 2-4 hr in hexane. n-Butyllithium in hexane was added at 25°. The reaction of **1** with R'X was carried out in the solvent specified at 25°, unless otherwise mentioned.

[b] By GLC. The numbers in parentheses are isolated yields. The stereoisomeric purity in each case established by GLC, ^{1}H NMR and/or ^{13}C NMR is $\geq$98%.

[c] Under reflux. [d] trans-1,2,4-Nonatriene was formed exclusively. [e] 40°.

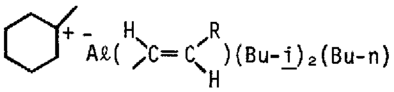
Interestingly, the reactions with tert-alkyl halides are rapid, but appear to follow considerably different reaction paths. For example, the reaction of **1** (R=n-C_4H_9-) with 1-methyl-

1-chlorocyclohexane yielded within 1 hour at 0° 1-methyl-1-*n*-butylcyclohexane (19%) and 1-methyl-1-isobutylcyclohexane (17%) along with 1-methylcyclohexane (40%) and methylcyclohexane (15%) without producing the desired 1-methyl-1-hexenylcyclohexane.



(2)

The transfer of the *n*-butyl or isobutyl group of **1** in preference to the alkenyl group appears unprecendented.[6] It seems difficult to rationalize the results in terms of any ionic two-electron transfer process. The relative transferability is consistent with a free-radical process. However, no homo-coupled product has been detected. The one-electron transfer mechanism involving **2** within a solvent cage seems to accommodate the experimental observations, although this point needs to be established by further studies.



2

The reaction of an alkenyltrialkylaluminate similar to **1** with aldehydes or carbon dioxide has previously been interpreted in terms of the predissociation of the *ate* complex into the corresponding alkenyllithium and trialkylalane.[6a] While such a mechanism cannot be ruled out on a rigorous basis, our attempt to promote the hypothetical dissociation reaction by the addition of an equimolar amount of *n*-butyllithium to **1** in hexane-ether mixture at 25° did not cause any noticeable change other than the well-documented slow reaction of *n*-butyllithium with ether.[7] Thus, the NMR features of both *n*-butyllithium (δ ≈ -1.2 ppm for 2 α-hydrogens) and **1** (δ = 6.2 - 6.3 ppm for 2 alkenyl hydrogens) remain unchanged on mixing. It is therefore likely that **1** is directly involved in the carbon-carbon bond-forming process.

ACKNOWLEDGMENTS

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