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Preliminary communication

STEREOCONTROLLED CARBOTITANATION OF ALKYNYLSILANES

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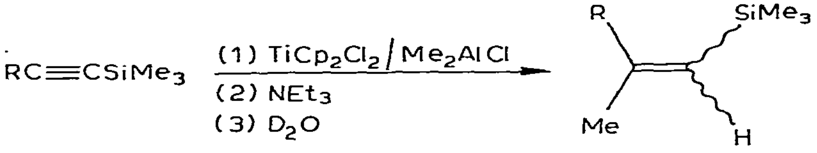
Summary

Carbometalation of alkynylsilanes with 1/1 titanocene dichloride/dialkylaluminum chloride is stereospecifically *cis*. The alkenyltitanium intermediate can be stereospecifically protonated by aqueous sodium hydroxide or iodinated. Addition of any Lewis base to the alkenyltitanium intermediate induces decomposition of this intermediate to give an alkene by hydrogen atom abstraction from the medium, with loss of stereochemistry.

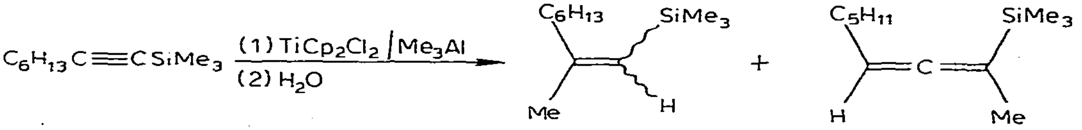
Carbometalation of alkynes is a versatile, new method for the stereospecific synthesis of trisubstituted alkenes. Organocopper species [1] and trialkylaluminum/zirconocene dichloride mixtures [2] are useful reagents for the stereospecific *cis* carbometalation of terminal alkynes. Carbometalation of alkynylsilanes is potentially valuable since the resulting alkenylsilanes undergo stereospecific electrophilic desilylation [3]. We have reported that nickel acetylacetonate/trimethylaluminum catalyzes the stereospecific *cis* addition of methylmagnesium bromide to alkynylsilanes [4]. The resulting alkenylmagnesium species can be trapped with a variety of electrophiles.

Eisch has reported that treatment of alkynylsilanes with 1 equiv. of titanocene dichloride and 1 equiv. of an alkylaluminum dichloride or dialkylaluminum chloride in methylene chloride for 12—25 h, followed by addition of triethylamine (a buffer to prevent desilylation during workup) and then water results in a mixture of stereoisomers in which the product of *trans* addition often predominates [5] (See eq. 1). Use of D_2O does not lead to deuterium incorporation. Negishi has reported that treatment of octynyltrimethylsilane with 2 equiv of a 1/1 mixture of titanocene dichloride/trimethylaluminum in 1,2-dichloroethane leads to a 30/70 mixture of allene and alkenylsilane of undefined stereochemistry [6] (See eq. 2). We felt that the apparent lack of stereospecificity, and differences in regiochemistry, warranted reinvestigation of the carbometalation of alkynylsilanes by titanocene dichloride/organoaluminum mixtures.

We wish to report that carbometalation of alkynylsilanes by dimethylaluminum chloride/titanocene dichloride is in fact stereospecifically *cis*.

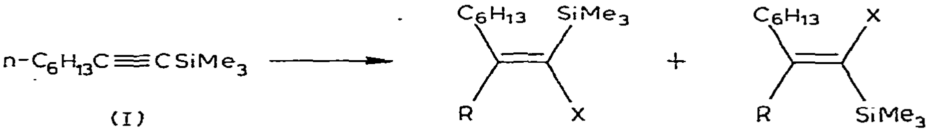


(1)



(2)

Treatment of octynyltrimethylsilane (I) in methylene chloride with 2 equiv. of a 1/1 mixture of dimethylaluminum chloride/titanocene dichloride for 1.5 h followed by addition of the reaction mixture to a large excess of 25% aqueous potassium hydroxide gives a 95/5 mixture of alkenylsilanes II and III in 93% yield. Quenching by addition to a saturated sodium bicarbonate solution gives 75% of a 95/5 mixture of II and III and 13% of 2-methyl-1-octene resulting from desilylation. Prolonged reaction time (2—3 days) prior to quenching does not lead to increased isomerization. Quenching by addition to 15% sodium deuteroxide in D_2O gives a 90% yield of a 95/5 mixture of IV and V with greater than 95% deuterium incorporation.



(3)

(II) R = Me, X = H (III)
(IV) R = Me, X = D (V)
(VI) R = Et, X = H (VII)
(VIII) R = Me, X = I (IX)

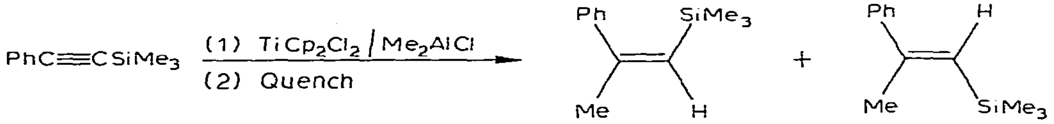
Reaction of I with 2 equiv. of 1/1 diethylaluminum chloride/titanocene dichloride for 2 h followed by quenching with aqueous potassium hydroxide gives a 95/5 mixture of VI and VII in 85% yield. Treatment of I with 2 equiv. of 1/1 ethylaluminum dichloride/titanocene dichloride for 2.5 h gives a similar mixture in 81% yield. Quenching with sodium deuteroxide in D_2O gives greater than 95% deuterium incorporation. This method thus allows the stereospecific introduction of alkyl groups containing β-hydrogen atoms.

Addition of triethylamine to the alkenyltitanium intermediates prior to quenching with sodium deuteroxide in D_2O gives mixtures of stereoisomers in which deuterium is not incorporated, as reported by Eisch [5]. Addition of other Lewis bases, i.e., trimethylamine, pyridine, and even tetrahydrofuran or ethylene oxide, to the reaction mixture prior to quenching with sodium deuteroxide in D_2O also leads to mixtures of stereoisomers in which deuterium is not incorporated. Lewis bases are known to coordinate strongly to aluminum and could disrupt an aluminum-titanium complex thus destabilizing the titanium—

carbon bond. Homolysis of this bond would give an alkenyl radical which could lose stereochemistry before abstracting a hydrogen atom from the reaction medium. Alternatively, Lewis bases could induce decomposition by attack at the β-carbon of the alkenyl group to give a carbenoid complex [7] which then decomposes. Apparently during quenching two competing processes occur, stereospecific protonation of the alkenyltitanium and Lewis base induced decomposition by hydrogen atom abstraction from the medium with loss of stereochemistry. In aqueous solution protonation is fast relative to Lewis base induced decomposition. Use of 0.1 equiv. titanocene dichloride and 2 equiv. of dimethylaluminum chloride results in only 10% reaction, even after 4 days, thus supporting the presence of the proposed alkenyltitanium intermediate rather than an alkenylaluminum intermediate.

For synthetic purposes it is desirable to be able to trap the alkenyltitanium intermediate with electrophiles other than a proton. Addition of the reaction mixture from octynyltrimethylsilane and dimethylaluminum chloride/titanocene dichloride to 8 equiv. of iodine in methylene chloride at –78°C, followed by addition to an aqueous solution of potassium hydroxide and sodium thiosulfate gives an 88/12 mixture of VIII [4] and IX [4] in 65% yield. These iodides are useful intermediates since VIII has been stereospecifically converted to the alkenyllithium by exchange with 2 equiv. of t-butyllithium in THF at –78°C [4]. Unfortunately the alkenyltitanium intermediate does not react with methyl iodide, carbon dioxide or methyl chloroformate and gives a complex mixture with acetyl chloride.

We have also studied the reaction of dimethylaluminum chloride/titanocene dichloride with phenylethynyltrimethylsilane. Quenching the reaction mixture after 2 h with 25% aqueous potassium hydroxide gives an 80/20 mixture of X and XI in 85% yield. Quenching with 15% sodium deuteroxide gives a 70/30 mixture of X and XI in 80% yield with ca. 70% deuterium incorporation. Less basic quenching media (sodium bicarbonate-*d* or potassium carbonate in D_2O) give 1/1 mixtures of X and XI with no deuterium incorporation. Apparently, the phenyl accelerates Lewis base induced decomposition so that stereospecific protonation of the alkenyltitanium species in aqueous base no longer dominates Lewis base induced decomposition.



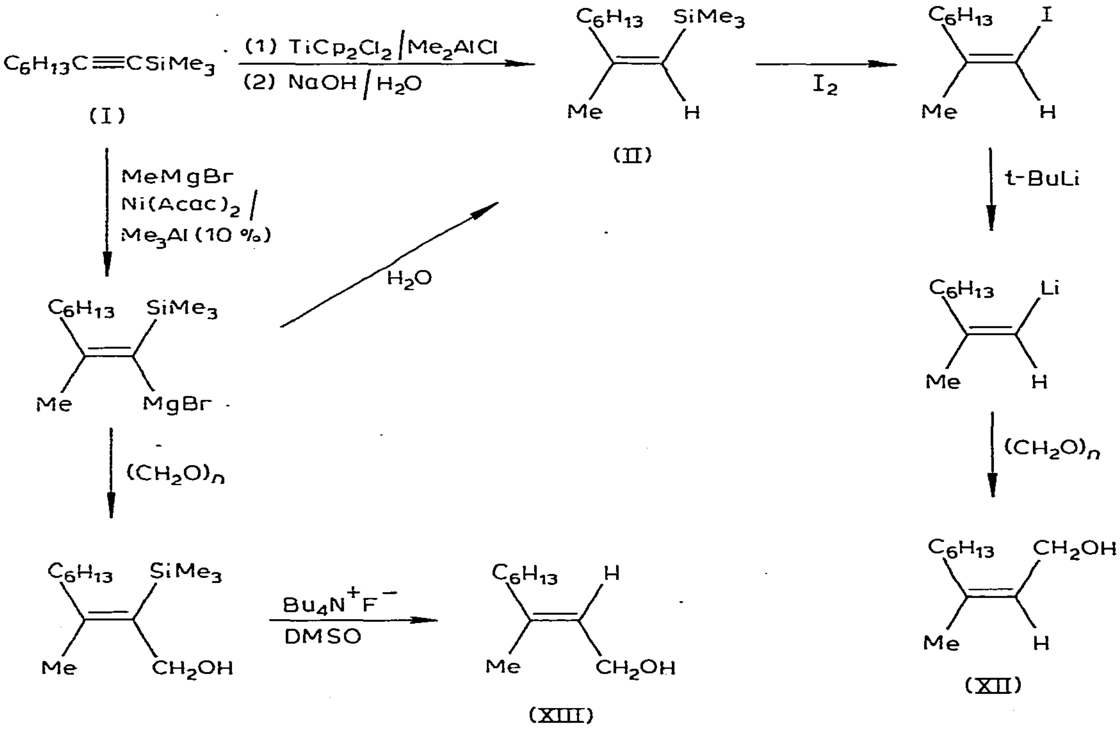
(4)

(X) (XI)

Reinvestigation of Negishi's reaction [6] of trimethylaluminum/titanocene dichloride with octynyltrimethylsilane indicates that this reaction is seven times slower than with dimethylaluminum chloride. The alkene which is formed is a 90/10 mixture of II and III along with the previously mentioned allene.

Negishi's alkyne carbometalation via trialkylaluminum/zirconocene dichloride has not been previously applied to alkynylsilanes. Reaction of alkynylsilane I with 1 equiv. of 2/1 trimethylaluminum/zirconocene dichloride for 3 h, followed by addition to 25% aqueous potassium hydroxide gives an 85% yield of a 5/5/1 mixture of II, III and 2-methyl-1-octene. No allene is formed. Quenching with basic D_2O gives greater than 80% deuterium incorporation. Quenching after 7 min (~50% reaction) gives a 5/4 mixture of II and III. Thus with zirconium, isomerization of the alkenylorganometallic and/or non-stereospecific carbometalation, rather than decomposition of the alkenyl species by hydrogen atom abstraction from the medium, leads to the mixture of isomers formed. Surprisingly, use of dimethylaluminum chloride in place of trimethylaluminum results in no reaction.

The ability to use carbotitanation of alkynylsilanes to produce alkenylsilanes stereospecifically is of synthetic value. For example, stereospecific iododesilylation of II [8] followed by transmetalation with t-butyllithium [9] and quenching with paraformaldehyde gives XII in 60% overall yield. We have also synthesized the stereoisomeric allylic alcohol XIII from octynyltrimethylsilane by nickel-catalyzed addition of methylmagnesium bromide, trapping with paraformaldehyde, and then desilylation with fluoride ion in dimethylsulfoxide [4]. Both stereoisomers are thus available from the carbometalation of a single alkynylsilane (see Scheme 1).



SCHEME 1

Our demonstration that carbotitanation is stereospecifically *cis* and that the alkenyltitanium intermediates can be stereospecifically cleaved with aqueous base or iodine makes this a versatile route to alkenylsilanes. It allows the use of alkyl groups with β-hydrogens and through the use of alkylaluminum dichloride allows efficient use of alkyl groups.

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