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THE PREPARATION OF 1,3-BIS(TRIMETHYLSILYL)ALLENE AND THE OBSERVATION OF THE ENANTIOMERS USING OLEFIN COMPLEXING CHIRAL SHIFT REAGENTS

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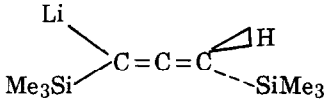
ABSTRACT: 1,3-Bis(trimethylsilyl)allene was prepared.

Lithiated allenes of type **1** have been used by two groups to form silylated enynes by reactions with



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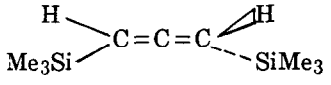

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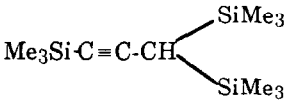
aldehydes and a ketone.[2] The allene structure **1** is chiral and potentially resolvable. A complication is that structure **1** could be in equilibrium with an achiral proparygyllithium structure. Still another possibility is that the lithiated species present may be an ion pair having allylic delocalization of the anionic charge. In this connection it is relevant that Okamura and coworkers[3] have found a reaction in which a lithiated allene appeared to undergo an inversion of its configuration.

Since the complications mentioned above may not be present in all instances, it is interesting to speculate that optically stable chiral allenes related to **1** might be obtained in resolved form by kinetic resolutions. The previously reported preparations of enynes[2] might accomplish such resolutions if optically active ketone or aldehyde substrates were used. If metallated allenes could, in fact, be obtained in the resolved form, they might in turn be used to accomplish kinetic resolutions of appropriate racemic compounds arising in total syntheses of natural products.

The silylated allene **2** in which the metal of **1** is replaced by hydrogen should not be subject to racemization. Furthermore a reaction of silylated allenes with ketones has been reported by Danheiser's group.[4] The Danheiser reaction of **2** should lead to the same enyne obtainable from **1** (except for the absence of a silyl group on the alkyne). The use of resolved carbonyl compounds could lead to the kinetic resolution of **2**. Accordingly we desired to investigate **2** as a synthetic equivalent of the chiral metallated allene **1**. The desired allene **2**, however had previously been obtained only once in

small amounts. Skell and Owen obtained it by the reaction of a few milligrams of C-3 fragments from a carbon arc with a large excess of trimethylsilane at liquid nitrogen temperature.[5]

A logical precursor of **2** was the trisilylated compound **3**, previously reported as a component of a complex mixture obtained by silylation of tetralithiated propyne.[6] We obtained **3** by the reaction of lithiated **4** (which has been depicted as **1**)[2] in ether with Me_3SiCl.



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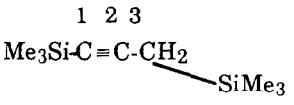

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Although gamma attack with double bond shift is the usual (but not always exclusive) result of reactions of allylsilanes and propargylsilanes with electrophiles,[7] protiodesilylation of **3** with trichloroacetic acid in methylene chloride gave 69 percent alpha attack! Subsequent studies showed that the desired allene **2** was also formed (14%), along with 17 percent of mono-trimethylsilylallene which, presumably, arose by desilylation of **2**.

Analogy with reactions of hindered ketones with metallated propargyl-allyl systems suggested that the use of hindered acids might give increased yields of allene. However both trichloroacetic acid and sulfonic acid ion exchange resin gave predominantly alpha attack to yield **4**.

A report[8] that saturated aqueous sodium sulfate acts as a hindered protonating agent prompted us to investigate the protonation of the lithiated propargylsilane **1**. This and other protonating agents gave the desired allene **2** with the propargylsilane **4** in ratios sometimes exceeding 50 percent (Table). In a reaction starting from 1.75 g of **4**, lithiation with t-BuLi (THF) followed by addition of H_2O-Na_2SO_4 at -78°C and warming gave 1.4 g (80%) of the distilled mixture of **2** and **4**.

Table 1. Allene to propargylsilane ratio from protonation of **1**

Source	Ratio
Na_2SO_4-H_2O	55/45
H_2O	53/47
TMEDA/H_2O	52/48
3-(Trifluoroacetyl)-d-camphor	63/37
Ethyl n-butylmalonate	41/59
Bio-Rad Resin	47/53
TFA	26/74

The mixture of 2 and 4 was separated by injection of 100 mg portions on a HPLC analytical reverse phase column with methanol water (90:10) carrier.

We studied the analysis of 2 by nmr chiral shift reagents. Most such analyses depend upon complexation with oxygen functionality, but recently analyses of chiral olefins have been accomplished using both silver and lanthanide complexes, both now commercially available.[9] We found that the olefinic hydrogen singlet of 2 was, in fact, split into two peaks showing only slight broadening (figure), whereas the Me_3 Si peak was only broadened at 90 MHz. Our result may represent the first analysis by complexation to an allenic center, although a chiral allene complexed through an oxygen has been analyzed by a chiral shift reagent.[10]

Our first attempt to carry out a $TiCl_4$ catalyzed reaction of 2 with the chiral ketone obtained from the ozonolysis of vitamin D_3 apparently led to no reaction under Danheiser's conditions.[4] However studies are continuing using other substrates.

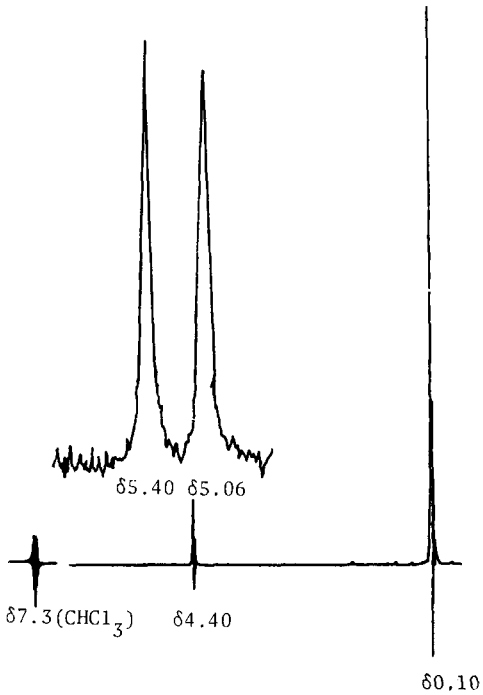

Figure. (A) ^1H NMR spectrum (90 MHz) of $(CH_3)_3SiCH=C=CHSi(CH_3)_3$. (B) Inset: Expansion of =CH region in the presence of the silver salt of 1,1,1,2,2,3,3-heptafluoro-7,7-dimethyloctane-4,7-dione(AgFOD) and tris[3-(heptafluoropropylhydroxymethylene)-d-camphorato, yttlerbium III derivative. Four μl of the allene and 10 mg of each shift reagent was added to 0.5 ml $CDCl_3$ containing $CHCl_3$ for the lock.

Experimental

To a stirred solution of 1,3-bis(trimethylsilyl)propyne (4) (1.75 gm, 9.5 mmol) dissolved in tetrahydrofuran (100 ml) was added t-butyllithium (0.61 gm, 9.5 mmol, 4.8 ml of a 2.0M pentane solution) at -78°C under an argon atomosphere. The resulting yellow solution was stirred at -78°C for 1 hr. At the end of this period, sodium sulfate decahydrate (6.50 gm, 20 mmol) was added in one portion

and the mixture stirred at -78°C for an additional hour. The mixture was transferred to a separatory funnel, diluted with enough water to dissolve the solid sodium sulfate and extracted with ether (3 x 125 ml). The combined ethereal extracts were washed with water and dried over magnesium sulfate. Filtration, solvent removal and vacuum distillation (80-90°C at 35 mm) afforded at 55:45 mixture of **2** and **4** (1.40 gm, 80%).

The mixture of **2** and **4** was separated by injection of 100 mg portions on an HPLC analytical C18 reverse phase 5 μ radial pak column with methanol-water (90:10) carrier. The combined fractions were taken into methylene chloride (50 ml), washed with water (2 x 25 ml) and brine (25 ml) before drying over magnesium sulfate. Removal of the solvent in vacuo and short path distillation afforded pure **2** (0.40 gm, 23%): bp 87-90°C (35 mm); ^{1}H NMR ($CDCl_3$) δ 0.10 (s, 9, Me_3), 4.39 (s, 1, CH); ^{13}C NMR ($CDCl_3$) δ -.74 (CH_3), 72.0 CH=), 211.5 (=C=); IR(film) 2960, 1910, 1295, 835 $cm.^{-1}$.

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