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CONJUGATE ADDITION OF DITRIMETHYLSILYLVINYL CUPRATES: PROTECTED ACYL ANION AND ENOLATE CARBANION EQUIVALENTS.

Robert K. Boeckman, Jr.* and Kenneth J. Bruza

Department of Chemistry, Wayne State University, Detroit, Michigan 48202

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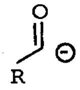
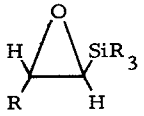
Considerable effort in the past few years has been devoted to the development and study of synthetic equivalents of acyl carbanions (1) in which nucleophilic reactivity is imparted to centers which ordinarily possess electrophilic characteristics.[1] Among the solutions reported to date, with the exception of the reports by Mukiayama[1b] and Schlessinger,[1e] no simple equivalent undergoes conjugate addition in a synthetically useful manner.

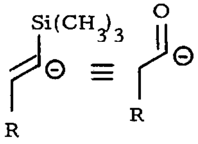


(1)



(2)

Since the work of Eisch[2] and Stork[3] had demonstrated that epoxy silanes (2) are efficient precursors of carbonyl compounds under acidic conditions, we were attracted to the possibility that halovinyltrimethyl silanes could be transferred 1,4 via the derived diorganocuprate complexes. The various isomers of the vinyl silane carbanions are by epoxidation and conversion to the carbonyl compound then the equivalent of acyl carbanions as well as aldehyde and methyl ketone enolates (3-5).[4]



R = H, alkyl

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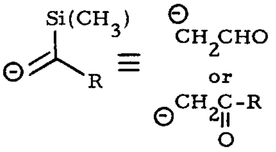

R = H, alkyl

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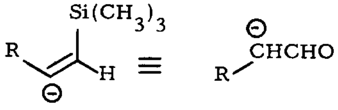
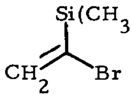


R = alkyl

(5)

The halovinyltrimethyl silanes are rendered even more attractive by the fact that the carbonyl compounds generated are conveniently differentiated and that vinyl silanes are stable to a variety of reaction conditions.[5]

Literature reports indicated that the required vinyl lithium reagents were not available in synthetically useful yields via direct reaction with lithium metal.[6] However, we have found that they may be prepared in high yield by exchange with 2 equivalents of tBuLi at -78° (in ether) then warming to -20° for 1-2 hrs.[7] The known halosilanes 6[8] and 7[9] were converted to the lithium reagent (2 eq) and thence to the diorgano cuprate with CuI (1 eq) at -50 to -20° in THF for 15-30 min. These cuprates formed characteristically deep green solutions and appeared to be quite thermally stable. This is not unexpected as silicon appears able to stabilize adjacent carbanions significantly.[10] Treatment of these solutions with 1 mole equivalent of 2-cyclohexen-1-one at -78° then warming to -10° over approximately 1 hr, afforded on NH_4Cl-NH_4OH workup the desired ketovinyl silanes 8 and 9 in > 90% yield. Ketones (8) and (9) were identified by their spectral characteristics,[11] and were contaminated only by small amounts of impurities apparently traceable to coupling of the untransferred vinyl group.



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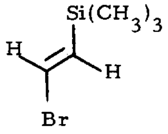

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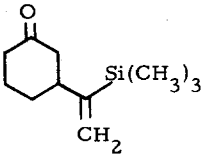

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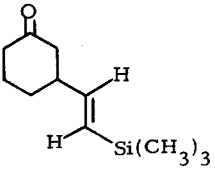
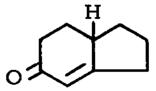


(9)

We then set out to determine whether these reagents were useful for the synthetically important introduction of angular substituents in polycyclic systems. Treatment of hydrindenone (10) in a similar way with the cuprate reagent derived from (7) affords the desired hydrindanone (11)[11] in 63% yield. Since branched alkyl groups are known to add sluggishly at best to angular positions, we were gratified to find that the reagent derived from (6) affords hydrindanone (12)[11] in 56% yield.

Extension of this process to substituted halo vinyl silanes requires the synthesis of three basic types of halovinyl silanes. It has been found that the methods utilized for the parent compounds are suitable with some modifications[12] for the preparation of typical members of the class (13) and (14). To date an efficient synthesis of the third structural type (15) has not been realized. Generation of the cuprate reagents from 13 and 14 proceeds as outlined above and addition products (16) and (17) are produced in 82 and 70% yields respectively. Thus far suitable conditions for the addition of the more highly hindered cuprates derived from 13 and 14 to hydrindenone 10 have not been found, however, efforts toward this end as well as toward the synthesis of 15 are continuing.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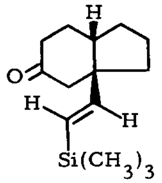
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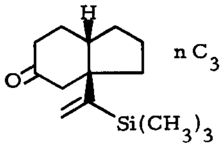
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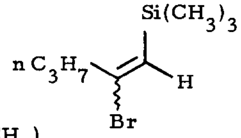
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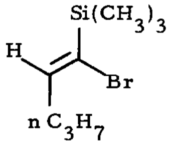
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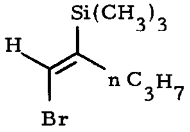
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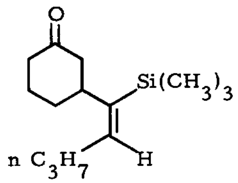
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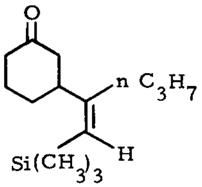
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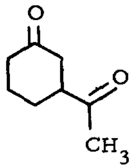
Conditions for the transformation of typical ketones (9) and (9) to compounds (18) and (19) have been developed. Direct epoxidation ($m\,Cl\phi CO_3H$ in CH_2Cl_2 at 25°) and acid treatment is not possible. The free carbonyl undergoes Baeyer Villager oxidation preferentially,[13] an indication of the unreactivity of the vinyl silanes. Ketalization followed by epoxidation ($\begin{matrix}CH_2OH\\ |\\ CH_2OH\end{matrix}/\phi H/pTs\phi H$; $m\,Cl\phi CO_3H/CH_2Cl_2/25^\circ$) affords the epoxy ketals (20) and (21) in good yield (60-70% overall). Treatment with aqueous acid at $0^\circ \rightarrow 25^\circ$ ($HClO_4$ in aq THF or $BF_3 \cdot Et_2O$ in aq CH_3OH) then affords the dicarbonyl compounds (18) and (19) in



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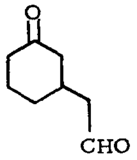

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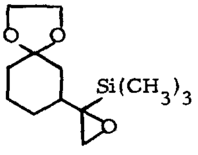

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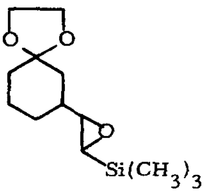

(21)

moderate yield.[11,14] Efforts are underway to improve the latter conversion as well as to allow the transformation of epoxy silanes to other functional groups.

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13. Another instance of this has been noted: G. Stork, private communication.
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