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THE STEREOSPECIFIC SYNTHESIS OF VINYL HALIDES USING A VINYLSILANE AS THE SYNTHETIC PRECURSOR

R. Bryan Miller* and Thomas Reichenbach

Department of Chemistry, University of California
Davis, California 95616

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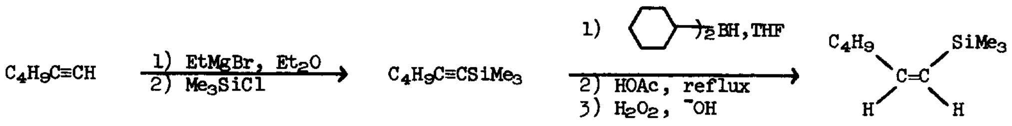
Although much is known about the properties and chemistry of vinylsilanes,[1,2] relatively little use has been made of them in organic synthesis.[3] We describe here the use of a vinylsilane as the precursor to the stereospecific synthesis of vinyl halides.

The vinylsilanes can be easily prepared from the corresponding acetylene either by the addition of trialkylsilanes to terminal acetylenes in the presence of choroplatinic acid[4] yielding the trans-1-alkenyltrialkylsilane, or by the semireduction of easily available 1-trimethylsilylacetylenes. We chose the latter procedure in our study (see Scheme I).

Scheme I



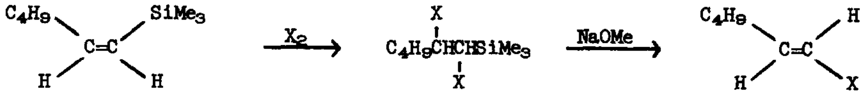
1

2

Reaction of 1-hexyne with ethyl magnesium bromide in ether followed by addition of trimethylchlorosilane gave the 1-trimethylsilyl-1-hexyne(1) in 61% yield. Although Stork[3a] had employed semihydrogenation using a poisoned palladium catalyst for reduction of the triple bond, we found that hydroboration-protonolysis[5] was a convenient method of producing the vinylsilane. Thus, compound 1 was reacted with dicyclohexylborane in tetrahydrofuran followed by protonolysis with refluxing acetic acid. (In terms of a practical workup it was necessary to oxidize the remaining organoboron compounds with hydrogen peroxide and base.) In this manner, *cis*-1-trimethylsilyl-1-hexene(2) was obtained in 67% yield.

Conversion of the *cis*-vinylsilane into either *trans*-vinyl bromide or *trans*-vinyl chloride was accomplished by use of two well known reactions (see Scheme II).

Scheme II



2

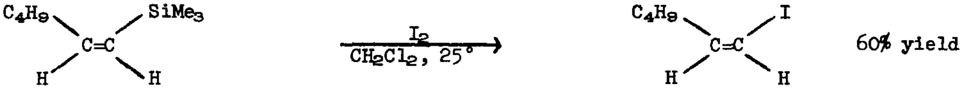
3, X = Cl

4, X = Br

The addition of halogen to the double bond was carried out by adding one equivalent of a carbon tetrachloride solution of the halogen to a methylene chloride solution of the vinylsilane 2 at low temperature (X = Cl at -78° and X = Br at -23°). The dihalides,[6a] obtained in greater than 98% yield, were used without further purification, and the elimination was performed by reaction with methanolic sodium methoxide at room temperature.[7] The *trans*-1-chloro-1-hexene(3),[6] obtained in 75% overall yield, and the *trans*-1-bromo-1-hexene(4),[6] obtained in 80% overall yield, were shown to have the assigned stereochemistry by comparison with authentic samples of the *cis*- and *trans*-vinyl halides.[8]

Attempts to prepare the *trans*-vinyl iodide by the above procedure failed in that the initial diiodide could not be isolated. Instead, the product of the reaction of compound 2 with iodine in dichloromethane at room temperature was *cis*-1-iodo-1-hexene(5)[6] (see Scheme III);

Scheme III



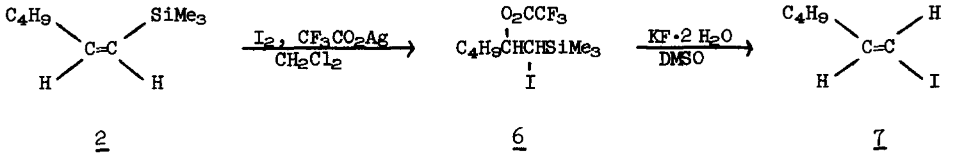
2

5

again the stereochemistry was proved by comparison with authentic samples of the *cis*- and *trans*-vinyl iodides.[8] The direct formation of the vinyliodide (5) and the *cis* stereochemistry might have come from a four-centered elimination of trimethyliodosilane from the unstable diiodide adduct.[9]

Finally, the *trans*-vinyl iodide was obtained (see Scheme IV) by reaction of compound 2 with a mixture of iodine and silver trifluoroacetate[10] in dichloromethane to give an adduct 6[8a] in 48% yield. After several unsuccessful attempts at elimination, it was found that reaction of compound 6 with potassium fluoride dihydrate[11] in dimethyl sulfoxide gave an 80% yield of *trans*-1-iodo-1-hexene(7); again the stereochemistry was proved by comparison with authentic samples of the *cis*- and *trans*-vinyl iodides.[8]

Scheme IV



From the above results it can be seen that the vinylsilanes are indeed useful synthetic precursors. The presence of the trimethylsilyl group not only allows for the elimination reactions to be stereospecific but also seems to exert a directing effect on the mode of addition in the iodine-silver trifluoroacetate reaction since only small amounts of the positionally isomeric adduct were observed.

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2. A. W. P. Jarvie, Organometal. Chem. Rev. A, **6**, 153 (1970).

3. For some examples, see (a) G. Stork and E. Colvin, J. Amer. Chem. Soc., **93**, 2080 (1971); (b) J. J. Eisch and M. W. Foxton, J. Org. Chem., **36**, 3520 (1971); (c) R. F. Cunico and E. M. Dexheimer, J. Amer. Chem. Soc., **94**, 2868 (1972); (d) G. Stork and B. Ganem, ibid., **95**, 6152 (1973).

4. Cf. R. A. Benkeser, M. L. Burrows, L. E. Nelson, and J. V. Swisher, J. Amer. Chem. Soc., **83**, 4385 (1961).

5. For use of dicyclohexylborane in this type of reduction, see: H. C. Brown and G. Zweifel, J. Amer. Chem. Soc., 83, 3834 (1961).

6. Satisfactory (a) nuclear magnetic resonance and infrared spectra and (b) elemental analysis and/or mass spectral data were obtained for these compounds.

7. For a discussion of the mechanism, see reference 2 and references cited therein.

8. We are grateful to Professor George Zweifel, University of California, Davis for supplying both samples and spectra of these vinyl halides.

9. For examples of the four-centered elimination in β-chlorosilanes, see I. M. T. Davidson, M. R. Jones, and C. Pett, J. Chem. Soc. (B), 937 (1967) and references cited therein.

10. D. G. Hey, G. D. Meakins, and M. W. Pemberton, J. Chem. Soc. (C), 1331 (1966).

11. For use of this reagent in eliminations of β-haloalkenylsilanes, see ref. 3c.