Stereochemistry of Acidolysis of Cyclohept-2-enyl-silanes and -stannanes

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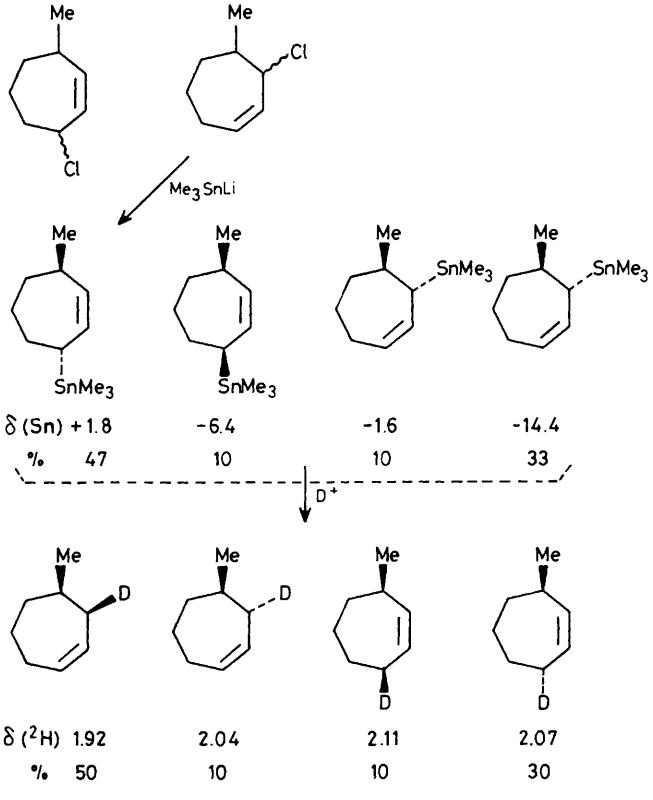
Direct ^2H n.m.r. analysis of the ^2H-substituted 3- and 4-methylcycloheptenes produced by acid cleavage (CF_3CO_2D) of mixtures of 4- and 7-methylcyclohept-2-enyltrimethyl-silanes and -stannanes confirms stereospecific γ-*anti* attack by the electrophile.

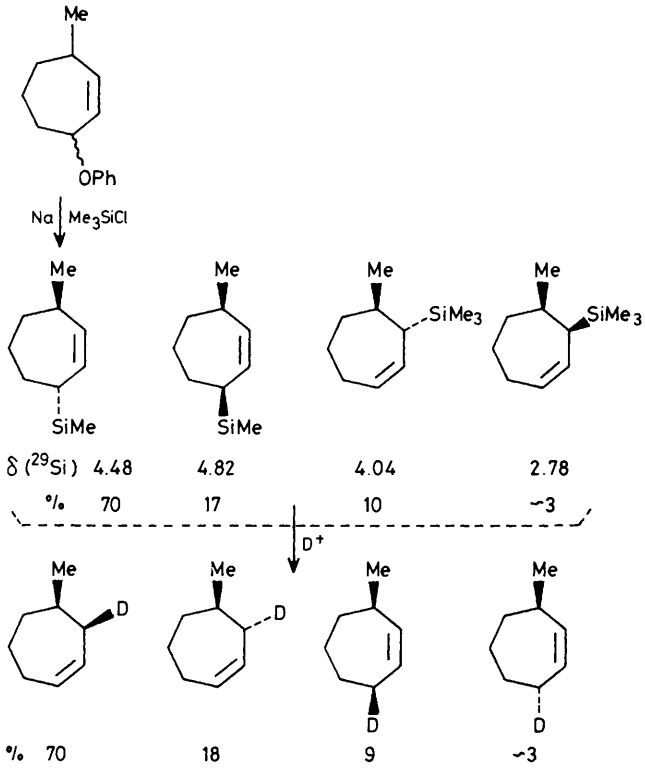
The S_E' reaction of allylic silanes and stannanes is of fundamental importance[1] and if stereochemically reliable can transfer chirality three places along a carbon chain. In acyclic and most cyclohex-2-enyl systems,[3] the γ-*anti* mode of substitution is highly preferred, but in some cyclopent-2-enyl,[1b,4] and some cyclohex-2-enyl cases,[5] the stereochemistry is variable and attributable to the nature of the electrophile, steric factors, and ring-size effects. To provide information on this latter aspect and in anticipation that this S_E' reaction may have synthetic value in seven- and medium-sized rings, we have examined the stereochemistry of acidolysis of some methyl substituted cyclohept-2-enyltrimethyl-silanes and -stannanes, and have determined that the γ-*anti* stereocourse is followed.

Stannylation of mixtures of *cis*- and *trans*-4- and -7-methylcyclohept-2-enyl chlorides (with Me_3SnLi in tetrahydrofuran, THF) provided a four component mixture of the corresponding allylic trimethylstannanes which were characterised by their ^1H, ^{13}C, and ^{119}Sn n.m.r. spectra.[6] To permit identification of the stannane isomers, 4-methylcyclohept-2-enone was reduced with $LiAlD_4$, chlorinated, and trimethylstannylated, to provide specifically deuteriated sets of regioisomers, which were identified on the basis of ^2H–^{119}Sn couplings in the ^{119}Sn n.m.r. spectrum.[6] Distinction, then, between the *cis*- and *trans*-isomers of each regioisomeric set was based on the ^{119}Sn and ^{13}C chemical shifts and certain ^{13}C–^{119}Sn coupling constants.[6] This information is summarised in Scheme 1.

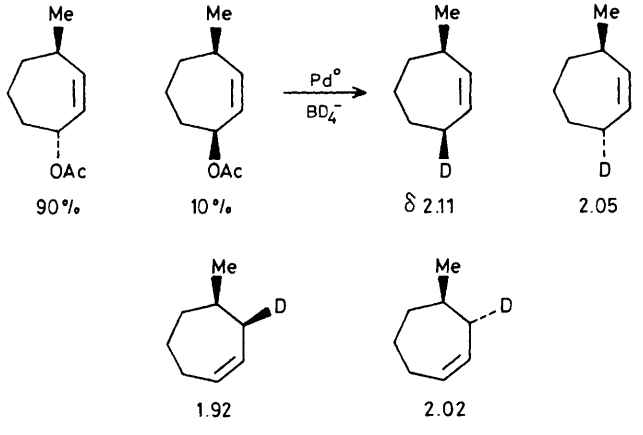


Scheme 1. ^{119}Sn Shifts are relative to internal Me_4Sn.

Treatment of 4-methylcyclohept-2-enyl phenyl ether (*cis*–*trans*-mixture) with sodium and trimethylchlorosilane[7] provided a mixture of the four allylic silanes which were just resolved by capillary v.p.c., and the mixture was purified by preparative v.p.c. Consideration of the ^{13}C, ^1H, and ^{29}Si



Scheme 2. ^{29}Si Shifts are relative to internal Me_4Si.



Scheme 3

n.m.r. data[7,8] led to the stereochemical assignments in Scheme 2, and these were supported by the fact that protonolysis of the mixture provided *ca.* 90% of 4-methylcycloheptene together with 3-methylcycloheptene.[7]

The possible products of acidolysis (with CF_3CO_2D) are *cis*- and *trans*-3-deuterio-4-methylcycloheptenes and *cis*- and *trans*-7-deuterio-3-methylcycloheptenes (Schemes 1 and 2) and, indeed, such cleavage of the stannane and silane mixtures provided ^2H n.m.r. product spectra consisting of four signals in the δ 1.9—2.2 region, as well as ^{13}C n.m.r. signals appropriate for γ-regiospecificity and monodeuteriation. Stereochemical determinations require specific assignments of the four ^2H n.m.r. signals and this was achieved as below. Reduction of predominantly *trans*-4-methylcyclohept-2-enyl acetate (90:10) with $Pd(Ph_3P)_4$ and $NaBD_4$ provided the 3- and 4-methylcycloheptenes† which exhibited two major signals (together ~90%) at δ(^2H) 1.92 and 2.11 p.p.m. and two minor signals (~10%) at δ(^2H) 2.02 and 2.05 p.p.m. The evidence is that this mode of reduction of allylic acetates incorporates ^2H *trans* to the acetate,[9] and coupled with the assignments of the H-7 signals in 3-methylcycloheptene (δ 2.05 and 2.11; 400 MHz; spin decoupling) leads to the assignments in Scheme 3.

The integrated ^2H n.m.r. spectra of the cleavage products of the silane and stannane mixtures (% of each deuteriomethylcycloheptene is shown below the isomeric composition of the reactants in Schemes 1 and 2) require the interpretation that each of the isomeric 4- and 7-methylcycloheptenyl-silanes and -stannanes experiences γ-*anti* attack by the deuteriated acid. The favoured conformation of cyclohept-2-enylmetallics (^1H and ^{13}C n.m.r. studies)[10] involves a preferred *quasi-axial* metal group orientation in the chair arrangement. This may be associated with relief of metal–H_2 eclipsed interaction (when *quasi-equatorial*) and maximisation of σ–π interaction, the apparent origin of γ-*anti* electrophile delivery.

This cleavage is being examined with other electrophiles, and extended to medium-ring derivatives to discern any transannular influences on this substitution.

The authors are grateful to the Australian Research Grants Committee for funding part of this work.

Received, 17th February 1986; 214

† Authentic 3-methylcycloheptene was obtained from 3-bromocycloheptene and dimethylcopperlithium; a mixture of 3- and 4-methylcycloheptene (~50:50) was obtained by dehydration ($KHSO_4$) of 3-methylcycloheptanol.

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