

STEREOSPECIFICITY IN THE SYNTHESIS OF ALLYLSILANES FROM TERTIARY ALLYLIC ACETATES¹

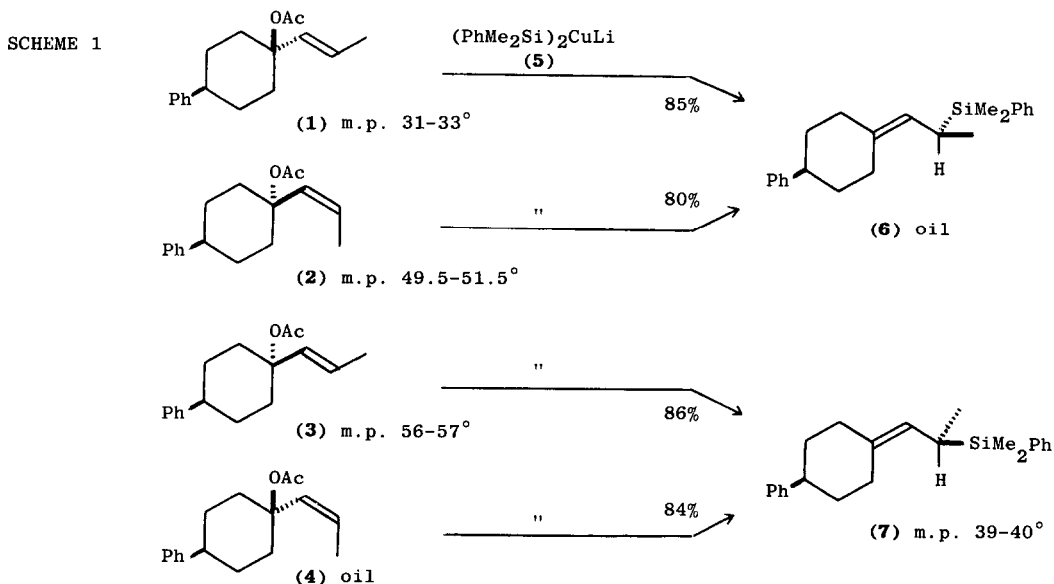
Ian Fleming* and Nicholas K. Terrett

University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, England

Summary—The tertiary allylic acetates (1-4) and the propargylic acetates (14 and 15) react with our silyl-cuprate reagent (5) to give, in a cleanly *anti* manner, the stereodefined allylsilanes (6 and 7) and allenylsilanes (16 and 17).

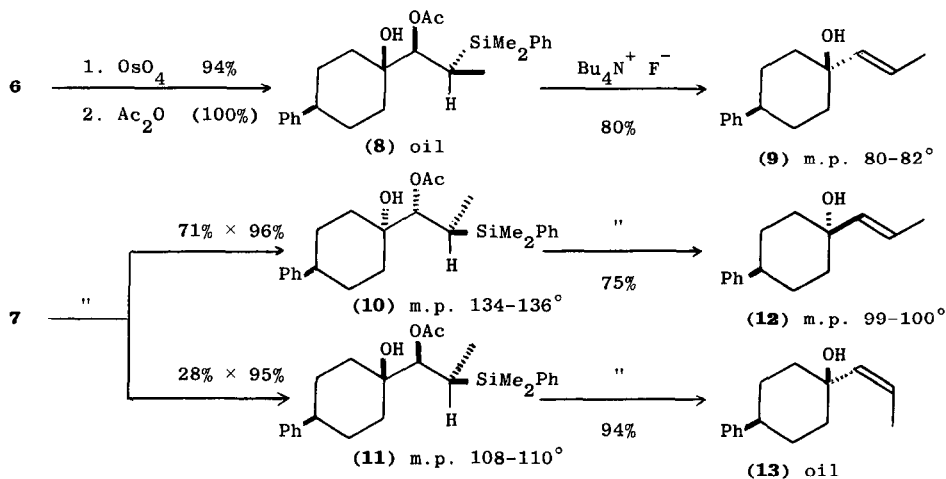
As Kumada has recently pointed out,² the stereochemistry of the S_E2' reactions of allylsilanes has been little studied because of the dearth of stereochemically defined allylsilanes. We now report the stereospecific synthesis of the allylsilanes (6 and 7). The availability of these allylsilanes allows us not only to study the intrinsic stereochemistry of the S_E2' reaction, but also to gain some insight into just how powerfully controlled the stereochemistry is when it is set in competition with other forces.³

The allylic acetates (1-4) were prepared by standard methods, and each was treated with our silyl-cuprate reagent (5), which we already knew⁴ gave allylsilanes from tertiary allylic acetates. In each case, the reaction was stereospecifically *anti* (Scheme 1), and there was no de-



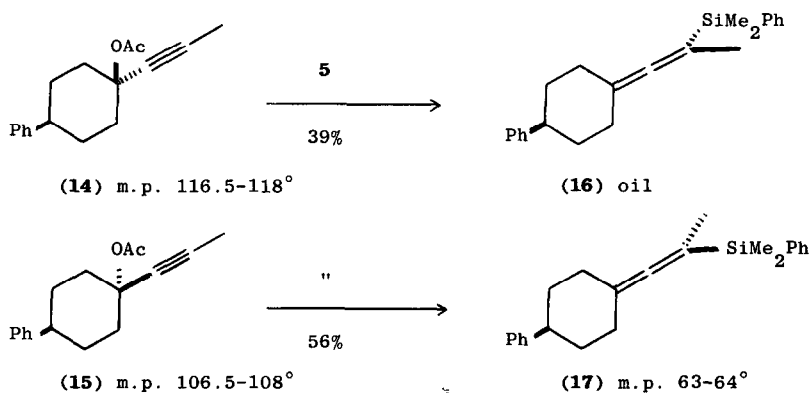
tectable cross-contamination (¹³C-NMR). The structures of the allylsilanes were proved (Scheme 2) by successive osmylation (known⁵ to be *syn* stereospecific), acetylation, and fluoride ion-induced elimination (assumed⁶ to be *anti* stereospecific). That the overall displacements (1 or 2 → 6 and 3 or 4 → 7) are *anti* is of course the expected result, by analogy with the corresponding reaction of alkyl-cuprates.⁷

SCHEME 2



The corresponding reaction of the propargylic acetates (14 and 15) was also stereospecifically *anti*, giving the stereodefined allenylsilanes (16 and 17) (Scheme 3). The structures of these compounds were determined by an X-ray crystal structure⁸ on the crystalline isomer (17).

SCHEME 3



NOTES and REFERENCES

- No reprints available.
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- This elimination has not been proved in the literature to be *anti* stereospecific, although analogies do exist.⁹ Support for the *anti* nature of the elimination comes from our observation that Peterson elimination of the minor diol (11, H for Ac), produced by osmylation of 7, gave the axial alcohol with a *trans* double bond (9). (The other two diols did not undergo Peterson eliminations.) Proof of the *anti* stereospecificity for fluoride-induced elimination with an acetate leaving group was obtained in other but unrelated work.¹⁰
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(Received in UK 6 July 1983)