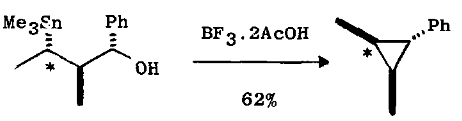
Tetrahedron Letters,Vol.26,No.32,pp 3857-3858,1985 0040-4039/85 $3.00 + .00
Printed in Great Britain

THE STEREOCHEMISTRY OF ATTACK BY A CARBON ELECTROPHILE ON A TIN-CARBON BOND[1]

Ian Fleming* and Michael Rowley
University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, England

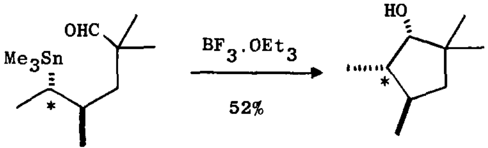
Summary—In the cyclisation of the 5-stannyl aldehyde (**3**), the cyclopentanol ring (**4**) is formed with retention of configuration at the carbon * bearing the stannyl group.

The reaction of organometallic carbon nucleophiles with carbon electrophiles usually takes place with retention of configuration. Examples of such reactions include the carboxylation of cyclopropyl[2] and norbornyl lithium compounds and Grignard reagents,[3] and the reactions of cyclohexyl[4] and acyclic[5] lithium compounds with a range of carbon electrophiles. The only known exceptions to this generally reliable pattern are the cyclisations of γ-stannyl[6,7] alcohols (and related γ-boronyl derivatives[8]) to cyclopropanes. These reactions regularly take place stereospecifically with inversion of configuration at C*, as in the example (**1** → **2**).



1 **2**

Inversion of configuration at C*



3 **4**

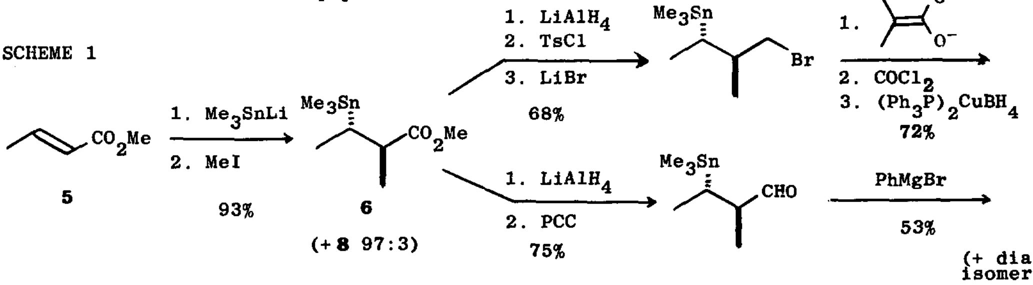
Retention of configuration at C*

We now report that this anomaly is associated with the formation of the three-membered ring, and not with the nature of the metal: we find that the aldehyde (**3**) cyclises to give very largely[9] the alcohol (**4**), in a reaction which involves retention of configuration at C*.

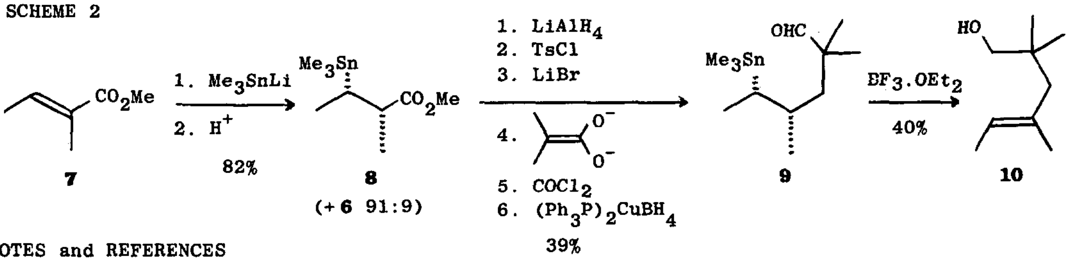
We prepared the alcohol (**1**) and the aldehyde (**3**) by the reactions shown in Scheme 1, in which we set up the two chiral centres using our earlier observation of highly diastereoselective alkylation (**5** → **6**) of β-stannyl enolates.[6,10] The diastereoselectivity was 97:3 in favour of the ester (**6**). The relative stereochemistry in **6** followed from the method of synthesis, and we confirmed it by the conversion (**1** → **2**), since this reaction, although anomalous in the sense mentioned above, is nevertheless stereochemically reliable.[6,7] Furthermore, an alternative sequence (Scheme 2) gave us a diastereoisomer (**8**), as a result of the highly diastereoselective (91:9) protonation (**7** → **8**).[6] We converted this ester into the aldehyde (**9**), diastereoisomeric with the aldehyde (**3**). However, this aldehyde did not cyclise on treatment with Lewis acid. Instead it gave the open-chain alcohol (*E*-**10**)[11] as a result of a stereoselective *anti* hydride delivery, for which there is precedent,[12] but hitherto incomplete stereochemical detail. This result prevents us from claiming, in Zimmerman's sense,[13] a truly stereospecific reaction for the conversion (**3** → **4**).

We prepared the alcohol (**4**) independently, by reduction of the corresponding ketone, which gave a mixture of the alcohol (**4**) and its diastereoisomer at C-1 in a ratio of 6:94. The stereochemistry of these two alcohols followed from a series of NOE-difference spectra, which we shall describe in a full paper.

SCHEME 1



SCHEME 2



NOTES and REFERENCES

1. No reprints available.
2. H. M. Walborsky, F. J. Impastato, and A. E. Young, *J. Am. Chem. Soc.*, **86**, 3283 (1964).
3. H. M. Walborsky and A. E. Young, *J. Am. Chem. Soc.*, **86**, 3288 (1964); F. R. Jensen and K. L. Nakamaye, *ibid.*, **88**, 3437 (1966); D. E. Applequist and G. N. Chmurny, *ibid.*, **89**, 875 (1967).
4. W. H. Glaze and C. M. Selman, *J. Org. Chem.*, **33**, 1987 (1968); J. S. Sawyer, T. L. Macdonald, and G. J. McGarvey, *J. Am. Chem. Soc.*, **106**, 3376 (1984).
5. W. C. Still and C. Sreekumar, *J. Am. Chem. Soc.*, **102**, 1201 (1980).
6. I. Fleming and C. J. Urch, *Tetrahedron Lett.*, **24**, 4591 (1983); *J. Organomet. Chem.*, **285**, 173 (1985).
7. D. D. Davis and H. T. Johnson, *J. Am. Chem. Soc.*, **96**, 7576 (1974); J. F. Kadow and C. R. Johnson, *Tetrahedron Lett.*, **25**, 5255 (1984).
8. H. L. Goering and S. L. Trenbeath, *J. Am. Chem. Soc.*, **98**, 5016 (1976); J. A. Marshall and J. H. Babler, *J. Chem. Soc., Chem. Commun.*, 993 (1968).
9. Another alcohol is formed in minor amounts (~10% of the amount of **4**). It has C*H*OH at δ 3.34 (J 8 Hz), whereas **4** has δ 3.18 (J 9.3 Hz). This alcohol is not the diastereoisomer of **4** at C-1, which has δ 3.14 (J 8.9 Hz), but we were unable to isolate it, or even confirm that it is one of the two alcohols which could have been formed by inversion of configuration at C*.
10. G. J. McGarvey and J. M. Williams, *J. Am. Chem. Soc.*, **107**, 1435 (1985).
11. We proved the geometry of the double bond by an NOE experiment.
12. E. Murayama, M. Uematsu, H. Nishio, and T. Sato, *Tetrahedron Lett.*, **25**, 313 (1984).
13. H. E. Zimmerman, L. Singer, and B. S. Thyagarajan, *J. Am. Chem. Soc.*, **81**, 108 (1959), footnote 16.

(Received in UK 31 May 1985)