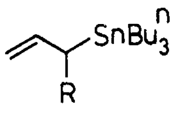
Tetrahedron Letters,Vol.26,No.43,pp 5327-5330,1985 0040-4039/85 $3.00 + .00
Printed in Great Britain

REGIOSELECTIVE SYNTHESIS OF α-SUBSTITUTED ALLYL- AND HOMOALLYL-STANNANES BY SELENOXIDE ELIMINATION

Vincent J. Jephcote and Eric J. Thomas*
The Dyson Perrins Laboratory, South Parks Road, Oxford, OX1 3QY.

Summary: α-Substituted allylstannanes (6) were prepared from selenides (5) via selenoxide elimination, and were found to be stable to 1,3-allylic rearrangement in non-polar solvents (T ≤110°C). Terminal homoallylstannanes (10) were similarly obtained from the methylated selenides (8), but other alkylated selenides (13) and (17) gave mixtures of allyl- and homoallyl-stannanes in which the allylstannanes predominated.

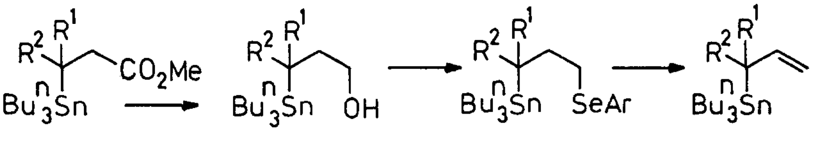
Allylstannanes are being developed into useful synthetic reagents, in particular thermal and Lewis acid catalysed reactions with aldehydes provide homoallylic alcohols stereoselectively,[1,2] and free-radical catalysed reactions with alkyl halides provide a method for replacing the halogen by an allylic group.[3] Several procedures are known for the preparation of allylstannanes, but in general these give the regioisomer (2) with the tin substituent at the less substituted end of the allyl unit,[4] e.g. the allyl acetate - allylstannane conversion recently reported by Trost,[5] or they are non-regioselective giving mixtures of α- and γ-substituted allylstannanes (1) and (2).[6] The exception is the α-ethoxyallylstannane (1; R=OEt) which has been prepared by treatment of chloroethoxymethyl-tri-n-butylstannane with vinylmagnesium bromide, but which was found to be rather unstable, isomerizing to the vinyl ether (2; R=OEt) on chromatography or on standing at room temperature for a few days.[7] We now describe regioselective syntheses of α-substituted allyl- and homoallyl-stannanes which are based upon the selenoxide elimination procedure recently developed for the preparation of substituted allylsilanes,[8] together with some preliminary observations on the chemistry and stability of the allylstannane products.



(1)

(2)

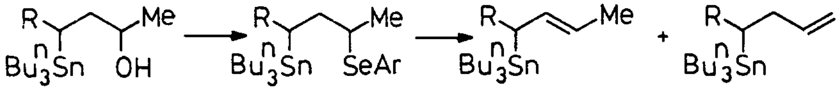
Lithium aluminium hydride reduction of the β-tri-n-butylstannyl esters (3)[9] gave the alcohols (4) in good yield (70-75%). Treatment of these alcohols with ortho-nitrophenyl selenocyanate - tri-n-butylphosphine gave the selenides (5) which were oxidized using m-chloroperoxybenzoic acid in a two-phase system (CH_2Cl_2-H_2O-$NaHCO_3$) to provide the α-substituted allylstannanes (6). Using this procedure α-phenyl-, α-methyl- and α,α-dimethyl-allylstannanes were obtained in reasonable yields (55-60%) after purification by flash chromatography on base ($KHCO_3$) washed silica.



(3) (4) (5) (6)

R^1	R^2	Isolated Yields (%)		
		(4)	(5)	(6)
Me	H	75	66	59
Ph	H	71	69	56
Me	Me	72	57	57

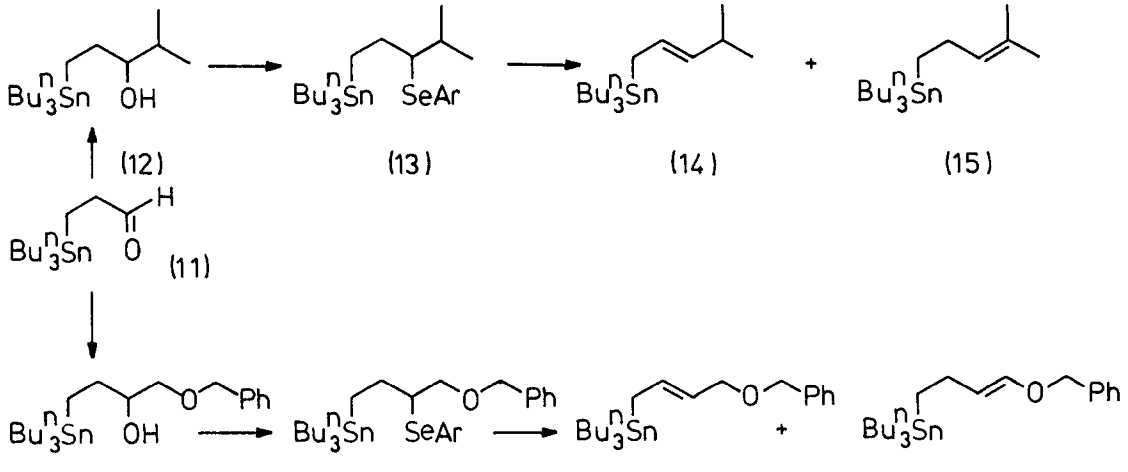
When applied to secondary o-nitrophenylselenides, mixtures of allyl- and homoallylstannanes were obtained, the regioselectivity of elimination depending upon the nature of the substituent α to selenium. With methyl substituents, homoallylstannanes were obtained with good regioselectivity. Thus the alcohols (4) were oxidized (N-chlorosuccinimide, dimethyl sulphide, toluene) to provide aldehydes which gave inseparable mixtures of the secondary alcohols (7) on treatment with methyl magnesium iodide. These alcohols were converted into the o-nitrophenyl selenides (8) as before, and the selenides oxidized to give mixtures of the allyl- and homoallyl-stannanes (9) and (10) in which the homoallylstannanes (10) predominated.



(7) (8) (9) (10)

R	Isolated Yields (%)			Ratio
	(7)	(8)	(9)+(10)	(9) : (10)
H	28	42	62	0 : 100
Me	73	75	75	1 : 3
Ph	68	60	60	1 : 10

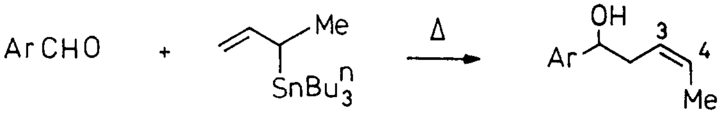
The regioselective elimination of selenoxide away from the tri-n-butylstannyl substituent is consistent with the latter being a π-donor.[10] However this regioselectivity is quite finely balanced. With an α-isopropyl substituent, e.g. in (13), more elimination occurs towards the tin, a 3:1 mixture of allyl- to homoallyl-stannanes, (14) to (15), being obtained. Similarly the α-benzyloxymethylselenide (17), prepared by addition of benzyloxymethyl lithium (from PhCH$_2$OCH$_2$SnBu$_3^n$ and Bu^{n}Li) to aldehyde (11) followed by treatment with *o*-nitrophenylselenocyanate and tri-*n*-butylphosphine, gave a 10:1 mixture of the allyl- and homoallyl-stannanes (18) and (19).[11]



(12) (13) (14) (15) (11) (16) (17) (18) (19)

The stability of the α-substituted allylstannanes (6) was then briefly investigated in view of the literature reports of facile 1,3-allylstannane isomerization.[12] In our hands, in non-polar solvents, the allylstannanes (6) were found to be quite stable. Thus the α-methyl- and α,α-dimethyl-allylstannanes (6; R^1=Me, R^2=H; R^1=R^2=Me) were unaffected by heating under reflux in toluene for 21h, although some decomposition was observed in refluxing xylene. The α-phenylallylstannane (6; R^1=Ph, R^2=H) was slightly less stable, *ca*. 25% decomposition together with some isomerization occurring in benzene after heating for 22h under reflux. However faster 1,3-isomerization of the α-methylallylstannane was observed in methanol.[12]

Finally a 1:1 mixture of the α-methylallylstannane (6; R^1=Me, R^2=H) and *p*-nitrobenzaldehyde was heated in benzene under reflux to see whether the thermal metallo-ene reaction would compete with stannane isomerization. In the event, after 6h, a single product was isolated (66%) and identified as the *cis*-alkenol (20). Similarly, in toluene heated under reflux, benzaldehyde was converted into alkenol (21).



(20) Ar = *p*-NO$_2$C$_6$H$_4$

(21) Ar = C$_6$H$_5$

Aspects of the chemistry of the α-substituted (6) and related allylstannanes, are under further investigation.

Acknowledgements

We thank the S.E.R.C. for support (to V.J.J.), Dr. A.E. Derome and Mrs. McGuinness for n.m.r. spectra, and Dr. R.T. Aplin for mass spectra.

Notes and References

1. Y. Yamamoto, H. Yatagai, Y. Naruta, and K. Maruyama, J.Am.Chem.Soc., 102, 7107 (1980); Y. Yamamoto, H. Yatagai, Y. Ishihara, N. Maeda, and K. Maruyama, Tetrahedron, 40, 2239 (1984); G.E. Keck and E.P. Boden, Tetrahedron Lett., 25, 265, 1879 (1984); G.E. Keck and D.E. Abbott, ibid, p. 1883; G.E. Keck, D.E. Abbott, E.P. Boden, and E.J. Enholm, ibid, p. 3927.
2. V.J. Jephcote, A.J. Pratt, and E.J. Thomas, J.Chem.Soc.,Chem.Commun., 800 (1984); A.J. Pratt and E.J. Thomas, J.Chem.Soc., Chem.Commun., 1115 (1982).
3. G.E. Keck and J.B. Yates, J.Am.Chem.Soc., 104, 5829, (1982).
4. D. Seyferth, K.R. Wursthorn, and R.E. Mammarella, J.Org.Chem., 42, 3104 (1977); S.J. Hannon and T.G. Traylor, J.Chem.Soc.,Chem.Commun., 630 (1975); Y. Ueno, S. Aoki, and M. Okawara, J.Am.Chem.Soc., 101, 5414 (1979).
5. B.M. Trost and J.W.Herndon, J.Am.Chem.Soc., 106, 6835, (1984).
6. E. Matarasso-Tchiroukhine and P. Cadiot, J.Organomet.Chem., 121, 155, 169 (1976); Y. Naruta and K. Maruyama, J.Chem.Soc.,Chem.Commun., 1264 (1983).
7. J.P. Quintard, B.-Elissondo, and M. Pereyre, J.Org.Chem., 48, 1559 (1983).
8. I. Fleming and D. Waterson, J.Chem.Soc., Perkin I, 1809 (1984).
9. Prepared by conjugate addition of tri-*n*-butyltin lithium to the corresponding α,β-unsaturated ester.
10. W. Hanstein, H.J. Berwin, and T.G. Traylor, J.Am.Chem.Soc., 92, 7476 (1970).
11. The allylstannane (18) consisted of an 85:15 mixture of *trans*- and *cis*-isomers, whereas the homoallylstannane (19) comprised an 75:15 mixture of *trans*- and *cis*-isomers.
12. J.A. Verdone, J.A. Mangravite, N.M. Scarpa, and H.G. Kuivila, J.Am.Chem.Soc., 97, 843 (1975); B.M. Trost and E. Keinan, Tetrahedron Lett., 21, 2595 (1980).
13. Alkenols (20) and (21) were assigned the *cis*-stereochemistry shown by analogy, and on the basis of coupling constant data, $J_{3,4} \sim 11$ Hz. Less than 0.5% of any other regio- or stereoisomer could be detected by ^{1}H n.m.r.

(Received in UK 12 August 1985)