Synthesis of (±)-Lavandulol and its Related Homoallylic Alcohol *via* Allyl Transfer from Sulphur to Tin[1]

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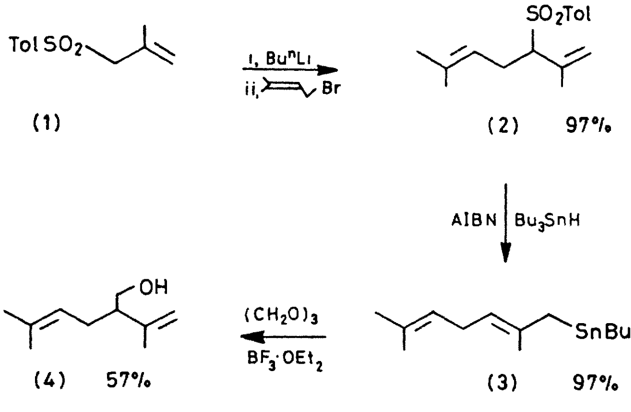
Summary (±)-Lavandulol and related homoallylic alcohols were prepared by the stannolysis of allylic sulphones and the subsequent hydroxymethylation of the resulting allylic stannanes with trioxan–$BF_3{\cdot}OEt_2$.

The synthetic utility of sulphur-stabilized carbanions has been extensively investigated; their use provides a useful technique for carbon–carbon bond formation.[2] Recent developments in this area involve the additional use of transition metal or organometallic chemistry.†

We report here a new approach to the synthesis of (±)-lavandulol (**4**) (an important class of perfumery compound) and related homoallylic alcohols based upon a regiospecific interconversion from an allyl sulphone into allylstannane, as outlined in Scheme 1. We used 2-methylprop-2-enyl tolyl sulphone (**1**) as the starting material since it can be regiospecifically α-prenylated in high yield in the usual manner.[3]

Stannolysis of the resulting allyl sulphone (**2**) was easily performed under mild conditions.[4] Thus, a mixture of the allyl sulphone (**2**) (3·59 mmol), tri-n-butyltin hydride (7·18 mmol), and azobis(isobutyronitrile) (AIBN) (10 mg) in dry benzene (3 ml) was refluxed under a nitrogen atmosphere for 2 h. After the completion of the reaction, the solvent was evaporated off and (**3**) was distilled at 150—155 °C and 0·05 mmHg (kugelrohr); 1·44 g (97%), *m/e* (M^+) 414; ^{1}H n.m.r., δ ($CDCl_3$) 0·60—0·90 (38H, m), 2·65 (2H, t, *J* 8 Hz, CH_2), and 5·00 (2H, =CH).



Scheme 1. Tol = Tolyl.

Although there have been several recent reports on the condensation of allylsilanes[5] or allylstannanes[6] with carbonyl compounds, such as aldehydes or ketones, in the presence of Lewis acids, such as titanium tetrachloride, it is surprising that no reports of the reaction of allylsilanes (stannanes) with formaldehyde, which is the simplest carbonyl species, have appeared.

Attempted reaction of solid paraformaldehyde or gaseous formaldehyde with the allylstannane (**3**) failed to give the desired hydroxymethylated product (*i.e.*, lavandulol).

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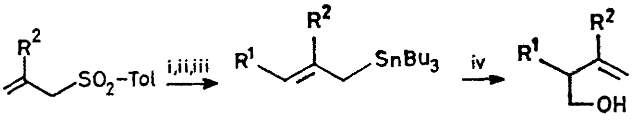
† For example, Trost and his co-workers have developed a synthetic method based upon the combination of the chemistry of organic sulphur and palladium; see B. M. Trost, *Tetrahedron*, 1977, **33**, 2615.

However, by using trioxan the condensation was found to work well, yielding (±)-lavandulol (**4**) in a reasonable isolated yield. Thus, a mixture of the allylstannane (**3**) (2·42 mmol) and trioxan (1·22 mmol) in dry methylene chloride (10 ml) was stirred under a nitrogen atmosphere at room temperature. To this solution, boron trifluoride–ether (7·33 mmol) was added slowly, the mixture stirred for 1 h, and then water (10 ml) added. The mixture was then stirred for 1 day. Tri-n-butyltin fluoride was filtered off, the organic layer was separated, and the aqueous layer extracted with methylene chloride (3 × 10 ml). The combined organic layer was dried over $MgSO_4$. The solvent was evaporated off and lavandulol (**4**) was distilled at 125—128 °C and 6 mmHg (kugelrohr); 0·21 g (57%); *m/e* (M^+) 154; i.r. ν_{OH} 3350 cm^{-1}; ^1H n.m.r., δ ($CDCl_3$) 1·65 (3H, s, Me), 1·73 (6H, s, Me), 2·00—2·54 (4H, m, C*H*,C*H*$_2$, O*H*), 2·59 (2H, d, *J* 6 Hz, OCH_2), and 4·67—5·32 (3H, m, C*H*=, =C*H*$_2$).‡



(**5**) (**6**)

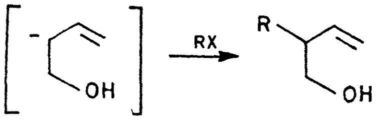
SCHEME 2. Reagents: i, Bu^nLi; ii, R′X; iii, Bu_3SnH; iv, $BF_3·OEt_2$, trioxan. For convenience, only the major stereoisomer is shown.

The related homoallylic alcohols (**6**) were prepared similarly from (α-alkylated)allyl tolyl sulphones[4] *via* the allylstannanes (**5**) (Scheme 2). The results are summarized in the Table.

TABLE. Hydroxymethylation of the allylic stannanes (**5**) (Scheme 2).

		Alcohol (**6**)	
R^1	R^2	% Yield	B.p./°C, *p*/mmHg
$Me[CH_2]_5$	H	50	110—114, 18
$Me[CH_2]_7$	H	72	105—110, 5
$PhCH_2$	H	70	105—108, 3
$Me_2C{=}CHCH_2$	Me	57	125—128, 6

The overall reactions reported here may be considered to be equivalent to those of the unusual carbanion synthon



(A)

SCHEME 3.

(A) (Scheme 3), since the substituents R are originally derived from alkyl halides.

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‡ All new compounds obtained here had satisfactory physical and spectral data. (±)-Lavandulol (**4**) was identified by comparison of its spectral data with reported data. Y. Yukawa and S. Ito, 'Spectral Atlas of Terpenes and Related Compounds,' Hirokawa, Tokyo, 1973, p. 104.

[1] For Part 4 of the series 'Synthetic Reactions using Organotin and Sulphur Compounds,' see Y. Ueno, H. Sano, and A. M. Okawara, *Tetrahedron Lett.*, 1980, 1767.

[2] E. Block, 'Reactions of Organosulfur Compounds,' Academic Press, New York, 1978, pp. 36—90.

[3] D. Savoia, C. Trombini, and A. Umani-Ronchi, *J. Chem. Soc., Perkin Trans.* 1, 1977, 123.

[4] Y. Ueno, S. Aoki, and M. Okawara, *J. Am. Chem. Soc.*, 1979, **101**, 5414.

[5] For a leading review see T. H. Chan and I. Fleming, *Synthesis*, 1979, 761.

[6] Y. Naruta, S. Ushida, and K. Maruyama, *Chem. Lett.*, 1979, 919; A. Hosomi, H. Oguchi, M. Endo, and H. Sakurai, *ibid.*, 1979, 977.