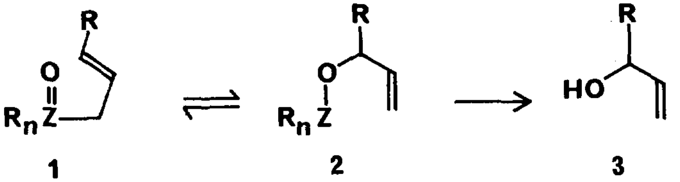
Tetrahedron Letters No. 42, pp 4089 - 4092.
© Pergamon Press Ltd. 1978. Printed in Great Britain.

0040-4039/78/1015-4089$02.00/0

CONNECTIVE SYNTHESIS OF ALLYL ALCOHOLS FROM ALLYL PHOSPHINE OXIDES

Reinhardt R. Arndt[1] and Stuart Warren,*
University Chemical Laboratories, Lensfield Road, Cambridge CB2 1EW

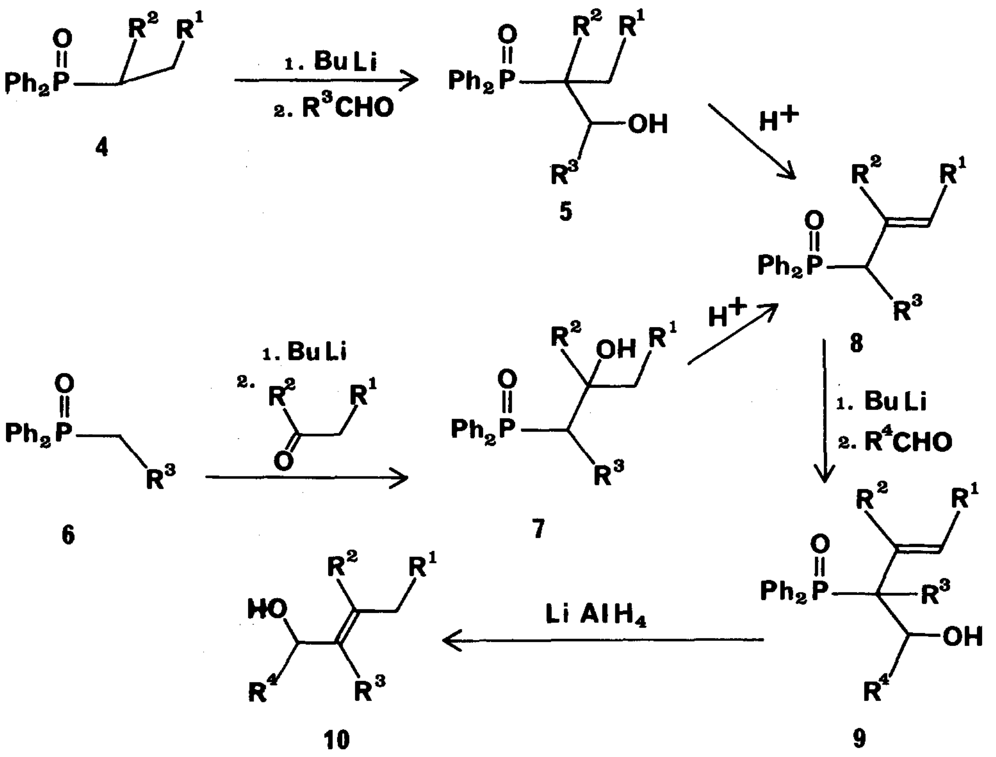
Allyl alcohols [e.g. (3)] may be made from allyl sulphoxides[2] (1, Z = S), but not directly from allyl phosphine oxides (1, Z = P) since the [2,3] sigmatropic rearrangement occurs only in the reverse direction[3] (2 → 1). We now report that allyl alcohols can be made from allyl phosphine oxides in a reaction sequence (scheme) involving a further extension of the carbon skeleton.



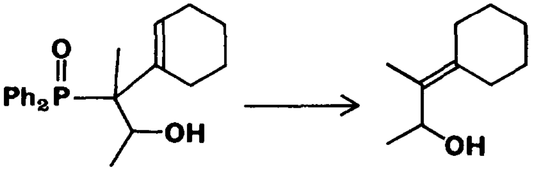
Allyl phosphine oxides (8) can be made from alkyl phosphine oxides (4) or (6) with (5 → 8) or without (7 → 8) diphenylphosphinoyl (Ph_2PO) migration.[4] Addition of aldehydes to the anions of (8) usually gives the α-adducts (9), precursors of dienes by completion of the Horner-Wittig reaction.[5]

The adducts (9) are homo allylic alcohols but reduction with lithium aluminium hydride gives allylic alcohols (10) (e.g., $R^2 = R^3 = R^4 = Me$, R^1 = n-pentyl, 93%) with loss of the Ph_2PO group and transposition of the double bond. Reductive cleavage of the C-P bond in an allyl phosphine oxide has been observed before[6] and reductive cleavage of allyl phosphoric acid derivatives has been used as an olefin synthesis.[7]

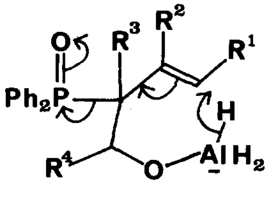
Scheme



We find that substituted allyl phosphine oxides e.g., (8, $R^1 = Pr^i$, $R^2 = Me$, $R^3 = PhCH_2$) do lose the Ph_2PO group on reduction with $LiAlH_4$ but that mixtures of isomeric (regio- and geometrical) olefins result. By contrast the alcohols (9) give single regioisomers of (10) even when the resulting double bond is exo to a six-membered ring (11 → 12). We therefore tentatively suggest that one or both oxygen atoms (13, only one shown) coordinate to the aluminium atom and help it to deliver hydride ion to the remote end of the double bond.

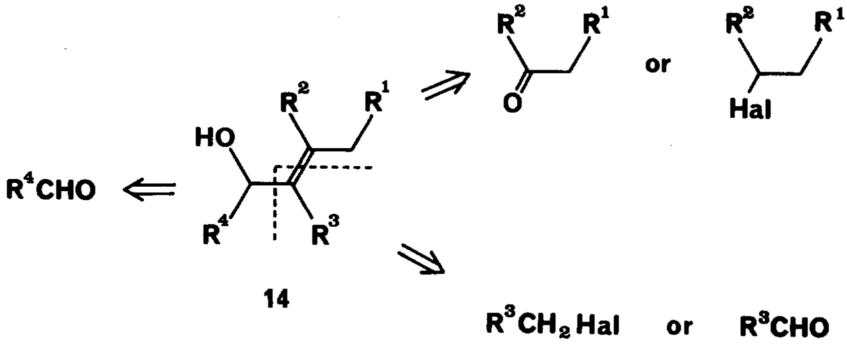


11 12



13

The reaction is regiospecific and stereoselective, only one isomer - presumably *E*- of the product being formed, e.g. (10, $R^1 = Pr^i$, $R^2 = R^3 = R^4 = Me$, 80%), from either diastereoisomer of (9). The sequence provides a general synthesis of allyl alcohols from three components - two carbonyl compounds and an alkyl halide (14). A typical procedure follows.



14

3-Cyclohexylidene-butan-2-ol. - 2-(Cyclohex-1-enyl)-2-diphenylphosphinoyl-1-phenylpropan-1-ol[5](11) (250 mg) in dry tetrahydrofuran (20 mls) was stirred overnight with $LiAlH_4$ (180 mg). The reaction mixture was quenched with water, extracted with ether, and the organic layers dried and concentrated *in vacuo*. Chromatography (silica column eluted with CH_2Cl_2) and distillation gave the allyl alcohol (12) (86 mg, 78%), b.p. 90° C/16 mm Hg, *m/e* 154 (M^+), δ 1.0 (3H, d, *J* 6 Hz, *Me*CHOH), 1.5 (1H, s, OH), 1.65 (3H, s, MeC=C), 1.6 (6H, m, CH_2), 1.8 (4H, m, allylic CH_2 in ring), 4.1 (1H, q, *J* 6 Hz, MeC*H*OH).

Acknowledgement

We thank the British Council for financial assistance.

References

(1) Permanent address; Department of Chemistry, Rand Afrikaans University, Johannesburg, South Africa.

(2) D. A. Evans and G. C. Andrews, *Accounts Chem. Res.*, 1974, **7**, 147.

(3) A. W. Herriott and K. Mislow, *Tetrahedron Letters*, 1968, 3013.

(4) A. H. Davidson, C. Earnshaw, J. I. Grayson, and S. Warren, *J.C.S. Perkin 1*, 1977, 1452 and references therein.

(5) A. H. Davidson and S. Warren, *J.C.S. Perkin 1*, 1976, 639.

(6) M. P. Savage and S. Trippett, *J. Chem. Soc. (C)*, 1967, 1998.

(7) K. Kondo, A. Negishi, and D. Tunemoto, *Angew. Chem. Internat. Edn.*, 1974, **13**, 407; K. Kondo, A. Negishi, and Y. Inoue, *Japan Kokai*, 76, 125, 006; *Chem. Abs.*, 1977, **86**, 155344.

(Received in UK 2 August 1978; accepted for publication 24 August 1978)