THE DIMESITYLBORON GROUP IN ORGANIC SYNTHESIS 7.   A UNIQUE VARIANT OF THE
BORON-WITTIG REACTION[1] WHICH STEREOSELECTIVELY YIELDS 1,2-DIOLS

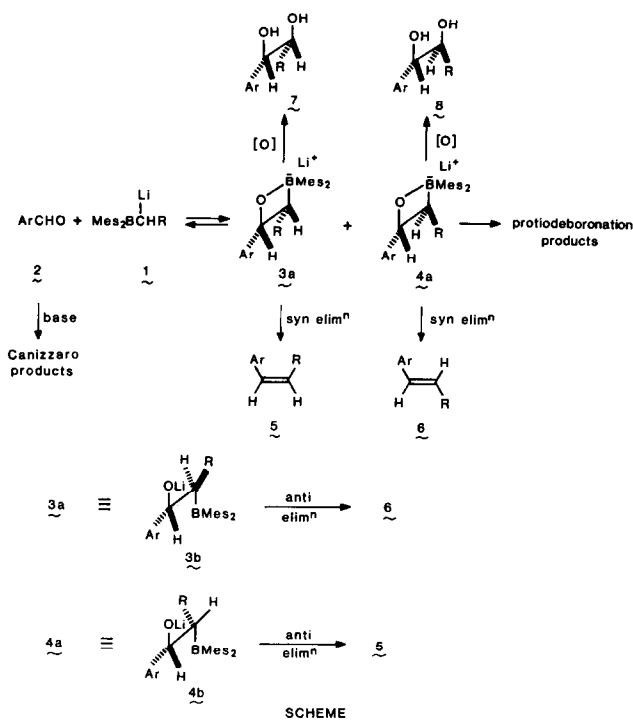Andrew Pelter[*], Dieter Buss and Andrew Pitchford

Department of Chemistry, University College of Swansea, Singleton Park, Swansea SA2 8PP

Low temperature oxidation of the intermediates in the Wittig reactions of aryl
aldehydes with carbanions stabilised with an adjacent dimesitylboron group leads stereo-
selectively to erythro-1,2-diols.   The mechanistic implications for the boron-Wittig
reactions are discussed.

It has been recently pointed out[2] that "though the Wittig reaction has played a
prominent role in synthetic chemistry for several decades, yet a clear mechanistic under-
standing of its stereochemistry has failed to emerge".   "Stereochemical drift"[3] has been
invoked to explain product ratios which are affected by solvent, cation, temperature and the
presence or absence of salts[4].   In the case of the silicon-Wittig reaction (Peterson
reaction) some understanding and useful chemical reactions have resulted from detailed
examination of the reactions of the intermediate β-hydroxysilanes and their salts[5].

We recently introduced[1] the condensations of aldehydes and ketones with anions
stabilised by an adjacent dimesitylboron group as a useful boron analogue of the Wittig
reaction.   We envisaged (Scheme) the reactions as proceeding via intermediate cyclic
anionic oxaboratanes, 3a and 4a which undergo syn-elimination to yield alkenes 5 and 6
respectively, such proposals being paralleled by those put forward for the Wittig[3] and
Peterson reactions[6].   We pointed out that the intermediates in the boron-Wittig reactions
would be sterically more compressed than those of the phosphorus and silicon analogues and
that the boron reaction might therefore be more stereoselective.   In particular the threo-
oxaboratanes, 4a should be thermodynamically more stable than the erythro-compounds, 3a.
In apparent confirmation, the condensation of benzaldehyde (2, Ar = Ph) with 1 (R = Hept^n)
gave only the E-alkene, 6 (Ar = Ph, R = Hept^n)[1].   The yield however was not good (ca. 40%
isolated) and the alkene was accompanied by products arising from protiodeboronation[5a] and
Canizzaro reactions involving benzaldehyde plus 3a and 4a acting as base.

In order to understand the course of the boron-Wittig reaction and to control the
various processes we decided to examine the oxaboratanes 3 and 4 in more detail.   Somewhat
to our surprise carrying out the reaction (Ar = Ph, R = Me) at -78°C followed by trapping by

ArCHO + Mes$_2$BCHR ⇌ ... + ... → protiodeboronation products

2　　**1**　　**3a**　　**4a**

7　　8

[O]　　[O]

base

Canizzaro products

syn elim^n　　syn elim^n

5　　**6**

3a ≡ ... **3b** $\xrightarrow[\text{elim}^n]{\text{anti}}$ **6**

4a ≡ ... **4b** $\xrightarrow[\text{elim}^n]{\text{anti}}$ **5**

SCHEME

silylation (Me$_3$SiCl) gave <u>erythro</u>-1-phenyl-1-trimethylsilyloxy-2-dimesitylborylpropane (50%

isolated). This corresponds to **3a** rather than **4a**, our expected product.

Another way of obtaining insight into the reaction would be to utilise the facile

oxidative cleavage of the C-B bond to produce 1,2-diols **7** and **8** which could then be examined

by standard methods. The oxidation of organoboranes proceeds with retention of

configuration[7] and so the configurations of the 1,2-diols should give information about the

precursors, **3** and **4**. Moreover, this reaction, if successful, would be a variant of the

Wittig type process <u>that would be unique to the boron-Wittig reaction</u> and might represent a

useful 1,2-diol synthesis.

We therefore condensed benzaldehyde with **1** (R = Me) at -120°C and directly oxidised the

reaction mixture by slow addition of cold, alkaline hydrogen peroxide. <u>Work-up gave no</u>

<u>alkene</u> but instead 84% isolated yield of **7** and **8** (Ar = Ph, R = Me) in a ratio of 92:8 (Table,

entry 1). The predominance of the <u>erythro</u>-isomer corresponds well with the silylation

result (incidentally proving that the oxidation has gone with retention of configuration) and

shows that 1,2-diol formation is not only feasible, but an efficient new reaction. The

products of this reaction (entry 1) are known and well characterised[8] and so serve as a

standard for determination of _erythro_, _threo_ ratios (Table). At temperatures between
-120°C to -45°C the _erythro:threo_ ratio varied from 10:1 to 4:1, probably indicating a
degree of reversibility in the formation of the oxaboratanes leading to stereochemical
drift. At room temperature only Canizzaro products result in this case.

TABLE

Production of 1,2-Diols, 7, 8, by oxidation of boron-Wittig intermediates

Entry	Ar	R	Yield % (h,temp)[a]	e:t[b]	δ(J.Hz) for H-1	
					erythro	threo
1	Ph	Me	84(1h,-120°C)	92:8	4.62(4)	4.25(8)
2	p-MeC$_6$H$_4$	Me	80(3h,-78°C)	91:9	4.54(4)	4.20(8)
3	p-ClC$_6$H$_4$	Me	86(1h,-78°C)	91:9	4.51(4)	4.16(8)
4	p-MeOC$_6$H$_4$	Me	84(6h,-78°C)	>99:<1[c]	4.52(4)	
5	p-NO$_2$C$_6$H$_4$	Me	78(8h,-120°C)	98:2	4.81(4)	
6	2,4,6-TriMeC$_6$H$_2$	Me	54(6½h,-78°C)	>99:<1[c]	4.79(7)	
7	Ph	Hept^n	80(5h,-78°C)	92:8	4.6(4)	4.36(8)

a) All yields are of isolated, characterised diols. b) Determined by h.p.l.c., ^{13}C n.m.r,
^{1}H n.m.r. c) No _threo_-product could be detected by any method.

Entries 2 and 3 show that satisfactory results are obtained with substrates that might
undergo anion exchange, while entries 4 and 5 show that different polar groups not only do
not adversely affect the product yield but enhance the stereoselectivity of the reaction.
The reaction with mesitaldehyde (entry 7, Table), carried out to test the effect of using a
sterically hindered arylaldehyde, gave a diol with an H-1 δ value characteristic of an
erythro-diol, but a coupling constant like that of a _threo_-product. The ^{13}C n.m.r. signals
for C-1 and C-2 are characteristic of an _erythro_-product. The conformation of
butan-1,2-diols is dominated by intramolecular hydrogen bonding[9] and in ethan-1,2-diol the
conformation is known to be the result of interplay between gauche interactions and
intramolecular hydrogen bonding[10]. On this basis the larger H-1, H-2 coupling of
erythro-diols as compared with _threo_-diols is readily explained. However models indicate
that in any conformation of _erythro_-1-(2,4,6-trimethylphenyl)propan-1,2-diol
(7, Ar = 2,4,6-trimethylphenyl, R = Me) that allows intramolecular hydrogen bonding, there
is a severe and unavoidable interaction between one of the two _ortho_-methyl groups and the
aliphatic C-3 methyl group. The aromatic ring on C-1 and the methyl group on C-2 must be
anti-, even though this precludes intramolecular hydrogen bonding. The resultant con-
formation has H-1 and H-2 almost _anti_, with a correspondingly large coupling constant. It
is noteworthy that the coupling constants of 1,2-diols are also strongly affected by

solvents that discourage intramolecular hydrogen bonding[8b].

Another point of great interest involves entry 7, in which the same components that yield _trans_-alkene at room temperature[1] give an excellent yield of _erythro_-diol at low temperatures. This implies either that there is stereochemical drift or that the intermediates 3 and 4 exist in the acyclic forms 3b and 4b which undergo _anti_-elimination, a type that is well precedented in organoborane reactions[11].

As regards the new process the situation is unequivocal. It represents a novel route of high stereoselectivity to _erythro_-1,2-diols, and is a variant of the Wittig type reactions available only to the boron-Wittig reaction. We are investigating its extension to condensations with ketones and other types of aldehyde.

The mechanism(s) of the boron-Wittig reaction remains a fascinating topic with such questions as whether the intermediates 3 and 4 exist in open or ring forms, whether they undergo _anti_- or _syn_-eliminations, effects of salts and temperature being under active investigation.

REFERENCES

1. A. Pelter, B. Singaram and J.W. Wilson, _Tetrahedron Lett._, 1983, 24, 635.

2. B.E. Maryanoff, A.B. Reitz and B.A. Duhl-Emswiler, _J.Amer.Chem.Soc._, 1985, 107, 217.

3. B.E. Maryanoff, A.B. Reitz, M.S. Mutter, R.R. Inners and H.R. Almond Jr., _J.Amer.Chem.Soc._, 1985, 107, 1068.

4. _inter alia_. M. Schlosser, _Top.Stereochem._, 1970, 5, 1; I. Gosney and A.G. Rowley, in 'Organophosphorus Reagents in Organic Synthesis', J.I.G. Cadogan. Ed., Academic Press, New York, 1979, p. 17-153; J.D. Thacker, M.-H. Whangbo and J.J. Bordner, _J.Chem.Soc.Chem.Commun._, 1979, 1072; H.J. Bestmann, _Pure.Appl.Chem._, 1979, 51, 515; 1980, 52, 771; E. Vedejs, G.P. Meier and K.A.J. Snoble, _J.Amer.Chem.Soc._, 1981, 103, 2823; M. Schlosser and B. Schaub, _ibid_, 1982, 104, 5821; G.A. Olah and V.V. Krishnamurthy, _ibid_, 1982, 104, 3987.

5. (a) P.F. Hudrlik in "Organosilicon Compounds in Organic Synthesis" in "New Applications of Organometallic Reagents in Organic Synthesis", D. Seyferth, Ed., Elsevier, Amsterdam, 1976, p. 127-159. (b) P.F. Hudrlik, A.M. Hudrlik and A.K. Kulkarni, _J.Amer.Chem.Soc._, 1982, 104, 6809 and references quoted therein.

6. P.F. Hudrlik and D. Peterson, _J.Am.Chem.Soc._, 1975, 97, 1464.

7. A. Pelter and K. Smith, 'Comprehensive Organic Chemistry', Vol. 3, D.N. Jones (Ed.), Pergamon Press, Oxford, 1979, p. 813-815.

8. (a) G.H. Schmid, _Canad.J.Chem._, 1968, 46, 3415. (b) C. Zioudrou and P. Chrysochou, _Tetrahedron_, 1977, 33, 2103.

9. W.K. Busfield, M.P. Ennis and I.J. McKewen, _Spectrochim.Acta._, 1973, 29A, 1259.

10. D.R. Traux and H. Wieser, _Chem.Soc.Rev._, 1976, 5, 411.

11. G. Zweifel, H. Arzoumanian and C.C. Whitney, _J.Amer.Chem.Soc._, 1967, 89, 3652.