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Hindered Organoboron Groups in Organic Chemistry. 21. The Reactions of Dimesitylboron Stabilised Carbanions with Oxiranes[1]

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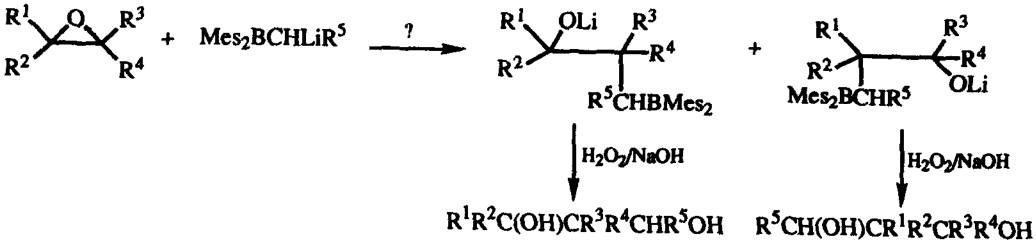
Abstract. Dimesitylboron stabilised carbanions react with oxiranes to give products that can be oxidised to 1,3-diols. The reactions are, in general, under steric rather than electronic control, and proceed smoothly for all but tetrasubstituted oxiranes. Some unusual stereoselective effects have been observed.

Introduction. Alkyldimesitylboranes readily yield stable anions that react as nucleophiles with alkyl halides.[2] Oxidation of the products yields alcohols *so making Mes_2CHLiR equivalent to RCHOH*. We next turned our attention to the reactions of $Mes_2BCHLiR$ with oxiranes which, we hoped, would proceed as outlined in Scheme 1.



Scheme 1

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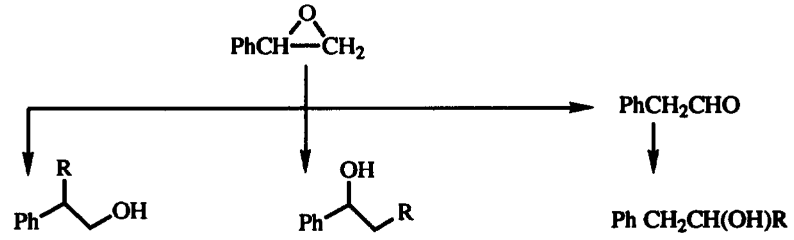
[a] Previously Gina F. Bugden.

Oxiranes are important synthetic intermediates due to their ready and many reactions with nucleophiles.[3] Such reactions can include attack by heteroatoms such as HO^-[4], AcO^-[5], Hal^-[6-8], $PhNH^-$[9], $MeSe^-$[10], Me_3Sn^-[11], NC^-[12]. Carbon-carbon bonds may be produced by reaction with organometallics[13] such as organolithium reagents[14,15] or Grignard reagents.[16] The former have limited synthetic utility whilst the latter are subject to competing reactions arising from the Lewis acidity of RMgX and the various species present due to the usual Grignard equilibria. Copper catalysed reactions of Grignard reagents with oxiranes proceed smoothly[17] as do the reactions of a wide variety of copper reagents.[18-22] Typical reagents are Li_2CuR_2[23,24,25], RCuCNLi[26], $R_2Cu(CN)Li_2$[27] and $R_2CuLi.BF_3$.[27] Complexities arising from the regiochemistry of the reactions as well as from rearrangement to carbonyl compounds followed by further reactions are well illustrated by comparing results for the attack on phenyloxirane by a variety of reagents[23,24,26] (Scheme 2).

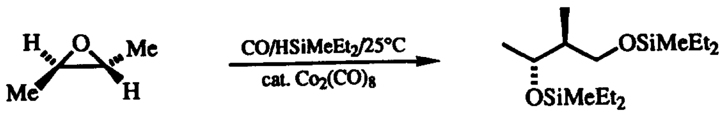


			Ph $CH_2CH(OH)R$
Me_2Mg	100	0	0
MeMgBr	50	0	50
MeCu(CN) Li	81	18	0
$Bu^nCu(CN)$ Li	74	12	0
$Bu^n_2Cu(CN)$ Li_2	8	85	0

Scheme 2

Organoalanes react mainly at the carbon atom most able to stabilise a positive charge, that is the reactions are electronically controlled.[28]

Stabilised carbanions such as enolate anions react with oxiranes[29] and such reactions are pathways to lactones,[30] butenolides[31] and α-methylene-γ-butyrolactones.[32] However, we have found only one example of a reaction (eq. 1) that gives 1,3-diol derivatives from oxiranes by a C-C bond formation. The mechanism of that reaction is clearly different from that envisaged in Scheme 1, and it is limited to the introduction of hydroxymethylene groups.[33]



(1)

The 1,3-diol grouping is present in many natural products and its synthesis has received much attention. 3-Hydroxyketones may be reduced to either *anti*-[34] or the *syn*-1,3-diols[35,36] and 3-hydroxyesters,[37], 1,3-diketones,[38], 3-ketoesters[39] and α-hydroxyoxiranes[40,41] are also reduced, some in a stereoselective fashion, to 1,3-diols. Hydroboration of suitable unsaturated alcohols[42,43], followed by oxidation can yield 1,3-diols in a selective fashion. One method that involves C-C bond formation is the regiospecific reaction of $LiCuMe_2$ with (α-hydroxymethyl)oxiranes,[44] readily available in homochiral form.[45]

For this investigation we chose to study as typical carbanions, $Mes_2B\bar{C}H_2$ (1) and $Mes_2B\bar{C}HCH_3$ (2). In the latter case there could be stereochemistry associated with the $CH_3CHBMes_2$ group being introduced, and as the oxidation of the B-C bond proceeds with retention of configuration, this will be reflected in the stereochemistry of the 1,3-diol end product. In general, attack on oxiranes by nucleophiles proceeds with inversion of the oxirane carbon atom to which the new bond is being made. To analyse the stereochemistry of our products we made their phenylboronates, which have the advantage over benzilidene derivatives that no new chiral centre is introduced and nor is there an additional aliphatic carbon atom. The ^1H nmr of the phenylboronates can be indicative of the stereochemistry,[46] and in addition, Hoffmann[46,47] pointed out that the 1,3-diols exist in hydrogen bonded conformations approximating to a chair cyclohexane, and that the 1,3-*anti*-isomer (*threo* in Hoffmann's convention) will always have one axial substituent at either the 1- or 3-positions. The 1,3-*syn* (erythro)-isomer has two equatorial substituents at these positions. This results in $(\delta_C\text{C-1} + \delta_C\text{C-3})\mathit{syn} > (\delta_C\text{C-1} + \delta_C\text{C-3})\mathit{anti}$, and holds not only for the diols themselves[47] but also for their phenylboronate derivatives,[46] which have the further advantage of giving molecular ions in their mass spectra. The oxiranes investigated are shown in Figure 1. All were purchased or made by conventional methods.[48]

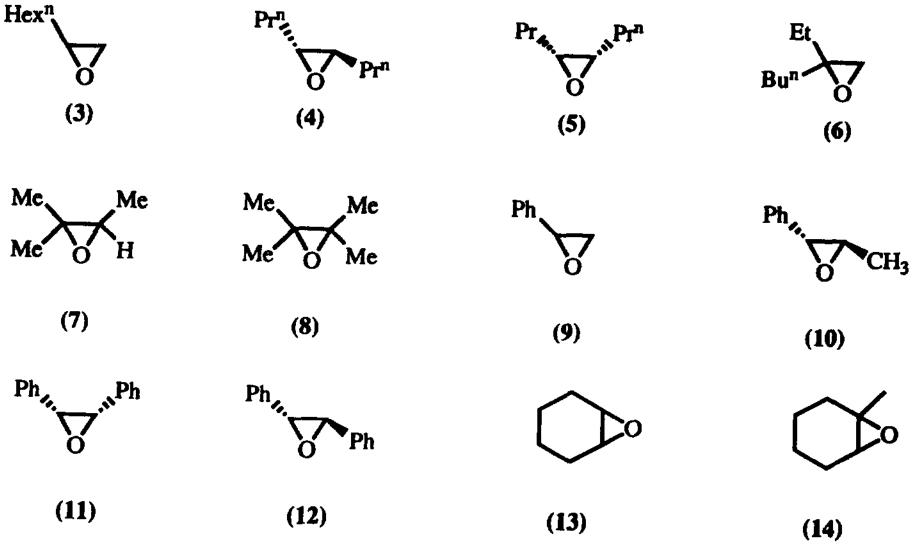


Figure 1

A preliminary investigation to test Scheme 1 using the reactions of phenyloxirane with anions (1) and (2) in THF showed that the condensation reactions were exothermic and proceeded to give diols (15) and (16) in good isolated yields after oxidation (Table 1, experiments 1,2). The disubstituted oxirane (4) reacted more slowly with (1) but with a slight excess of anion gave the 1,3-diol (17) in excellent yield (experiments 3,4,5). In this study no effort was made to optimise the conditions for each reaction, but for comparison purposes the conditions used in Table 1 were utilised plus, in some cases, heating at 60°C for 6h. The latter conditions emphasise the advantages of the use of boron-stabilised carbanions, which are stable up to more than 100°C.

Table 1

Preliminary reactions of Mes_2BCH_2Li (1) and $Mes_2BCHLiCH_3$ (2) with oxiranes

Exp.	Anion	Oxirane	Time (h)	Temp °C	Anion : Oxirane	Product[a]	% Yield[b]
1	(1)	(9)	2	25	1 : 1	$PhCHOH(CH_2)_2OH$ (15)	81
2	(2)	(9)	2	25	4 : 3	$PhCHOHCH_2CH(CH_3)OH$ (16)	81
3	(1)	(4)	2	25	1 : 1	$Pr^nCHOHCHPr^nCH_2OH$ (17)	41
4	(1)	(4)	18	25	1 : 1	(17)	87
5	(1)	(4)	18	25	4 : 3	(17)	95

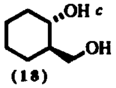
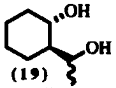
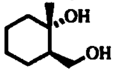
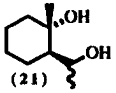
[a] In this and all subsequent Tables, "product" refers to the ***1,3-diols obtained on oxidation.***

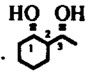
[b] In this and all subsequent Tables, "yield" refers to ***isolated*** yield of 1,3-diol based on starting oxirane.

Reactions with cyclohexene oxide (13) and 1-methylcyclohexene oxide (14). The reactions of (1) and (2) with (13) showed that substitution by the stabilised carbanions proceeded with inversion at the oxirane carbon atom being attacked (Table 2, experiments 6 and 7). The reaction of (1) and (2) with (14) showed that trisubstituted oxiranes react readily with these bulky anions. The reactions were regiospecific at the least substituted carbon atom and gave only two products in each case, these being equal amounts of the 1,3-*syn*- and 1,3-*anti* diols (19) and (21). Structures were assigned using ^{13}C nmr spectra of the diols and their phenyl boronates (22) and (23) in conjunction with the Hoffmann criteria (Table 3).

Table 2

Reactions of carbanions (1) and (2) with oxiranes (13) and (14)[a]

Exp.	*Anion*	*Oxirane*	*Time (h)*	*Temp (°C)*	*Product*	*Syn:anti* [b]	*Yield (%)*
6	(1)	(13)	2	25	 (18)	-	82
7	(2)	(13)	18	25	 (19)	1:1	68
8	(1)	(14)	2	25	 (20)	-	82
9	(2)	(14)	18	25	 (21)	1:1	62

a) Oxirane : Anion ratio always 1:1 b) Defined as 1,3-*syn* or 1,3-*anti*. eg.  is *syn* (19)

c) In this and all subsequent formulae only *relative* configurations are indicated.

Table 3

^{13}C nmr values[a)] *for (19) and (21) and their derived phenylboronates (22) and (23)*

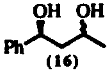
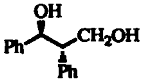
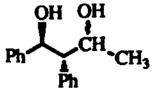
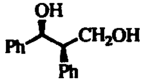
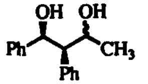
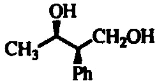
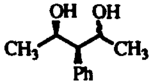
Compound	C-1	C-3	Summation
syn-(19)	76.1	71.3	147.3
anti-(19)	73.4	69.5	142.9
syn-(22)	74.9	70.1	145.0
anti-(22)	72.8	69.5	142.3
syn-(20)	77.6	74.4	152.0
anti-(20)	77.1	72.6	149.7
syn-(23)	73.2	70.7	143.9
anti-(23)	73.1	69.3	142.4

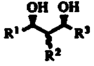
[c)] In this and all subsequent Tables, ^{13}C values are in p.p.m.

Reactions with oxiranes substituted by one or more phenyl groups. These studies are summarised in Table 4.

Table 4

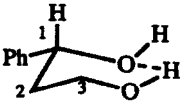
Reactions of anions (1) and (2) with phenyl substituted oxiranes

Exp.	*Anion*	*Oxirane*	*Time (h)*	*Temp (°C)*	*Product*	*syn:anti* [a]	*Yield (%)*
1	(1)	 (9)	2	25	Ph CHOH$(CH_2)_2$OH (15)	-	81
2	(2)	(9)	2	25	 (16)	4 : 3	81
10	(1)	 (11)	18	25	 (24)	-	82
11	(2)	(11)	18	25	 (25)	7 : 1	37
12	(1)	 (12)	18	25	 (26)	-	93
13	(2)	(12)	6	60	 (27)	4 : 3	31
14	(1)	 (10)	2	25	 (28)	-	94
15	(2)	(10)	18	25	 (29)	9 : 1	72

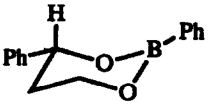
a) In this and subsequent Tables *syn* and *anti* are defined for the relationship of the 1,3-diol unit eg.  is *syn* in the Table.

The reactions of (1) and (2) with phenyloxirane (9) are exothermic and proceed as expected to give diols (15) and (16) in good yields. The assignments of structure to the components of (16) are made on the basis of Hoffmann's criteria for the diols and their derived phenylboronates (30) and (31) (Figure 2). The similar data for the diols and boronates supports the view[47] that the diols exist in a hydrogen bonded pseudo chair form.

Experiment 1



(15)

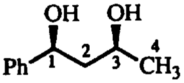


(30)

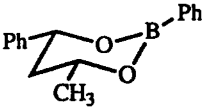
	^{1}H	^{13}C	^{1}H	^{13}C
1	4.84dd, J_1 = 12, J_2 = 4	72.79	5.16dd, J_1=9, J_2=4	72.8
2	1.6 - 1.0m	40.57	1.8 - 2.4m	35.27
3	3.72t, J=6	60.25	4.0 - 4.2m	60.98

Experiment 2

Major product. 1,3 -*syn* -(**16**) = (**16s**)



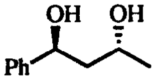
(16s)



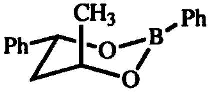
(31s)

	^{1}H	^{13}C	^{1}H	^{13}C
1	4.5 - 4.9m	74.07	4.94dd, J_1=13, J_2=3	73.31
2	1.6 - 1.9m	46.96	1.8 - 1.2m	45.33
3	3.4 - 3.7m	67.77	3.8 - 4.2m	68.12
4	1.08d, J=6	23.58	1.23d, J=6	22.97
		C-1 + C-3 = 141.84		C-1 + C-3 = 141.43

Minor product. 1,3 -*anti* -(**16**) = (**16a**)



(16a)



(31a)

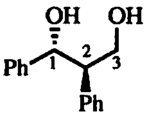
	^{1}H	^{13}C	^{1}H	^{13}C
1	a	70.92	5.21t, J=5	70.51
2	a	46.72	a	40.36
3	a	64.70	3.9 - 4.4m	64.33
4	a	23.28	1.23d, J=6	22.40
		C-1 + C-3 = 135.62		C-1 + C-3 = 134.84

[a] Indistinguishable from major isomer.

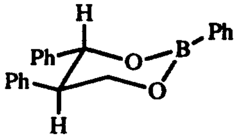
Figure 2.

The reactions of *cis*-1,2-diphenyloxirane (11) and the *trans*-isomer (12) with (1) (experiments 10 and 12) allowed a check on whether inversion occurred during attack on an acyclic system, as both isomers (24) and (26) are known.[60] The data are given in Figure 3. The H-1 coupling constants together with the Hoffmann criteria show conclusively that the reactions have gone with clean inversion. In this case the criteria are used to establish 1,2-stereochemistry as only (33) can have a C-1 axial phenyl group.

Experiment 10



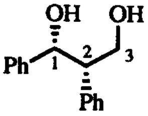
(24)



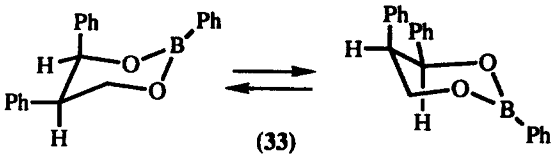
(32)

	^{1}H	^{13}C	^{1}H	^{13}C
1	4.88d, J=10	79.28	5.04d, J=10	78.49
2	3.02m	56.64	2.9m	57.08
3	3.98dd, 3.90dd	66.10	4.1m	66.08
		C-1 + C-3 = 145.38		C-1 + C-3 = 144.57

Experiment 12



(26)



(33)

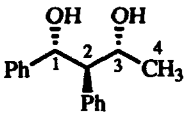
	^{1}H	^{13}C	^{1}H	^{13}C
1	4.9d, J=6	75.18	5.2d, J=4	72.20
2	3.05dd, J_1=16, J_2=8	54.92	3.52m	47.11
3	3.65m	65.52	4.1-4.4m	62.56
		C-1 + C-3 = 140.70		C-1 + C-3 = 139.76

Figure 3

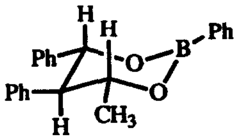
In experiments (11) and (13), attack by carbanion (2) sets up a new chiral centre associated with the $Mes_2BCH(CH_3)$ group and then with the $CH(OH)CH_3$ group produced from it on oxidation. Experiment (11) gave only two diols in a 7:1 ratio! As the H-1 coupling constants of both diols were 11Hz and of the boronates was 10Hz, the reactions have gone with clean inversion of configuration, and therefore the isomerism is associated with the nucleophile. The major isomer is 1,3-*syn*-(**25**) (*e.g.*, 1,2-*anti*-2,3-*anti*-1,2-diphenylbutan-1,3-diol) and the minor isomer is (**25a**), using Hoffmann's criteria[47] (Figure 4).

Experiment 11

Major isomer, 1,3-syn



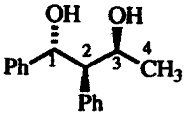
(**25s**)



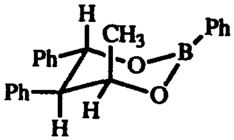
(**34s**)

	^1H	^{13}C	^1H	^{13}C
1	4.96d, J=10	80.44	5.08d, J=10	78.95
2	2.76t, J=10	60.12	2.57t, J=9	58.73
3	4.2 - 4 6m	72.83	4.2 - 4.6m	72.18
4	0.9d, J=6	22.41	1.12d, J=6	21.27
		C-1 + C-3 = 153.27		C-1 + C-3 = 151.13

Minor isomer, 1,3-anti



(**25a**)



(**35a**)

	^1H	^{13}C	^1H	^{13}C
1	5.12d, J=10	78.39	5.54d, J=8	75.47
2	2.8m	58.33	a	53.40
3	4.2 - 4.6m	66.94	a	68.02
4	1.1d, J=6	20.62	1.24d, J=6	19.03
		C-1 + C-3 = 145.33		C-1 + C-3 = 143.49

[a] Hidden by signals of main isomer.

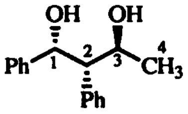
Figure 4

The stereoselectivity exhibited in experiment 11 is both unusual and exciting. Some other reactions of disubstituted oxiranes show a similar stereoselectivity and are discussed later.

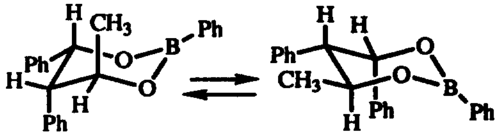
The *trans*-oxirane (12) reacted very slowly with anion (2) (experiment 13) to give (27) on oxidation, as a 4:3 mixture of (27a) and (27s) (Figure 5). The stereoselectivity drops considerably in the reaction of (12) with (2) as compared with the reaction of (11) with (2), a drop paralleled in the rates of reactions.

Experiment 13

Major product, 1,3 - anti



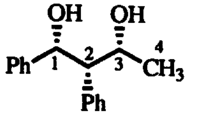
(27a)



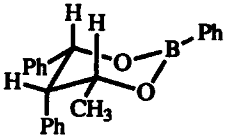
(35a)

	^{1}H	^{13}C	^{1}H	^{13}C
1	5.14d, J=4	74.56	5.31d, J=4	77.52
2	2.6 - 2.9m	60.05	3.1 - 3.35m	54.6
3	4.2 - 4.4m	68.28	4.4 - 4.7m	67.4
4	0.98d, J=6	22.08	2.28d, J=7	21.6
		C-1 + C-3 = 142.84		C-1 + C-3 = 144.92

Minor product, 1,3 - syn



(27s)



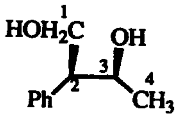
(35s)

	^{1}H	^{13}C	^{1}H	^{13}C
1	5.19s	76.14	5.66d, J=3	76.81
2	2.6 - 2.9m	59.86	3.1 - 3.35m	52.4
3	3.8 - 4.1m	68.78	4.8 - 5.0m	71.56
4	0.92d, J=6	21.97	2.20d, J=6	20.60
		C-1 + C-3 = 144.92		C-1 + C-3 = 148.37

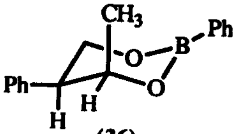
Figure 5

The result of experiment (14) was surprising. For the first time in this series of experiments, attack had occurred at the oxirane carbon bearing the phenyl group. Presumably with somewhat equally bulky groups at C-1 and C-2 of the oxirane, electronic control predominates. Only *one* diol was detected in the product, there being no indication of the other regioisomer (Figure 6).

Experiment 14



(28)



(36)

	^{1}H	^{13}C	^{1}H	^{13}C
1	3.6 - 4.1m	63.28	4.0 - 4.6m	62.36
2	2.6 - 2.9m	54.30	3.19dt	45.86
3	3.9 - 4.25m	68.15	4.0 - 4.6m	70.75
4	1.06d, J=6	20.42	1.08d, J=6	17.90

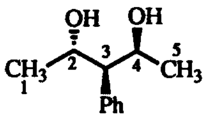
Figure 6

In all our previous diols containing a PhCHOH group, (*e.g.* (15), (16), (25), (26) and (27) and their boronates, whether 1,3-*syn* or 1,3-*anti*, the aliphatic ^{13}C signal for the PhCHOH grouping never appeared lower than 74.5 ppm. However, the simple PhCH groups of (24), (25), (26), (27) show at between 54.9 ppm and 60.1. Moreover, in the phenylboronates this signal may shift to lower field as for (26) in which it shifts from 52.92 ppm to 47.11 ppm, very similar to the values found in (28) and (36). We also had many examples of compounds with CH_3CHOH groups with a mean value of 68.2 ppm for the diols and 68.7 in the phenylboronates. In addition, the very similar picture that arises from comparisons of the ^{1}H nmr spectra makes our assignment firm.

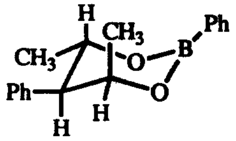
Reaction of oxirane (10) with (2) (experiment 15) gave a 9.1 mixture of (29a) and (29s))! Attack was, as before, on the carbon bearing the phenyl group and proceeded with inversion. Structural assignment was made easy in that the minor isomer was a *meso*-compound and readily distinguished. Data is given in Figure 7, exact assignments being by analogy with compounds previously synthesised in this study. In addition to the usual data all isomers of (29) and the boronate (37) give a base peak in the mass spectrum at m/z 118 (PhCH=CHCH$_3$) a property in common with all the isomers of (25) and (27) and their boronates. We do not know the conformation of (37s), which may exist as a half-boat with all substituents ψ-equatorial.

Experiment 15

Major isomer, 2,4-anti



(29a)

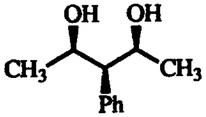


(37a)

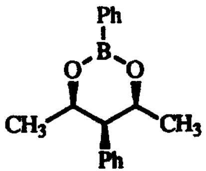
	^1H	^{13}C	^1H	^{13}C
1	1.04d, J=6	20.23*	1.27d, J = 5.6	18.06
2	4.15 - 4.5m	68.33✱	4.5 - 4.9m	70.64
3	2.52dd, $J_{2,3}$ = 10; $J_{3,4}$ = 3	59.20	2.98dd, $J_{2,3}$=12; $J_{3,4}$=4	53.74
4	4.15 - 4.5m	67.75✱	4.2 - 4.4m	67.18
5	1.03d, J=6	22.36*	1.20d, J=6	22.04
		C-2 + C-4 = 136.08		137.82

*,✱ - Interchangeable assignments.

Minor isomer, 2,4-syn (meso)



(29s)



(37s)

	^1H	^{13}C	^1H	^{13}C
1,5	1.82d, J=6	20.72	1.09d, J=6	20.54
2,4	4.15 - 4.5m	70.26	a	71.21
3	2.38t, J=4	58.34	2.76t, J=4	51.38
		C-2 + C-4 = 140.52	C-1 + C-3 =	142.42

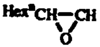
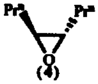
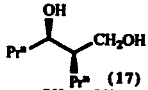
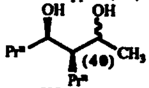
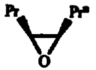
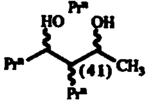
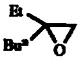
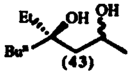
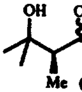
[a] Covered by multiplet of major isomer.

Figure 7.

We next turned to a study (Table 5) of the aliphatic acylic oxiranes (3) - (8) (Figure 1). Characterisation of products, and particularly assignment of stereochemistry to isomers, was not straightforward. Isomers rarely gave distinguishable ^1H nmr and h.p.l.c. of the diols or phenyl boronates only infrequently gave separations. In general we were forced to rely upon ^{13}C nmr spectra as a guide, reinforced by ^1H coupling constants, when available.

Table 5

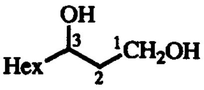
Reactions of alphatic acyclic oxiranes with anions (1) and (2)

Exp.	*Anion*	*Oxirane*	*Time (h)*	*Temp (°C)*	*Product*	*syn:anti*	*Yield (%)*
16	(1)	 $\underset{\mathrm{O}}{\mathrm{Hex^{n}CH{-}CH}}$ (3)	2	25	$\mathrm{Hex^{n}CHOH(CH_2)_2OH}$ (38)	-	90
17	(2)	(3)	2	25	$\mathrm{Hex^{n}CHOHCH_2CH(Me)OH}$ (39)	5 : 6	85
5	(1)	 (4)	18	25	 (17)	-	95
18	(2)	(4)	6	60	 (40)	10 : 1	50
19	(2)	 (5)	18	25	 (41)	a	37
20	(1)	 (6)	2	25	$\mathrm{Bu^{n}(Et)COH\ (CH_2)_2OH}$ (42)	-	78
21	(2)	(6)	18	25	 (43)	b	72
22	(1)	 (7)	2	25	$\mathrm{Me_2C(OH)CH(Me)CH_2OH}$ (44)	-	64
23	(2)	(7)	6	60	 (45)	2 : 3[c]	53

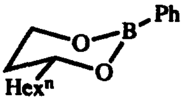
a) Complex mixture of many isomers. b) Could not be assigned. c) Refers to 1,2-*syn* and 1,2 - *anti*.

Reaction of *n*-hexyloxirane (3) with Mes_2BCH_2Li (1) (Table 5, experiment 16) was exothermic and regiospecific, and oxidation of the product gave nonan-1,3-diol (38) in 90% yield (Figure 8).

Experiment 16



(38)



(46)

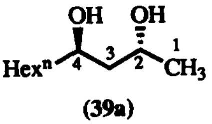
	^1H	^{13}C	^1H	^{13}C
1	3.6 - 3.9m	60.76	3.7 - 4.1m	61.37
3	3.7 - 4.1m	71.10		71.37
2	2.5 - 2.8m	38.65	2.6 - 2.8m	37.20

Figure 8

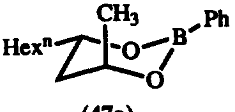
The reaction of (3) with anion (2) was also regiospecific and yielded a 5 : 6 mixture of 1,3-*syn* and 1,3-*anti*-diols (39). (Table 5, experiment 17). The configurations were assigned on the basis of the usual ^{13}C nmr criteria (Figure 9).

Experiment 17

Major isomer, 2,4-anti



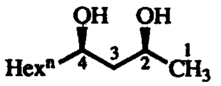
(39a)



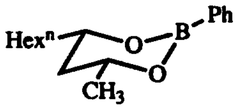
(47a)

	^1H	^{13}C	^1H	^{13}C
1	a	23.50	a	22.70
2	3.8 - 4.4	65.09	3.8 - 4.4	64.40
4		69.02		68.40
3	1.7t, J=6	44.56	a	37.82
		C-2 + C-3 = 138.1		C-2 + C-4 = 133.37

Minor isomer[b] *2,4-syn*



(39s)



(47s)

	^{13}C	^{13}C
1	a	23.23
2	68.76	68.11
4	72.67	71.82
3	44.56	40.89

C-2 + C-3 = 141.43

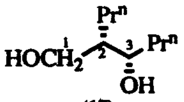
C-2 + C-4 = 139.93

[a] Could not be assigned.

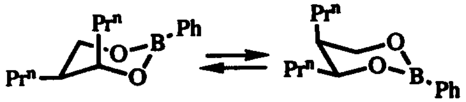
Figure 9

Trans-1,2-di-*n*-propyloxirane (4) reacted with inversion with anion (1) to give diol (17) on oxidation in 95% yield (Figure 10). The same oxirane reacted with inversion with (2) and gave (40s) and (40a) only in a ratio of 10:1 (Figure 10), this being yet another example of a highly selective reaction with a disubstituted oxirane. Compound (40s) is almost a *meso*-compound and hence C-1 and C-3 have the same signal in the ^{13}C nmr.

Experiment 5



(17)



(48)

	^{1}H	^{13}C	^{1}H	^{13}C
1	3.9m, $J_1=8$, $J_2=4$, $J_3=2$	64.13	3.4 - 4.3	64.50
3	3.98 - 4.2m	73.73		75.95
2	1.9m	39.30	2.18d, J=7	44.17

Experiment 18

Major Product *Minor Product*

(40s) **(40a)**

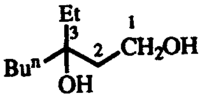
C-1 + C-3 = 146.90 C-1 + C-3 = 143.06

Figure 10

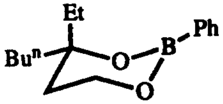
The reaction of (2) with *cis*-1,2-di-*n*-propyloxirane (5) (Table 5, experiment 19) was very slow, giving only 37% of product (41) after 18h at 25°C. The ^{13}C nmr spectrum of (41) was very complex. Thus in the δ 75-68 region there were peaks at 76.50, 74.90, 73.17, 72.73, 72.03, 71.21, 69.43 and 68.03. If the reaction had proceeded with inversion as usual, there would have been four peaks in this region and therefore the reaction has gone with retention as well as inversion, the only example of this that has been encountered. The rest of the spectrum was equally complex and the mixture was not analysed further. It is not clear why experiment 19 contrasts so greatly with experiment 18.

The reactions of (1) and (2) with the 1,1-disubstituted oxirane (6) proceeded, as expected, regiospecifically and in good yields. The reaction with (1) was highly exothermic. Experiment (21) gave a 1.7:1 mixture of diols, to which we have not been able to assign configurations. The ^{1}H nmr spectra of the diols completely overlapped and the Hoffmann criteria cannot be applied to these tertiary diols as either the 1,3-*syn* or 1,3-*anti*-diol or phenylboronates must have an axial alkyl group α- to an oxygen atom. The relevant data for experiments (20) and (21) are given in Figure 11.

Experiment 20



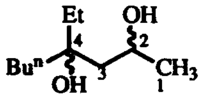
(42)



(49)

	^{1}H	^{13}C	^{1}H	^{13}C
1	3.8t, J=5	58.99	4.05t, J=5	58.84
2	2.69t, J=7	39.72	2.74t, J=5	34.07
3	-	75.50	-	74.30

Experiment 21



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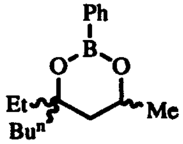


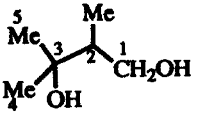
(50)

		^{13}C	^{13}C
Major isomer			
	2	64.33	65.19
	3	41.92	45.32
	4	74.77	75.58
Minor isomer			
	2	64.33	65.20
	3	42.03	45.37
	4	74.85	75.68

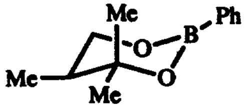
Figure 11

Experiments (22) and (23) show that reactions with a trisubstituted aliphatic oxirane proceed reasonably and that the products can be oxidised to 1,3-diols. Product (45) consisted of a mixture of 1,2-*syn* and 1,2-*anti* diols in the ratio of 2:3. These could not be characterised by ^{13}C nmr, but instead by extensive decoupling of the ^1H nmr of the diols (Figure 12).

Experiment 22



(44)

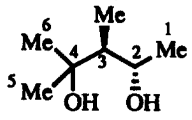


(51)

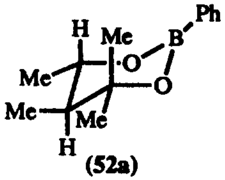
	^1H	^{13}C	^1H	^{13}C
1	3.5 - 3.7m	65.68	H_{ax}, 4.82dd, J=11;10; H_{eq}, 4.8t, J=8	64.96
2	1.4 - 1.9m	44.08	1.6 - 1.9m	40.40
3	-	74.43	-	73.71
4)	1.18s	29.16	a	29.02
5)	1.22s	24.02	a	22.94
6	0.86d, J=6	12.93	0.79d, J=6	12.26

Experiment 23

Major isomer, 2,3-anti



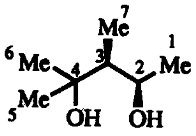
(45a)



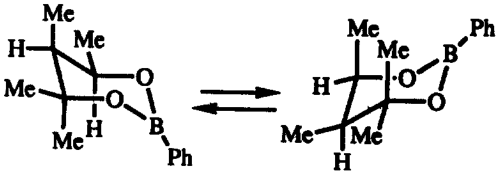
(52a)

	^{1}H	^{13}C	^{1}H	^{13}C
1	0.74d, J=6	22.72	1.28d, J=6	21.55
2	3.7 - 3.92, sext, $J_{2,3}$= 11	70.91	4.82, sext	69.96
3	1.4 - 1.7m	49.38	1.2 - 1.7m	47.58
4	-	75.03	-	74.02
5)	[a]	22.99	[a]	23.23
6)	[a]	30.14	[a]	29.19
7	[a]	13.62	0.82d, J=6	12.90

Minor isomer, 2,3-syn



(45s)



(52s)

	^{1}H	^{13}C	^{1}H	^{13}C
1	0.96d, J=6	21.56	1.34d, J=6	19.33
2	4.2 - 4.5 sext, $J_{2,3}$=3	67.25	5.48 sext	67.26
3	2.1 - 2.3m	46.22	1.2 - 1.7m	41.62
4	-	73.70	-	75.53
5)	[a]	28.45	[a]	27.81
6)	[a]	29.30	[a]	30.15
7	[a]	6.68	0.83d, J=6	6.71

[a] Could not be distinguished in general C-H envelope.

Reaction of (1) with tetramethyloxirane (8) was slow and after 6h at 60°C only 14% of a complex diol product was isolated, after oxidation. Carbanion (2) did not react at all with (8), showing the limitations of the reactions of the bulky dimesitylboron stabilised carbanions (1) and (2).

Conclusion.

Anions (1) and (2) are versatile reagents for the direct, one-pot introduction of an hydroxymethyl or an hydroxyethyl group into a wide range of mono, di- and tri-substituted oxiranes. The reactions are generally regiospecific and proceed, with one exception, with inversion of configuration. Some disubstituted oxiranes react with (2) with good stereoselectivity with respect to the hydroxyethyl group finally produced. This is a most novel and potentially valuable phenomenon, the cause of which requires further investigation. In all, the reactions have good synthetic potential.

We thank the SERC for support of this work.

Experimental

Technical Information

Infra-red spectra were recorded on a Pye Unicam SP1050 infra-red spectrometer using NaCl cells with neat liquids or solutions and KBr disks with solids. The polystyrene absorbances at 1603 cm^{-1} and 1494 cm^{-1} were used as references. Proton nmr were recorded on a Hitachi Perkin-Elmer R-24B spectrometer at 60 MHz, a Varian HA-100 spectrometer at 100 MHz and a Bruker WM-250 spectrometer at 250 MHz using $CDCl_3$ as solvent and Me_4Si as reference, except where stated. Carbon (^{13}C) nmr were recorded on a Varian XL100 or a Bruker WM-250 Fourier transform nmr spectrometer, using $CDCl_3$ as a solvent and Me_4Si as an internal standard, except where stated. Low resolution mass spectra and accurate mass measurement were recorded on an AEI MS9 mass spectrometer.

Melting points were recorded on a Gallenkamp Hot Stage apparatus and were uncorrected. Boiling points were determined by Kugelrohr distillation and the temperature given is that of the Kugelrohr oven. Thin layer chromatography was performed on silica gel (Merck) mounted on aluminium cards with fluorescent indicator (254 nm). Hplc were recorded using an LDC (Milton Roy constametric spectromonitor and C1-10 recorder apparatus using hypersil 5μ columns with efficiency N=55,580 plates/metre. Short flash chromatography was carried out on Keselgel 60G silica (Merck) on a 2' x 1" sintered (Grade 4) column using diethyl ether/petroleum mixtures under water vacuum pressure. Spinning chromatography (Chromatotron) separations used a circular plate of 2mm silica gel (with $CaSO_4$. 0.5 H_2O, Type 60 TLC, Merck) impregnated with a fluorescent indicator. G.l.c. were recorded on a Varian-Vista with a Varian CDS 401 recorder, using 10 foot steel columns with 5% SE30 on Chromosorb 9. Microanalyses were by Mr. O. Hughes (U.C. Swansea).

All reactions involving organoboranes were carried out using purified anhydrous reagents, unless otherwise stated. Reactions involving the use and production of air and water sensitive compounds were carried out under a static pressure of argon or nitrogen used directly from the cylinder through a glass line directly connected *via* a three-way tap to a vacuum pump. The preparation and purification of reagents for use in reactions of organoboron compounds have been reviewed.[49] Solvents were treated as follows.[50] THF was purified first by passing through dry, neutral alumina under nitrogen or agon. Sodium (2g per litre) and benzophenone (8g per litre) were then added to the THF in a still and the mix stirred under argon to give a purple solution of the sodium benzophenone ketyl. The THF was then distilled from the ketyl, under argon, as required. Glyme, diethyl ether, petroleum ether and cyclohexane were passed through an alumina column, stirred for 16 hours with calcium hydride and distilled from calcium hydride under nitrogen or argon. Carbon tetrachloride and ethyl acetate were purified by distillation from phorphorus pentoxide. Methanol was dried and purified by distillation from magnesium methoxide.

Mesityl bromide was distilled under nitrogen, at reduced pressure, prior to use. All other reagents were distilled under nitrogen prior to use. Solutions of *n*- and *t*-butyllithium in hexanes and methyllithium in ether were obtained from Aldrich and standardised every three to four weeks by direct titration of the carbon-lithium bond with butan-2-ol using 1,10-phenanthroline as indicator.[51] Oxiranes were prepared by standard methods[52-54] and distilled under water pump pressure, *via* a drying line, prior to use. They were stored over 4Å molecular sieves in dry flasks with detachable trap adaptors protected by two serum caps. B-methyl- and B-Ethyl-dimesitylborane[2] were dried in a drying pistil at 35°C/2mm Hg for 2h prior to use.

Experimental Procedures

The equipment and techniques involved in laboratory operations with air sensitive substances have been surveyed.[49] All glassware was oven dried (typically >24 hours at 120°C) assembled hot, and allowed to cool under a stream of nitrogen or argon introduced *via* needles inserted through serum capped inlets with outlets protected by inert oil bubble. Manipulation of liquids was carried out under an inert atmosphere, using syringes and double-ended needle techniques. Syringes and double-ended needles were flushed with nitrogen as they cooled. Solids were transferred, either in air without delay and flushed with nitrogen prior to reaction, or by using a dry box.

Unless otherwise stated, the apparatus for reactions at room temperature or below consisted of a septum capped flask equipped with a spiral inlet arm which is wholly immersed in the cooling bath.[55] The flask contained a coated magnetic follower to enable stirring of the reaction mixiture *via* an external magnetic stirrer. A bleed needle to an argon line was inserted through the cap to allow for any changes in the pressure within the vessel during reaction. The apparatus for reactions at elevated temperatures consisted of a two-necked round-bottomed flask; one neck equipped with a septum capped tap adaptor, the other with a septum capped reflux condenser carrying a nitrogen bleed. Again, a magnetic stirrer provided a method for agitation of the reaction mixture.

Procedure for the preparation of anions (1) and (2) derived from Mes$_2$BMe and Mes$_2$BEt respectively[2]

Bromomesitylene (1.1g, 5.5mmol) was made up to a 0.5M solution in a round-bottomed flask by addition of THF (11ml). The flask was cooled to -78°C and Bu^{t}Li (2 equiv. of a freshly standardised solution, normally about 1.8-2.0M in hexane, was added. The solution became pale yellow and a white solid precipitated. The mixture was stirred for 15 min at -78°C, then placed in a bath at 25°C for 15 min, during which the precipitate dissolved. The reaction mixture containing MesLi (5.5mmol) was transferred *via* a double-ended needle to the previously weighed out B-alkyldimesitylborane (5mmol) at 25°C, the mixture stirred for 1h and then used for further reaction.

General procedure for the reactions of oxiranes with dimesitylboron stabilised carbanions.

This is exemplified, with notes, for the reaction of phenyloxirane (9) with (dimesitylboryl)methyllithium, Mes$_2$BCH$_2$Li, (1).

Preparation of 1-phenylpropan-1,3-diol (15). (Experiment 1, Tables 1 and 4).

To a stirred solution of 5mmol of anion (1) in THF at 25°C, prepared as above, was added dry phenyloxirane (9) (0.57ml, 5mmol)[a] in a dropwise fashion. The reaction was exothermic and the mixtures changed from red to green. After addition was complete, the reaction was stirred for 2h at 25°C.[c] The flask was cooled to 0°C and 5M NaOH (6ml) was added followed by slow, careful addition of hydrogen peroxide (6ml, 50%, w/v).[d] The oxidation was exothermic during the addition and was completed by heating under reflux for 1h after addition of the peroxide was complete. The reaction mixture was then cooled to 25°C, added to sat. NH$_4$Cl (100ml) and extracted with ether (3 x 100ml). The combined ether extracts were dried (MgSO$_4$), filtered and concentrated to give crude product (2.35g). This was transferred with the aid of a little pentane to a column containing 40g of silica and eluted under water pump vacuum with pentane-diethyl ether mixtures. Any starting materials came through at once, and 2,4,6-trimethylphenol (hydroxymesitylene) was removed by ether-pentane mixtures varying from 1:9 to 1:1.
Further elution with neat ether (200ml) gave (15) (0.62g), essentially pure (hplc) as a yellow oil, b.p. 104-106°C/1mm Hg (lit.[56] b.p. 154-5°/5mm Hg). For ^{1}H, and ^{13}C nmr see Figure 2, experiment 1. ν_{max} 3500-3200 cm^{-1}, $M^{\cdot +}$ 152.0837, $C_9H_{12}O_2$ requires 152.0837, m.s. m/z 152(1), 151(4), 134(45), 105(69), 77(17), 43(100).

[a] Proportions of anion to oxirane varied between 1:1 and 5:4 and will be given in each case.
[b] With solid oxiranes, in particular, the anion solution is added to the weighed out oxirane.
[c] Three sets of conditions, 2h/25°C; 18h/25°C and 6h/60°C were used and are given in the Tables.
[d] Alternatively the peroxide may be added dropwise at 25°C. The reaction mixture becomes hot and is refluxed for 1h after addition, or left to stand for 15h at 25°C.

General method for the preparation of phenylboronates from 1,3-diols[57].

Preparation of 2,4-diphenyl-1,3-dioxa-2-boracyclohexane (30).

A dry round-bottomed 25 ml flask was charged with (15) (0.15g, 0.98mmol) and phenylboronic acid (0.13g, 1.08mmol) was added followed by dichloromethane (10ml). A magnetic stirrer bar and 4Å molecular sieves (0.5g) were added directly from an oven and the reaction was sealed and stirred well for 18h. The reaction mixture was then filtered and the sieves well washed with dichloromethane (3 x 20ml). The combined filtrates were concentrated to give crude product (0.21g, 81%). This was purified on a Chromatotron by elution with light petroleum/ether (6:1) to give (30) as a clear oil b.p. 138°C/0.4mm Hg. Found C, 75.95, H, 6.38% $M^{\cdot+}$ 238.1152; $C_{15}H_{15}O_2B$, requires C, 75.63, H, 6.30%, $M^{\cdot+}$ 238.1165. For ^1H and ^{13}C nmr see Figure 2, experiment 1. m.s. 239 (16) 238(98), 117(7), 106(21), 105(100), 104(69), 103(35), 91(33), 77(44). Accurate mass measurements gave 106.0416 (C_7H_6O), 105.0352 (C_7H_5O), 105.0512 (C_6H_6BO), 105.0706 (C_8H_9), 104.0429 (C_6H_5BO), 104.0621 (C_8H_8), 103.0531 ($C_6H_4{}^{11}BO$), 103.0466 $C_6H_5{}^{10}BO$, 103.0543 (C_8H_7).

Preparation of trans-*2-hydroxymethylcyclohexan-1-ol* (18). (Experiment 6, Table 2).

Ratio of anion (1) : oxirane (13) = 1:1. Isolated as a liquid (0.54g, 82%), b.p. 86-88°C/1.5mm Hg, (lit.[58] b.p. 104-110°C/3mm Hg. ν_{max} (film) 3600-3200 cm^{-1}. δ_H, 1.22(4H, m, H-5 and H-4), 1.66(4H, m, H-3 and H-6), 1.92(1H, m, H-2), 3.45(1H, m, H-1), 3.60(2H, m, H-2′), 5.38(2H, m, OH). δ_C 24.6, 25.2,(C-5, C-4), 27.5(C-3), 35.1(C-6), 46.1(C-2), 67.2(C-2′), 75.0(C-1).*

4,5-Cyclohexyl-2-phenyl-1,3-dioxa-2-boracyclohexane✱

Isolated as a white crystalline solid m.p. 99-103°C (0.62g, 69%). Found C, 72.51, H, 7.56%; $M^{\cdot+}$, 216.1328; $C_{13}H_{17}O_2B$ requires C, 72.22, H, 7.87%, $M^{\cdot+}$, 216.1322. δ_H 1.17(4H, m, H-8 and H-9), 1.50(4H, m, H-7 and H-10), 2.04(1H, m, H-5), 3.50(2H, m H-6, J_1=10, H-4), 3.84(1H, q ,J_1=10, J_2= 4, H-6), 7.24, 7.77(5H, m, ArH). δ_C 24.5, 25.0, 26.5 (C-8, C-9, C-10), 33.5(C-7), 42.6(C-5), 67.2(C-4), 75.2(C-6), 127.4, 130.4, 133.9 (aromatic). m.s. 217(14), 216(100), 215(27), 174(12), 173(89), 172(21), 160(19), 159(84), 158(20), 105(55), 104(28).

trans-*2-(1′-hydroxyethyl)cyclohexan-1-ol* (19). (Experiment 7, Table 1).

Ratio of anion (2) : oxirane (13) = 1:1. Isolated as a viscous oil (0.49g, 68%), b.p. 116-120°C/3mm Hg, which was a 1:1 mixture of (19s) and (19a). ν_{max} 3500-3100 cm^{-1}, δ_H, 1.15 (3H, d, J=6, H-2′), 1.40(4H, m, H-4, H-5), 1.60(4H, m, H-3, H-6), 3.64(1H, m, H-1′), 4.01(1H, m, H-1), 4.85(2H, OH) δ_C (19s) 20.8(C-2′), 24.7, 25.4(C-4,C-5), 25.7(C-3), 35.2(C-6), 49.7(C-2), 71.3(C-1′), 76.1(C-1) δ_C (19a) 18.5(C-2′), 24.7, 26.0(C-4,C-5), 27.1(C-3), 35.5(C-6), 50.3(C-2), 69.5(C-1′), 73.4(C-1).

6-Methyl-4,5-cyclohexyl-2-phenyl-1,3-dioxa-2-boracyclohexane (22).

Reaction carried out on (19) (0.49g, 3.4mmol) to give product (0.45g, 51%) as a white crystalline solid m.p. 106-108°C, which was a 1:1 *syn:anti* mixture. Found C, 73.17, H, 8.36%, $M^{\cdot+}$, 230.1478; $C_{14}H_{19}O_2B$ requires C, 73.04, H, 8.26%, $M^{\cdot+}$, 230.1478. δ_H 1.19, 1.13(3H, d, J=6, C-6′), 1.31(4H, m, H-8 and H-9), 1.64(4H, m, H-7 and H-10), 2.09(1H, m, H-5), 3.66(1H, m, H-6), 4.05(1H, m, H-4), 7.26, 7.80(5H, m, Ar-H). δ_C *(22s)* 20.6(C-6′), 24.4, 26.9, 27.0, (C-8, C-9, C-10), 34.2(C-7), 49.0(C-5), 70.1(C-6), 74.9(C-4), 127.3, 130.3, 133.9 (aromatic C) *(22a)*. 17.8 (C-6′), 24.4, 25.3, 25.6 (C-8, C-9, C-10), 33.7(C-7), 46.1(C-5), 69.5(C-6), 72.8(C-4), 127.3, 130.3, 133.9 (aromatic C).

2-Hydroxymethyl-1-methylcyclohexan-1-ol (20). (Experiment 8, Table 2).

Ratio of anion (1) : oxirane (14) = 1:1. Compound (20) was isolated as a colourless liquid, b.p. 117-119°C/3mm Hg/lit.[58], b.p. 79°/0.15mm Hg) (0.55g, 82%). ν_{max} 3600-3200 cm^{-1}, δ_H, 1.16(3H, s, H-1′), 0.9-1.9(m, ~9H), 3.48(1H, q, J_1=10, J_2=4, H-2′), 3.64(1H, q, J_1=12, J_2=10, H-2′), 4.28(br., OH), δ_C, 20.3(C-1′), 23.6, 25.5, 26.5(C-3, C-4), C-5), 41.8(C-6), 47.8(C-2′), 65.4(C-1′), 74.3(C-2). m.s. 126(12), 111(16), 83(14), 71(56).

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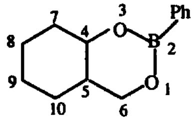
*All multiplicities in accord with assignments, in this and all subsequent ^{13}C nmr data.

✱ Numbering as shown.



4-Methyl-4,5-cyclohexyl-2-phenyl-1,3-dioxa-2-boracyclohexane

Carried out on **(20)** (0.4g, 2.8mmol). Compound **(22)** (1.33g, 46%) was isolated as white crystals m,.p. 109-111°C. Found C, 72.89, H, 8.78%, $M^{\cdot+}$ 230.1478; $C_{14}H_{19}O_2B$ requires C, 73.04, H, 8.26%, $M^{\cdot+}$ 230.1478. δ_H, 1.23(3H, s, H-4′), 1.44(4H, m, H-8, H-9), 1.74(5H, m, H-7, H-10, H-5), 3.6-3.9 (2H, m, H-6), δ_C, 20.0(C-4′), 23.5, 25.0, 25.5(C-7, C-8, C-9), 40.0(C-10), 45.3(C-5), 64.1(C-6), 73.0(C-4), 127.3, 130.3, 133.8 (aromatic C). m.s. 231(10), 230(56), 229(16), 215(55), 187(100), 186(23).

2-(1″-Hydroxyethyl)-methylcyclohexan-1-ol (21).* (Experiment 9, Table 2).

Ratio of anion (2) to oxirane (14) = 1:1. Pure (21) (0.49g, 62%) was isolated as white crystals m.p. 95°C, as a 3.2 mixture of *syn* and *anti*-isomers. ν_{max} 3600-3200 cm^{-1}, δ_H 0.82(3H ,d, J=6, H-2″) 1.15(3H, s, H-1"), 1.0-2.6(m, C-H), 3.65(1H, m, H-2′), 3.60-4.0(2H, br, OH). m.s. 95(13), 81(9), 71(23), 67(11), 58(23), 55(12), 43(100). **(21s)** had δ_C 15.2, 20.7(C-1′, C-2″), 23.0, 24.0(C-4, C-5), 30.9, 33.4(C-3, C-6), 43.5(C-2), 74.4(C-2′), 77.6(C-1). **(21a)** had δ_C 19.9, 21.0(C-1′, C-2″), 23.2, 24.2(C-4,C-5), 31.1, 32.9(C-3, C-6), 38.5(C-2), 72.6(C-2′), 77.1(C-1).

4,6-Dimethyl-4,5-cyclohexyl-2-phenyl-1,3-dioxaborocyclohexane (23).*

Usual procedure carried out on (21) (0.33g, 2.1mmol) to give (23) (0.28g, 47%) m.p. 115°C as a 3:2 mixture of **(23s)** and **(23a)**. Found C, 73.38, H, 8.72%, $M^{\cdot+}$, 244.1635; $C_{15}H_{21}O_2B$ requires C, 73.77, H, 8.61%, $M^{\cdot+}$, 244.1635. (23s), δ_H 1.24(3H, s, C-4′), 1.33(3H, d, J=6, H-6′), 1.0-2.4(~9H, m), 4.22(1H, quint, $J_{6,5}$=5, $6_{12,6}$=6, H-6). δ_C 21.1, 23.4(C-6′,C-4′), 23.5, 25.7, 26.2(C-8,C-9,C-10), 42.9(C-7), 47.9(C-5), 70.7(C-6), 73.2(C-4). **(23a)**. δ_H, 1.22(3H, d, J=6, H-6′), 1.38(3H, s, H-4), 1.0-2.4(~9H, m), 3.94(1H, sext. H-6). δ_C 18.4, 23.4(C-6′,C-4′), 23.5, 25.5, 25.7(C-8, C-9, C-10), 40.4(C-7), 52.0(C-5), 69.3(C-6), 73.1(C-4), 127.3, 130.2, 133.9 (aromatic C). m.s. (mixture of **(23s)** and **(23a)**). 244(28), 229(100), 228(25), 187(38), 186(10), 173(10), 105(22), 96(40).

1-Phenylbutan-1,3-diol (16). (Experiment 2, Table 4).

Ratio of (2):(9) = 1:1. Compound (16) (0.67g, 81%) was isolated as a pale yellow oil, b.p. 118-120°C/1.5mm Hg (lit.[59] 129-131°C/2mm Hg), as a 4:3 mixture of **(16s)** and **(16a)**. m.s. 166(2), 148(20), 107(100), 105(52), 104(25), 77(39). For ^{1}H and ^{13}C nmr see Figure 2.

6-Methyl-2,4-diphenyl-1,3-dioxa-2-boracyclohexane (31).

Prepared from (16) (0.43g, 2.6mmol) and isolated as a clear oil (0.47g, 70%), b.p. 146°C/0.5mm Hg. Found C, 76.13, H, 6.77% $M^{\cdot+}$, 252.1345; $C_{16}H_{17}O_2B$ requires C, 76.19, H, 6.75%, $M^{\cdot+}$, 252.1321. m.s. 253(14), 252(81), 209(14), 119(12), 107.0497(C_7H_7O) (54), 106(13), 105.0347(C_7H_50), 105.0512(C_6H_6OB), 105.0711(C_8H_9) (100). For ^{1}H and ^{13}C nmr see Figure 2.

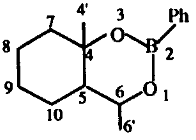
1,2-anti-*Diphenylpropan-1,3-diol* (24). (Experiment 10, Table 4).

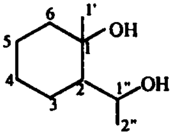
Ratio of (1) : (11) = 5:4. Compound (24) was isolated as yellow crystals (0.79g, 82%) m.p. 114-117°C, (lit.[60], m.p. 115-118°C.) ν_{max} (KBr), 3500-3200 cm^{-1} m.s. 180(4), 179(3), 107(10), 105(9), 104(100), 103(7), 79(11), 77(13). ^{1}H and ^{13}C nmr in Figure 3.

trans-*2,4,5-Triphenyl-1,3-dioxa-2-boracyclohexane* (32a).

Prepared from (24) (0.56g, 2.5mmol) and isolated as white crystals (0.39g, 64%), m.p. 164-5°C. Found C, 80.26, H, 6.11%, $M^{\cdot+}$, 314.1460; $C_{31}H_{19}O_2B$ requires C, 80.26, H, 6.05%, 314.1478. m.s. 315(5), 314(22), 105(10), 104(100). ^{1}H and ^{13}C nmr spectra in Figure 3.

* Numbering as shown





1,2-syn-*Diphenylpropan-1,3-diol* **(26)**. (Experiment 12, Table 4).

Ratio of **(1)** : **(12)** is 5:4. Compound **(26)** was isolated as white crystals m.p. 110-113°C (lit.^{60}, m.p. 112°C). ν_{max} (KBr), 3500-3200 cm^{-1}. m.s. 180(9), 179(11), 107(90), 105(77), 104(100), 103(57). ^{1}H and ^{13}C nmr spectra in Figure 3.

cis-*2,4,5-Triphenyl-1,3-dioxa-2-boracyclohexane* **(33)**.

Prepared from **(26)** (0.4g, 1.75mmol) as white crystals (0.56g, 92%) m.p. 162-3°C. Found C, 80.44, H, 6.08%, $M^{\cdot+}$, 314.1460, $C_{21}H_{19}O_2B$ requires C, 80.26, H, 6.05%, $M^{\cdot+}$, 314.1478. m.s. 315(4), 314(19), 313(4), 105(8), 104(100). ^{1}H and ^{13}C nmr spectra in Figure 3.

1,2-anti-*1,2-diphenylbutan-1,3-diol* **(25)**. (Experiment 11, Table 4).

Ratio of **(2)** : **(11)** = 5:4. Compound **(25)** (0.4g, 37%) was isolated as a white solid, m.p. 125-128°C as a mixture of the 1,2-*anti*-2,3-*anti*-isomer **(25s)** and the 1,2-*anti*-2,3-*syn*-isomer **(25a)** in a ratio of 7:1. ν_{max} (KBr), 3500-3200 cm^{-1}, m.s. 180(30), 179(20), 118(100), 117(33), 105(10), 91(5). ^{1}H and ^{13}C nmr in Figure 4.

4,5-trans-*6-Methyl-2,4,5-triphenyl-1,3-dioxa-2-boracyclohexane* **(34)**.

Prepared from **(25)** (0.24g, 1mmol) as a white, crystalline solid (0.32g, 73%) m.p. 172-174°C as a mixture of the *trans, trans*-isomer **(34s)**, and the *trans,cis*-isomer **(34a)**. Found C, 80.9, H, 6.22%, $M^{\cdot+}$ 328.1634, $C_{22}H_{21}O_2B$ requires C, 80.49, H, 6.40%, $M^{\cdot+}$ 328.1635. m.s. 328(10), 119(10), 118(100), 117(20). Based on ^{13}C nmr the mixture was **(34s)** : **(34a)** = 7.1. By hplc it was 11:1. ^{1}H and ^{13}C nmr of **(34s)** and **(34a)** in Figure 4.

1,2-syn-*1,2-Diphenylbutan-1,3-diol* **(27)**. (Experiment 13, Table 4).

Ratio of **(2)** : **(12)** = 5:4. Compound **(27)** (0.3g, 31%) was isolated as a crystalline solid m.p., 120-122°C as a mixture of the 1,2-*syn*-2,3-*syn* -isomer **(27s)** and the 1,2-*syn*-2,3-*anti*-isomer **(27a)** in the ratio of 4:5. ν_{max} (KBr), 3500-3200 cm^{-1}. m.s. 180(6), 179(6), 119(11), 118(100), 117(23), 105(12), 77(15). ^{1}H and ^{13}C nmr spectra in Figure 5.

4,5-cis-*6-Methyl,2,4,5-triphenyl-1,3-dioxa-2-boracyclohexane* **(35)**

Prepared from **(27)** (0.21g, 0.87mmol). Compound **(35)** (0.15g, 49%) was isolated as a white solid m.p. 170-173°C as a mixture of *cis, trans*- and *cis, cis*-isomers **(35a)** and **(35s)** in the ratio of 5:4 (^{13}C, ^{1}H). Found C, 80.5, H, 6.39%, $M^{\cdot+}$, 328.1634; $C_{22}H_{21}O_2B$ requires C, 80.49, H, 6.4%, $M^{\cdot+}$ 328.1635. m.s. 328(11), 119(10), 118(100), 117(18). ^{1}H and ^{13}C nmr spectra in Figure 5.

2,3-syn-2-Phenylbutan-1,3-diol **(28)**. *(Experiment 14, Table 4).*

Ratio of **(1)** : **(10)** = 1:1. The product (0.78g, 94%) was isolated as a clear oil, b.p. 107-110°C/1mm Hg (lit.^{59} b.p. 105-110°C/1mm Hg). ν_{max} 3500-3200 cm^{-1}. ^{1}H nmr and ^{13}C nmr in Figure 6.

cis-*5-Methyl-2,4-diphenyl-1,3-dioxa-2-boracyclohexane* **(36)**.

Prepared from **(28)**, (0.78g, 4.7mmol) as white crystals (0.8g, 68%) m.p. 123-125°C. Found C, 76.36, H, 6.67, $M^{\cdot+}$, 252.1345, $C_{16}H_{17}O_2B$ requires C, 76.19, H, 6.75%, $M^{\cdot+}$ 252.1322. m.s. 252(16), 105(11), 104.0622 (C_8H_9) (100). ^{1}H and ^{13}C nmr spectra in Figure 6.

2,3-syn-*3-phenylpentan-2,4-diol* **(29)**. (Experiment 15, Table 4).

Ratio of **(2)** : **(10)** = 5:4. Compound **(29)** (0.52g, 72%) was isolated as a white crystalline solid m.p. 101-102°C as a mixture of *syn-syn* isomer **(29s)** and *syn-anti*-isomer **(29a)** in the ratio of 1:9. ν_{max} (KBr) 3500-3200 cm^{-1}. m.s. 118(100), 117(50), 91(23), 43(30). ^{1}H and ^{13}C nmr spectra in Figure 7.

*4,5-*syn*-4,6-dimethyl-2,5-diphenyl-1,3-dioxa-2-boracyclohexane* (37).

Prepared from (29) (0.34g, 1.89mmol) as a white crystalline solid (0.25g, 45%) m.p. 131-132°C as a mixture (1:4) of 1,3-*syn*, (37s) and 1,3-*anti* (37a)-isomers. Found $M^{\cdot+}$ 266.1478, $C_{17}H_{19}O_2B$ requires 266.1478 m.s. 266(9), 119(15), 118.0765 (C_9H_{10}, $C_6H_5CH{=}CHCH_3$) (100), 117(20). ^{1}H and ^{13}C nmr spectra in Figure 7.

Nonan-1,3-diol, (38). (Experiment 16, Table 5).

Anion (1) : Oxirane (3) = 1:1. Pure (38) (0.72g, 90%) was isolated as a clear oil, b,.p. 88-92°C/1mm Hg (lit.[61] b.p. 90-92°C/0.8mm Hg). ^{1}H and ^{13}C nmr spectra in Figure 8.

4-Hexyl-2-phenyl-1,3-dioxa-2-boracyclohexane (46).

Prepared from (38) (0.46g, 2.6mmol) as a viscous oil (0.55g, 81%), b.p. 152-153°C/0.5mm Hg. Found C, 73.38, H, 9.45%, $M^{\cdot+}$ 246.1791. $C_{15}H_{23}O_2B$ requires C, 73.17, H, 9.35%, $M^{\cdot+}$ 246.1791. m.s. 246(17), 161(92), 160(26), 131(23), 105.0500 (C_6H_6BO) (52), 104.0426 (C_6H_5BO), 104.0617 (C_8H_8) (29) 91(100).

Decan-2,4-diol (39). (Experiment 17, Table 5).

Anion (2) : oxirane (3) = 1:1. Compound (39) (0.74g, 85%) was isolated as an oil b.p. 175-176°C/14mm Hg (lit.[62], b.p. 120-123°C/0.8mm Hg), which was a mixture of (39s) and (39a) (4:5). m.s. 115(11), 89(30), 71(51), 70(12), 58(20), 57(10), 45(100), 43(50), 41(30). ^{1}H and ^{13}C nmr are given in Figure 9.

4-Hexyl-6-methyl-2-phenyl-1,3-dioxa-2-boracyclohexane (47).

Prepared from (39) (0.43g, 2.5mmol) as a viscous oil (0.38g, 60%), b.p. 157-159°C/0.5mm Hg) as a mixture (5:6) of the 1,3-*cis*-isomer (47s) and the 1,3-*trans*-isomer (47a). Found C, 73.65, H, 9.70%, $M^{\cdot+}$ 260.1947; $C_{16}H_{25}O_2B$ requires C, 73.85, H, 9.62, $M^{\cdot+}$ 260.1947. m.s. 260(14), 175(72), 174(15), 105(100), 104(13). ^{1}H and ^{13}C nmr given in Figure 9.

syn-*2-Propylhexan-1,3-diol* (17). (Experiment 5, Table 5).

Anion (1) : oxirane (4) = 5:4. Compound (19) (0.53g, 95%) was isolated as a colourless liquid, b.,p. 96-99°C/1mm Hg (lit.[63], b.p. 118-120°C/3mm Hg). ν_{max} (film) 3600-3200 cm^{-1}. m.s. 117(10), 81(11), 73(34), 71(10), 70(100). ^{1}H and ^{13}C nmr given in Figure 10.

cis-*4,5-Di-*n*-propyl-2-phenyl-1,3-dioxa-2-boracyclohexane* (48).

Prepared from (17) (0.51g, 3.2mmol) and isolated as a viscous oil, b.p. 152°C/0.5mm Hg. Found C, 73.24, H, 9.61%, $M^{\cdot+}$ 246.1791. $C_{15}H_{23}O_2B$ requires C, 73.17, H, 9.35%, $M^{\cdot+}$ 246.1791. m.s. 246(26), 203(75), 202(18), 159(11), 147(49), 146(12), 117(11), 105(73), 104(26), 91(51), 81(22), 70(100). ^{1}H and ^{13}C nmr given in Figure 10.

*3-*n*-Propylheptan-2,4-diol* (40). (Experiment 18, Table 5).

Anion (2) : oxirane (4) = 5:4. Product (40) was isolated as a colourless oil (0.19g, 50%), b.p. 110-113°C/1mm Hg as a mixture of the 1,2-*syn*-2,3-*syn*-isomer (40s) and the 1,2-*syn*-2,3-*anti*-isomer (40a) in the ratio of 10:1. The mixture had ν_{max} (film) 3500-3200 cm^{-1}, δ_H 0.87 (6H, m, H-7, H-10), 1.32(12H, m, H-1, 5, 6, 8, 9), 3.44(1H ,m, H-2), 4.06(1H, m, H-4), 4.5(2H,s,OH). ^{13}C nmr given in Figure 10. m.s. 110(74), 95(50), 81(100), 68(93), 55(64), 41(45).

3-Ethylheptan-1,3-diol (42). (Experiment 20, Table 5).

Anion (1) : oxirane (6) = 5:4. The reaction gave (42) (0.50g, 78%) as a colourless liquid, b.p. 120-122°C/3mm Hg. ν_{max} (film) 3600-3200 cm^{-1}. m.s. 131(26), 115(57), 113(14), 103(62), 85(81), 59(23), 57(100), 55(44). ^{1}H and ^{13}C data given in Figure 11.

4-Butyl-4-ethyl-2-phenyl-1,3-dioxa-2-boracyclohexane **(49)**.

Prepared from **(42)** (0.5g, 3.1mmol). This gave **(49)** (0.54g, 63%) as an oil, b.p. 153°C/0.5mm Hg. Found C, 72.97, H, 9.26%, $M^{\cdot+}$ 246.1794. $C_{15}H_{23}O_2B$ requires C, 73.17, H, 9.35%, $M^{\cdot+}$ 246.179. m.s. 246(2),. 217(55), 216(13), 189(100), 188(25), 105(21), 104(9), 91 (11). ^1H and ^{13}C data given in Figure 11.

4-Ethyloctan-2,4-diol **(43)**. (Experiment 21, Table 5).

Anion **(2)** : oxirane **(6)** = 5:4. Pure **(43)** (0.5g, 72%) was isolated as an oil, b.p. 120-125°C/2.5mm Hg, which was a mixture of two isomers in the ratio of 2:3. m.s. 150(2), 149(18), 117(16), 115(30), 85(70), 83(10), 75(25). ^1H and ^{13}C data given in Figure 11.

4-Butyl-4-ethyl-6-methyl-2-phenyl-1,3-dioxa-2-boracyclohexane **(50)**.

Reaction carried out with **(43)** (0.44g, 2.5mmol) to give **(50)** (0.48g, 66%) as an oil, b.p. 158°C/0.6mm Hg as a 2:3 mixture of isomers. $M^{\cdot+}$ = 260.1934, $C_{16}H_{25}O_2B$ requires 260.1947. m.s. 260(1), 232(8), 231(58), 230(12), 204(13), 203(100), 202(24), 105(31). ^1H and ^{13}C data given in Figure 11.

2,3-Dimethylbutan-1,3-diol **(44)**. (Experiment 22, Table 5).

Anion **(1)** : oxirane **(7)** = 1:1. Pure **(44)** was isolated as a colourless liquid (0.37g, 63%), b.p. 58-60°C/3mm Hg (lit.[64] b.p. 108-112/7mm Hg). ν_{max} (film) 3500-3100 cm^{-1}. m.s. 118(2), 117(5), 99(8), 73(13), 70(55), 59(100), 56(75), 55(42). ^1H and ^{13}C data given in Figure 12.

4,4,5-Trimethyl-2-phenyl-1,3-dioxa-2-boracyclohexane **(51)**

Preparation used diol **(44)** (0.32g, 2.7mmol). Compound **(51)** was isolated as a viscous oil (0.34g, 54%), b.p. 140°C/2mm Hg. Found C, 70.59, H, 8.61%, $M^{\cdot+}$ 204.1339. $C_{12}H_{17}O_2B$ requires C, 70.59, H, 8.33%, $M^{\cdot+}$ 204.1322. m.s. 205(3), 204(30), 203(11), 189(39), 119(26), 118(30), 105(80), 104(28), 59(100). ^1H and ^{13}C data given in Figure 12.

2,3-Dimethylpentan-2,4-diol **(45)**. (Experiment 23, Table 5).

Anion **(2)** : oxirane **(7)** = 1:1. Pure **(45)** was isolated as a colourless liquid (0.37g, 56%), b.p. 60-63°C/3mm Hg (lit.[64], b.p. 109-112°C/12mm Hg), which was a mixture 2,3-*anti*-and 2,3-*syn*-isomers in the ratio of 2:3. m.s. 104(3), 103(3), 85(7), 83(5), 70(5), 60(17), 59(100), 55(12). ^1H and ^{13}C data given in Figure 12.

4,4,5,6-Tetramethyl-2-phenyl-1,3-dioxa-2-boracyclohexane **(52)**. (Experiment 23, Table 5).

Prepared using **(45)** (0.37g, 2.8mmol). Pure **(52)** was isolated, using a Chromatotron, as a viscous oil (0.52g, 74%), b.p. 150-154°C/3mm Hg as a mixture of 11:4 of the 5,6-*trans* to the 5,6-*cis*-isomer. Found C, 71.82, H, 8.97%, $M^{\cdot+}$ 218.1491. $C_{13}H_{19}O_2B$ requires C, 71.56, H, 8.72%, $M^{\cdot+}$ 218.1478. m.s. 219(4), 218(23), 189.1089 ($C_{11}H_{14}O_2B$) (22), 119.0843 (C_9H_{11}) (26), 118.0775 (C_9H_{10}) (11), 105.0526 (C_6H_6OB) (52). ^1H and ^{13}C data given in Figure 12.

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