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THE DIMESITYLBORON GROUP IN ORGANIC SYNTHESIS 8. PREPARATIONS OF 1,3-DIOLS FROM OXIRANES

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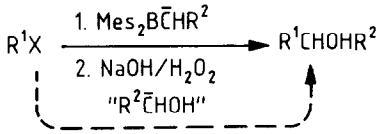
Alkyldimesitylboranes, yield anions[1], $Mes_2B\bar{C}HR$, that on reaction with oxiranes followed by oxidation give 1,3-diols. These anions are thus the operational equivalent of $R\bar{C}HOH$. The scope and limitations of the new process are delineated.

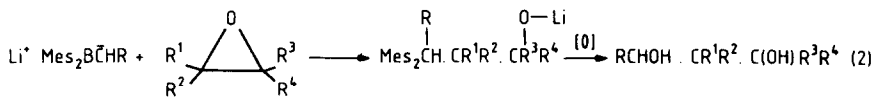
The ready availability of chiral and achiral oxiranes[2] together with their plethora of reactions[2,3,4], make them key intermediates in organic synthesis. In particular their reactions with nucleophiles are powerful tools for the regio- and stereospecific formation of carbon-carbon bonds[2,3,4,5] as well as for the introduction of new heteroatoms[6]. To obtain the synthetically important 1,3-diol system from oxiranes however an hydroxyl group must be already present α or β to the oxirane group. The reaction of such substrates with say metal alkyls[5,7,8] must then be regiospecific to prevent the formation of 1,2- or 1,4-diols and this has led to considerable problems. Alternative routes to 1,3-diols involve the reductions of 1,3-dicarbonyl compounds or β-hydroxycarbonyl compounds and there has been considerable progress in making such reductions stereospecific[9,10,11]. If the equivalents of $R\bar{C}HOH$ were readily available then their reactions with oxiranes would be conceptually advantageous inasmuch as; (i) no hydroxyl group would be present in the substrate and 1,2- or 1,4-diol production would not be a problem; (ii) the relative stereochemistry of two substituents of the product 1,3-diol is fixed assuming the normal S_N2 attack with inversion[4]; (iii) there is the possibility of some control of the stereochemistry of the entering centre relative to those already present.

With these considerations in mind we decided to investigate the interactions of anions derived from alkyldimesitylboranes[1] with oxiranes. We have already shown[12] that in alkylation reactions such anions are the operational equivalents of $R\bar{C}HOH$ (eq. 1).



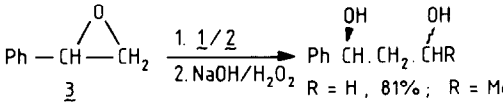
(1)

We now report that $Mes_2B\bar{C}H_2$, 1, and $Mes_2B\bar{C}HCH_3$, 2, react with oxiranes to give intermediates (not isolated) that on oxidation yield, 1,3-diols (eq. 2).



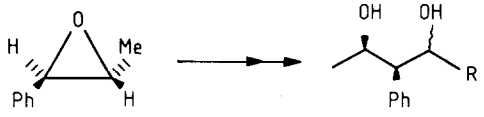
(2)

Phenyloxirane, 3, was our first substrate, chosen because steric and electronic effects are strongly opposed and nucleophilic attack frequently leads to mixtures[2,3,4,8]. Our results (eq. 3) show that the steric requirements of the reagents 1 and 2 predominate and excellent yields[a] result of 1,3-diols, produced by reaction at C-2. Little erythro:threo selectivity is shown in the reactions of 2.



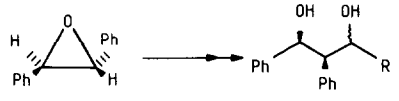
3 R = H, 81%; R = Me, 94% (e:t = 4:3) (3)

To our surprise reaction of trans-1-phenyl-2-methyloxirane, 4, with anions 1 and 2 was regiospecific in the opposite sense to that of phenyloxirane, attack being at C-1. Apparently the steric effects of the phenyl and methyl groups are roughly balanced and electronic effects dominate (eq. 4). The 4:1 ratio of erythro to threo 1,3-diols in the reaction of 2 with 4 is very promising and as yet, unoptimised.[b]



4 R = H, 94%; R = Me, 72% (e:t = 4:1)[c] (4)

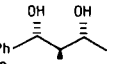
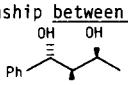
To test the steric tolerance of the reaction, 1 and 2 were reacted with trans- and cis-1,2-diphenyloxiranes, 5 and 6 (eq. 5 and 6).



5 R = H, 93%; R = Me, 31% (e:t = 2:3) (5)

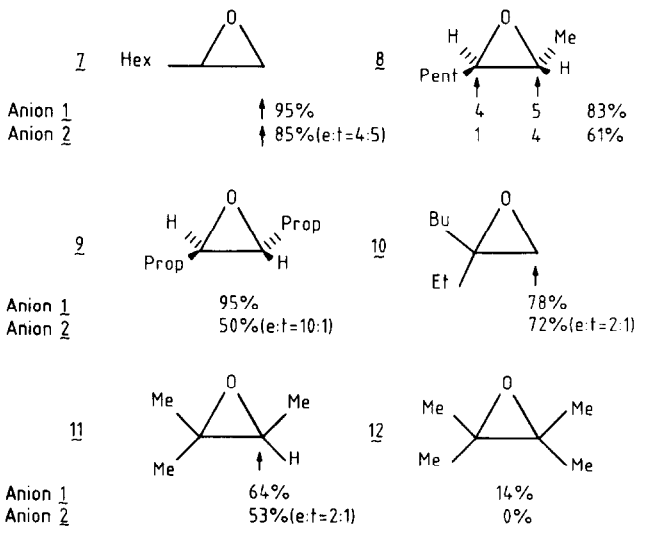
6 R = H, 82%; R = Me, 37% (e:t = 7:1) (6)

Two points emerge from reactions (5) and (6). (i) Anion 1 reacts well but 2, even under our best conditions of 6h at 60°C, at which temperature the anion is stable, did not give good yields of products. (ii) The e:t ratio of 7:1 in the reaction of 6 with 2 is

[a] All yields are of characterised, isolated products. [b] The terms erythro and threo in all cases are defined as the relationship between the two alcohol groupings, e.g.  is erythro and  is threo. The e:t ratio is established by ^{1}H and ^{13}C n.m.r. studies on the diols and derived phenylboronates and by h.p.l.c. studies on the latter compounds. [c] We assume that in the basic reaction conditions, inversion occurs at the oxirane carbon being attacked, even when this is benzylic. All our physical data agree with this assumption.

noteworthy. Attempts to increase the yields of products using Lewis acid catalysis will be reported separately.

We then examined a series of aliphatic oxiranes of differing steric requirements with the results shown in Scheme 1.



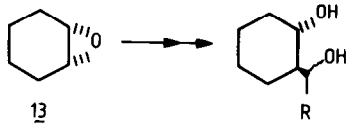
SCHEME 1

Anion 1 ($\check{C}H_2OH$ equivalent) reacts with all the epoxides but yields gradually decrease with increasing hindrance. However even with 11 there is an acceptable isolated yield of 64%. As expected 2 ($CH_3\check{C}HOH$ equivalent) is more subject to steric hindrance than 1 and in general gives lower yields of 1,3-diols. Even so 2 reacted with all oxiranes except 12 to give acceptable fields of 1,3-diols. We have not carried out rate studies but find that 1 reacts with 7, 8, 10 and 11 in 2h at 25°C but requires 18h at 25°C to react with 9 and even partly with 12. Anion 2 reacts with 7 in 2h at 25°C but needs 18h at 25°C to react with 8, 10 and 11, 6h at 60°C to react with 9, and refuses to react with 12. This suggests that with anions $Mes_2B\check{C}HR$ there will be good discrimination between oxiranes of differing steric requirements in the same molecule.

The next general point is that there is complete regiospecificity in the reactions of 1 and 2 with the unsymmetrical oxiranes 7, 10 and 11, with the least substituted carbon atom being the site of attack in each case. With oxirane 8, the reagents are being asked to discriminate between a methyl and a normal alkyl group. Anion 1 fails to do this but the selectivity shown by 2 is, to our knowledge, unprecedented, suggesting that $Mes_2B\check{C}HR$ may find very particular use in cases where delicate steric choices need to be made. We were not able to separate the products of the reaction of 8 with 2, but the ^{13}C n.m.r. suggests that the two 1,3-diols are present as single stereoisomers! In the same vein the 10:1 erythro:threo ratio in the reaction of trans-1,2-dipropyloxirane 9 with 2 is extremely promising as three contiguous asymmetric centres are set up in one process and with high selectivity (two centres completely selective, two centres 91:9 selective). This result

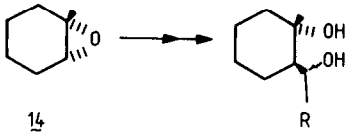
was unexpected in view of the low selectivity with trans- as compared with cis-1,2-diphenyloxirane. We have not, as yet, tested cis-1,2-dipropyloxirane, 9.

Cyclohexene oxiranes 13 and 14 react as expected[4] with 1 and 2 to yield trans-disubstituted cyclohexanes, with attack on 14 being completely regiospecific (eq. 7 and 8). Erythro and threo-diols are produced in almost equal amounts,



13 R

R = H, 82%
R = Me, 68%(e:t=1:1) (7)



14 R

R = H, 82%
R = Me, 68%(e:t=5:4) (8)

To summarise: anions derived from alkyldimesitylboranes react readily with most oxiranes without catalysis and with extremely high regioselectivity. Oxidation of the products yields 1,3-diols. The reactions are selective with regard to the rates of reactions with different types of oxirane and in some important cases give high erythro:threo ratios. The process uses $Mes_2B\bar{C}HR$ as the equivalent of $R\bar{C}HOH$ and represents an important new method for the production of 1,3-diols. Taken together with the preceding communication[13] which uses $Mes_2B\bar{C}HR$ as precursors of 1,2-diols this work emphasises the potential of boron stabilised carbanions in organic synthesis.

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