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Boron-Catalyzed Epoxidation of Olefins with *tert*-Butyl Hydroperoxide

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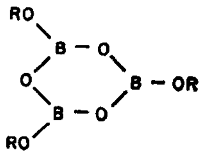
Cyclohexene and 1-octene have been epoxidized with *tert*-butyl hydroperoxide at 80°C, in the presence of several boron esters. The catalytic activities of the boron compounds are markedly dependent on their structures and are enhanced by the presence of electron-attracting substituents, which increase the electrophilicity of the boron atom.

Alkyl and aryl metaborates catalyze the epoxidation but are rapidly deactivated via alcoholysis to give the corresponding orthoborates, which are inactive. Orthoborate esters containing sufficiently strong electron-withdrawing groups (such as acetylacetonate or hexafluoroacetylacetonate) are, on the other hand, active catalysts. They are also deactivated during the reaction via alcoholysis and/or oxidative destruction of the ligands by hydroperoxide.

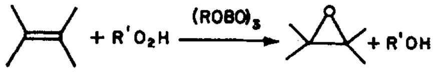
INTRODUCTION

The epoxidation of olefins with organic hydroperoxides is known (*1*) to be catalyzed by a variety of transition-metal complexes. If, as we recently suggested (*2*), the activities of these catalysts are related to their Lewis acidities, then nontransition-metal compounds possessing Lewis acid properties might also be expected to catalyze these reactions.

Wolf and Barnes (*3*) have recently described the epoxidation of olefins with alkyl hydroperoxides in the presence of cyclohexyl metaborate (IA). The metaborate was unable to effect the conversion of more than one equivalent of reactants due to its facile reaction with the co-product alcohol to afford the corresponding orthoborate, which was shown to be inactive.



I = $(\mathrm{ROBO})_3$; IA, R = cyclohexyl; IB, R = phenyl; IC, R = 2,6-di-*tert*-butyl-4-methylphenyl

 (1)

$$\tfrac{1}{3}(\mathrm{ROBO})_3 + \mathrm{R'OH} \rightleftharpoons \mathrm{RO(R'O)BOH} \overset{\mathrm{R'OH}}{\rightleftharpoons} \mathrm{RO(R'O)_2B} + \mathrm{H_2O} \quad (2)$$

It was of interest, therefore, to study the effect of the structure of the boron compound on its catalytic activity and stability.

METHODS

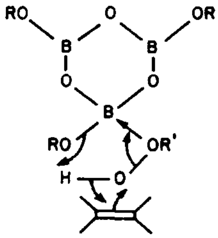
Materials. Cyclohexyl metaborate (*4*), phenyl metaborate (*5*), (2,6-di-*tert*-butyl-4-methyl)phenyl metaborate (*6*), and triphenyl orthoborate (7) were prepared by standard procedures. 2-Acetylacetonato-1,3,2-benzodioxaborole(III) was prepared by reaction of acetylacetone with 2,2′-oxy-bis-1,3,2-benzodioxaborole (*8*). Similarly, 2-hexafluoroacetylacetonato-1,3,2-benzodioxaborole(IV) was synthesized using hexafluoroacetylacetone in place of acetylacetone. The product was an oil, which could not be crystallized. For the epoxidation reactions (IV) was prepared *in situ*.

Procedure for epoxidation. A solution of the boron compound and *tert*-butyl hydroperoxide (0.5–4 and 4–40 mmol, respectively) in the olefin (20 ml) was allowed to react at 80°C under an atmosphere of nitrogen. The appearance of epoxide was followed by glc analysis (*2*) and the disappearance of hydroperoxide by iodometric titration.

Results and Discussion

Metaborates

The boron atom in trivalent boron compounds, such as borate esters, is trigonal co-planar and electron-deficient, and hence acts as a Lewis acid. Coordination of an alkyl hydroperoxide to the electrophilic boron atom renders the peroxidic oxygens more electrophilic, and thus more reactive towards olefins. Wolf and Barnes (*3*) suggested a mechanism involving transfer of an oxygen atom from a boron–hydroperoxide complex to the olefin via the cyclic transition state:



Both the ease of complex formation and the ease of subsequent reaction of the complex with an olefin are expected to increase with increasing Lewis acidity of the boron atom. In agreement with this we found that phenyl metaborate (IB) was significantly more active than cyclohexyl metaborate (IA) (see Table 1, Expts 1 and 2).

The results of an experiment with IB (Expt 2), where 2.4 mol of epoxide were produced per equivalent of IB, suggested that in these reactions metaborates can be used in less than stoichiometric amounts, i.e., as genuine catalysts. The effect of metaborates will depend on the relative rates of reactions (1) and (2) and only when the rate of alcoholysis of the metaborate [reaction (2)] is slow relative to that of epoxidation [reaction (1)] can the metaborate be expected to function as a catalyst in the usual sense.

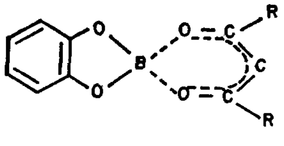
In general, metaborates are very sensitive to alcoholysis (*9*) and their reactivity is dependent on both electronic and steric factors. Since the sterically hindered metaborate (IC) is one of the most hydrolytically stable metaborates known, and therefore expected to be fairly resistant towards alcoholysis, we tested (IC) as an epoxidation catalyst.

Indeed, whereas the initial rate of epoxidation of cyclohexene with *tert*-butyl hydroperoxide in the presence of (IC) proved to be roughly the same as in the presence of (IB), the former catalyst had a longer lifetime (Expts 3 and 5). However, after forming 9.2 mol of epoxide per equivalent of (IC) the catalyst was deactivated.

The rate of epoxidation of 1-octene with *tert*-butyl hydroperoxide in the presence of (IC) was lower than that of cyclohexene, and gave a lower selectivity to epoxide (see Table 1), which is consistent with the lower reactivity of 1-octene to electrophilic attack.

Orthoborates

We attribute the reported (*3*) lack of activity of alkyl orthoborates to their Lewis acidity being lower than that of the corresponding metaborates (*9*). Nevertheless, orthoborates should be capable of functioning as catalysts if substituted with sufficiently strong electron-withdrawing groups to increase the electrophilic nature of the boron atom. Whereas no epoxidation was observed in the presence of triphenyl orthoborate (II, Expt 7), the orthoborates (III) and (IV), which contain the more strongly electron-attracting (compared to phenoxy) acetylacetonate and hexafluoroacetylacetonate ligands, were the most active of the compounds studied.



(III) R = CH_3; (IV) R = CF_3.

TABLE 1
BORON-CATALYZED EPOXIDATION OF OLEFINS AT 80°C

Expt	Catalyst, (Meq)	BuO_2H, (mmol)	Olefin[a]	Reaction time (hr)	BuO_2H consumed (%)	Epoxide yield (%)	Epoxide selectivity[b] (%)	Epoxide (mol/Eq of cat.)
1	IA (4.0)	4.0	C	15	99	82[c]	83	0.83
2	IB (1.0)	4.0	C	3	100	59[c]	59	2.4
3	IB (1.0)	10.0	C	6	—	26[d]	—	2.6
4	IC (1.0)	4.0	C	3	100	93	93	3.8
5	IC (1.0)	40.0	C	3	—	23[d]	—	9.2
6	IC (1.0)	4.0	O	9	33	23[d]	70	0.92
7	II (4.0)	4.0	C	3	—	Tr	—	—
8	III (0.5)	4.0	C	5	100	95	95	7.6
9	III (0.5)	50.0	C	20	—	48[d]	—	38
10	III (0.5)	4.0	O	50	100	41	41	3.3
11	IV (0.5)	40.0	C	22	80	56[d]	70	400

[a] C = cyclohexene; O = 1-octene.

[b] Based on BuO_2H consumed.

[c] Catalyst deactivated; addition of fresh *tert*-BuO_2H resulted in no further reaction.

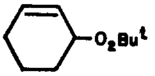
[d] Catalyst deactivated; addition of fresh catalyst resulted in further reaction.

The rate of epoxidation of cyclohexene in the presence of (IV) was about three times that in the presence of (III), which is consistent with the fact that the boron is more strongly electrophilic in (IV) than in (III).

In the epoxidation of cyclohexene, catalyzed by (III), 38 mol of epoxide were formed per equivalent of (III) before the reaction stopped. The infrared spectrum of the catalyst recovered from the reaction, after deactivation, showed that the catalyst no longer contained an acetylacetonate group. We believe that removal of the acetylacetonate group occurred via oxidative destruction by hydroperoxide rather than by alcoholysis. Oxidative destruction of acetylacetonate ligands by hydroperoxide was previously observed (*10*) in molybdenum-catalyzed epoxidations. The greater stability of hexafluoroacetylacetonate ligands, as reflected in the relatively long lifetime of (IV) compared to (III) (Expts 9 and 11), is in agreement with this view.

Side-Reactions

The major by-product formed in the reactions with cyclohexene was 3-*tert*-butylperoxy-1-cyclohexene (V). In addition, small amounts of 2-cyclohexen-1-ol 2-cyclohexen-1-one were produced. The formation of these three products is characteristic of a competing boron-catalyzed homolytic decomposition of the hydroperoxide (*10*). With less reactive olefins, such as 1-octene, the latter reaction predominates, leading to low epoxide selectivities.



(V)

Comparison of Boron with Molybdenum Catalysts

It is of interest to compare the activity of the boron catalysts with that of molybdenum catalysts. The latter are known (*2*) to be the most active catalysts for epoxidations with hydroperoxides. The second-order rate constants for the epoxidation of cyclohexene with *tert*-butyl hydroperoxide in the presence of (III) and $MoO_2(acac)_2$ are 2×10^{-5} M^{-1} s^{-1} ([catalyst] = 0.025 M) and 2.7×10^{-3} M^{-1} s^{1} ([catalyst] = 0.002 M), respectively. Molybdenum-catalyzed epoxidations are, thus, about 10^3 times faster than epoxidations performed with the active boron catalyst (III). This result is in agreement with the fact that, e.g., molybdenum (VI) oxide is a stronger Lewis acid than boron oxide (*11*).

CONCLUSIONS

The rates of boron-catalyzed epoxidations of olefins with hydroperoxides are dramatically influenced by the structure of the catalyst. Electron-attracting ligands, by increasing the electrophilicity of the metal atom, enhance the catalytic activity. Yet, even the most effective catalysts are about 10^3 times less active than conventional molybdenum catalysts. Moreover, the boron catalysts, in contrast to the molybdenum catalysts, have only a limited lifetime due to deactivation via alcoholysis and/or oxidative destruction of the ligands.

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