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Preliminary communication

AN ANOMALOUS COURSE FOR THE HYDROGEN PEROXIDE OXIDATION OF "ATE" COMPLEXES OF 9-BORABICYCLO[3.3.1]-NONANE

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Summary

In contrast to alkaline hydrogen peroxide oxidations of *B*-alkyl-9-borabicyclo[3.3.1]nonane (B-alkyl-9-BBN) derivatives, which yield only the corresponding alcohol and *cis*-1,5-cyclooctanediol, oxidations of the lithium-dialkyl-9-BBN "ate" complexes give a mixture of products containing substantial amounts of *cis*-bicyclo[3.3.0]octan-1-ol. The rearrangement of the bicyclo[3.3.1]nonyl structure to the bicyclo[3.3.0]octyl framework apparently involves an attack by the hydrogen peroxide on the bridgehead hydrogen of the organoborane followed by concurrent or subsequent bond migrating from boron to carbon.

The conversion of organoboranes to alcohols by oxidation with alkaline hydrogen peroxide is perhaps the most widely used reaction in the realm of organoborane chemistry. Its popularity as an analytical and preparative method stems from the fact that it conveniently and quantitatively transforms all of the alkyl groups on boron into alcohols while maintaining the regio- and stereochemical integrity of the functional carbon [1,2].

We wish to report an unusual rearrangement in the course of the hydrogen peroxide oxidation of lithium dialkyl "ate" complexes of 9-borabicyclo-[3.3.1]nonane**. The exceptional synthetic utility of this bicyclic borane system has been reported [1-5]. In the course of a detailed study of the

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[*] Graduate Research Assistant on grant GM 10937 from the National Institutes of Health.

[**] 9-Borabicyclo [3 3 1] nonane = 9-BBN

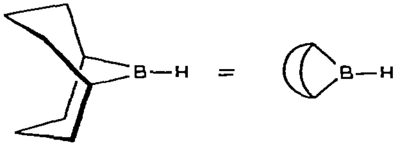
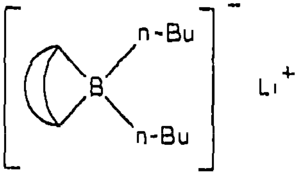
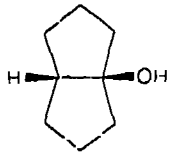
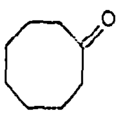
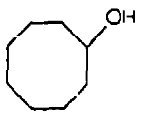
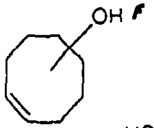
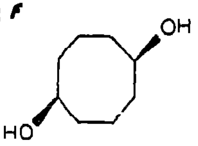


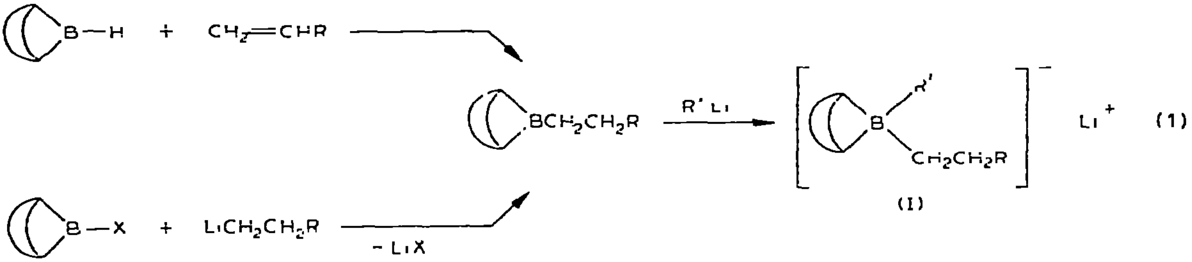
TABLE 1

HYDROGEN PEROXIDE OXIDATION OF 

Solvent[a]	Conditions[b]	Oxidation products[c,d]					
		n-BuOH[e]	 (II)	 (III)		 [f]	 (IV)
THF	Alkaline	92	27	68	0.7	1.3	7
Pentane	Alkaline	87	46	24	2	5	25
THF	Alkaline + EtOH	96	33	53	0.5	1.5	12
Pentane	Alkaline + EtOH	90	45	36	1.3	2.7	18
THF	Neutral + EtOH	95	65	14	0.6	3.4	18
Pentane	Neutral + EtOH	98	60	14	1	2	24
THF	Neutral	93	48	50	7[g]		2
Pentane	Neutral	85	61	8	5[g]		9

[a] The solvent in which the "ate" complex was prepared. [b] Alkaline: 1 equiv. 3 *M* NaOH and 4 equiv. 30% H_2O_2: Neutral: 4 equiv. 30% H_2O_2 only: EtOH: ~ 30% by volume of the origional mixture. [c] Yields by VPC analysis on 6 ft × 1/4 in. 10% XE-60, 6 ft × 1/4 in. 10% QF-1, and 24 ft × 1/8 in. 7.5% Glycerol. [d] Major products were isolated by preparative VPC and identified by comparison of their IR, NMR, and mass spectra with those of authentic materials. Minor products were identified by combined VPC mass spectrometry. [e] Yield based on two groups. [f] Isomer ratio not determined. [g] Sum of the saturated and unsaturated alcohols.

synthesis of those *B*-alkyl-9-BBN derivatives not available via hydroboration, we had occasion to prepare lithium dialkyl-9-BBN "ate" complexes (I) by two routes (eqn. 1) [5].



We undertook to confirm these structures by the usual oxidation with hydrogen peroxide. Surprisingly, the oxidations yielded major products other than those expected. Major components of the mixture from these oxidations proved to be *cis*-bicyclo[3.3.0]octan-1-ol (II) and cyclooctanone (III). Reexamination of the oxidation of several simple 9-BBN derivatives (*B*-n-butyl, *B*-H, *B*-OMe, and *B*-Cl) confirmed the formation of the expected *cis*-1,5-cyclooctanediol (IV) with only trace amounts of the anomalous products.

In a typical experiment, 5 mmol of *B*-n-butyl-9-BBN in 7.5 ml of dry, olefin-free pentane was treated with an equimolar amount (2.5 ml of 2.0 *M*) of carefully standardized n-butyllithium in hexane at −78° C [1]. Upon warming, a white precipitate of the "ate" complex separated. To the stirred slurry was added 3 ml of ethanol*. The solid dissolved without the liberation of gas or heat. The resulting clear solution was oxidized at room temperature by the dropwise addition of 2.25 ml (four equivalents) of 30% hydrogen peroxide**. In sharp contrast to the oxidation of simple organoboranes, an induction period was observed. However, after 5 to 10 minutes the reaction mixture began to boil, and each subsequent drop of peroxide produced the usual vigorous reaction. After the addition of 2.5 g of potassium carbonate, 10 ml of ether, and a suitable internal standard, VPC analysis revealed the presence of 66% II and 14% III, as well as other products (Table 1).

We thought that the unusual results might be due to the presence of hydrocarbon solvent. Accordingly, we prepared the "ate" complex in THF, obtaining a clear solution. The oxidation was carried out as previously described. An induction period was noted, and analysis showed the products to be similar. We then explored the possibility that the absence of the aqueous sodium hydroxide, normally used in the oxidation of simple R_3B, was the cause of the anomalous products. However, the addition of one equivalent of 3 *M* sodium hydroxide did not circumvent the formation of the unusual products. Other variations in the oxidation conditions only altered the distribution of products. However, II and III were always present in substantial amounts (Table 1).

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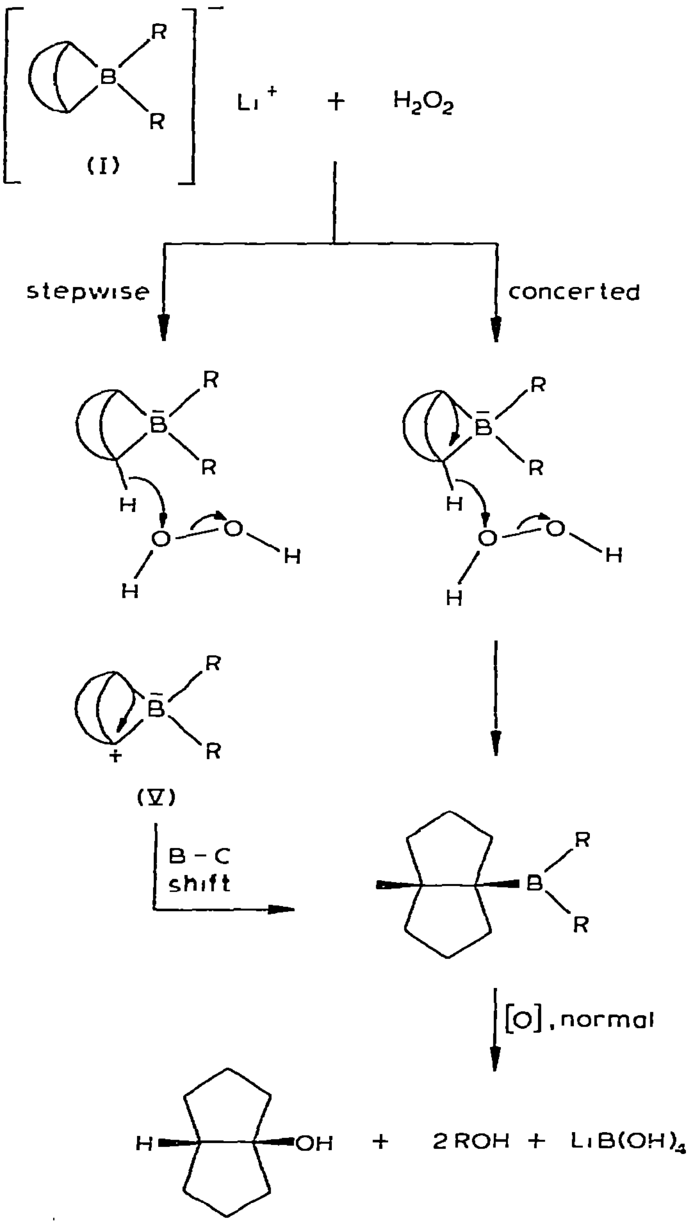
*Ethanol is usually added as a cosolvent when oxidations are carried out in non-polar solvents.

**Additional base was not added because one equivalent of base is formed during the oxidation.

The question arose as to whether the "ate" complexes were undergoing rearrangement prior to oxidation. The di-n-butyl complex was prepared by mixing the stoichiometric amounts of *B*-n-butyl-9-BBN and n-butyllithium in the desired solvent as described previously*. The product from pentane was isolated by removal of the solvent under vacuum at room temperature

SCHEME 1



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*Similar results were obtained with other *B*-alkyl-9-BBN derivatives and other primary lithium reagents, such as methyllithium.

The weight of this material corresponded exactly with that of the expected addition compound. However, when THF was used, removal of the solvent at 25 °C produced a viscous liquid corresponding in weight to the "ate" complex plus one equivalent of THF.

The infrared spectrum of the viscous liquid from THF corresponded exactly with that of the solid from the pentane reaction (mulled in Nujol) when the bands due to THF (and Nujol) were ignored. These spectra contained no absorptions in the boron hydride region (4-6 microns). The ^{11}B NMR spectra of the solution from the THF reaction and a THF or ethanol solution of the solid from the pentane reaction were identical [^{11}B NMR: δ + 18.5 ppm, singlet]. Also, the complex showed no ageing effect. Oxidation of samples which had been allowed to stir overnight in pentane or THF gave essentially the same results as freshly prepared samples. It is therefore reasonable to assume that the product is the same in both pentane and THF, that it is the simple addition compound, and that the rearrangement occurs during the oxidation.

Although we made no attempt to explore the mechanism, it appears that the formation of the bicyclic alcohol (II) must involve an attack by the hydrogen peroxide on the bridgehead hydrogen of the bicyclic "ate" complex with concurrent or subsequent migration of the boron-carbon bond (Scheme 1). If the migration step is not concurrent with the loss of the bridgehead hydrogen, a zwitterionic intermediate (V) like that originally proposed by Jager and Hesse must be implicated [6].

In any case, irrespective of the precise mechanism and timing, the reaction provides a new and convenient route to the bicyclo[3.3.0]octyl system.

Acknowledgement

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