

TRANSFER REACTIONS INVOLVING BORON—XIX

OXIDATION STUDIES INVOLVING MONO- AND BISBORONIC ACID DERIVATIVES OF THE PHENYLETHYL AND STYRYL SYSTEMS^{1, 2}

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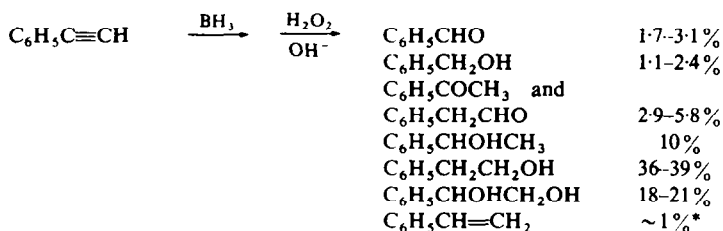
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Abstract—The oxidation of the 1- and 2-phenylethaneboronic esters (4 and 1), α - and β -styreneboronic esters (5 and 2), 2-phenylethane-1,1-bisboronic ester (3), and 1-phenylethane-1,2-bisboronic ester (6) with basic hydrogen peroxide and Fenton's reagent has been extensively studied. Compounds 1, 2, 4 and 5 undergo normal oxidations with basic hydrogen peroxide to give the expected alcohols and carbonyl compounds. Similar treatment of 3 gives a number of products of which the C—C bond cleavage products benzaldehyde and benzyl alcohol predominate (up to 60% and 20% respectively). Basic hydrogen peroxide oxidation of 6 similarly produces a number of products including benzaldehyde and acetophenone. Compounds 2, 3, 4 and 6 react with Fenton's reagent to produce a number of products including C—C bond cleavage and elimination products. Mechanisms are proposed for these oxidation reactions based on the known radical reactivity of compounds 1, 3, 4 and 6, the known chemistry involving Fenton's reagent, and oxidation studies of selected model systems with Fenton's reagent.

The following important conclusions may be drawn from this study: (1) Reactions with basic solutions of hydrogen peroxide may produce radical reactions involving hydroxyl and/or hydroperoxyl radical; (2) Reactions with Fenton's reagent involve both hydroxyl and hydroperoxyl radicals (the latter believed to be predominating) in addition reactions with olefins and radical combination reactions.

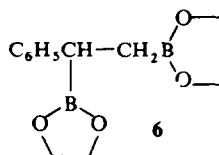
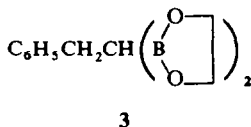
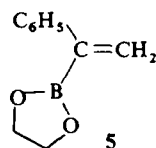
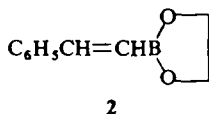
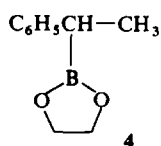
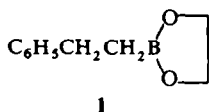
EARLIER investigations in our laboratories on the dihydroboration of acetylenes followed by basic hydrogen peroxide oxidation demonstrated that a number of products were formed including olefinic and C—C bond cleavage products.⁴ For example, the dihydroboration of phenylacetylene in tetrahydrofuran, followed by basic hydrogen peroxide oxidation, produced the products illustrated below.



Deuterium labelling studies showed that deuterium was introduced in both the 1- and 2-positions of the 1- and 2-phenylethanol. Based on the data obtained with this system, and other additional data obtained with other systems, mechanisms were proposed to account for the formation of the various products based on a variety of base-catalyzed reactions. It was noted however, that substantiation or refutation of the proposed mechanisms must await the synthesis of appropriate

* Styrene was formed in 12% yield when the hydroboration was carried out in diglyme.

model compounds for more detailed studies. The preceding article¹ describes the synthesis and chemical and physical characterization of the model compounds **1** through **6** related to the phenylacetylene system. A recent communication⁵ from our laboratories confirmed our earlier experimental observations and indicated that not all of the proposed base-catalyzed mechanisms were operative, but that some of the products were being formed in radical reactions as demonstrated by the use of Fenton's Reagent. This article describes in detail our oxidation studies of compounds **1** through **6** under normal basic hydrogen peroxide conditions and with Fenton's Reagent.



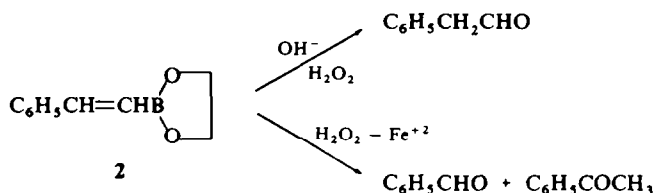
RESULTS

The normal oxidation of ethylene 2-phenylethaneboronate (**1**) with basic hydrogen peroxide produced 2-phenylethanol and only trace quantities of benzaldehyde, acetophenone, and phenylacetaldehyde. Treatment of **1** with Fenton's reagent produced substantial quantities of the abnormal oxidation products as indicated in Table 1. The total yield of the oxidation products was nearly 100% in all cases.

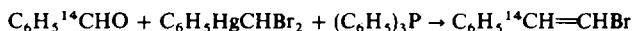
TABLE 1. OXIDATION PRODUCTS OF ETHYLENE 2-PHENYLETHANE-BORONATE (**1**)

Product	$\text{H}_2\text{O}_2\text{-OH}^-$	$\text{H}_2\text{O}_2\text{-Fe}^{+2}$
Benzaldehyde	trace	4.6%
Acetophenone	trace	8.9%
Phenylacetaldehyde	trace	3.2%
2-Phenylethanol	99%	82.3%

Oxidation of ethylene β -styreneboronate (**2**) with basic hydrogen peroxide gave essentially only phenylacetaldehyde, whereas treatment of **2** with Fenton's reagent gave benzaldehyde (60%) and acetophenone (36%).



The products derived from the oxidation of diethylene 2-phenylethane-1,1-bisboronate (**3**) with hydrogen peroxide in 20% sodium hydroxide and at pH 9, and with Fenton's reagent are tabulated in Table 2. Oxidation of 3-2- ^{14}C , prepared as outlined below beginning with benzaldehyde - α - ^{14}C and phenyl(dibromomethyl)-mercury⁶ to give β -bromostyrene- α - ^{14}C with conversion to 3-2- ^{14}C as described in the accompanying article,¹ with basic hydrogen peroxide produced benzaldehyde and benzyl alcohol which retained *all* of the ^{14}C . This experiment indicates that there



are no carbon skeletal rearrangements occurring during the reaction of **3** with Fenton's reagent.

TABLE 2. OXIDATION PRODUCTS OF DIETHYLENE 2-PHENYLETHANE-1,1-BISBORONATE (**3**)

Product	H_2O_2 - 20% NaOH	H_2O_2 (pH 9)	$\text{H}_2\text{O}_2 + \text{Fe}^{+2}$ ^a
Benzaldehyde	60	71	41
Benzyl alcohol	20	12	—
2-Phenylethanol	5	—	—
Phenylacetaldehyde	9	15	40
Acetophenone	1	2	19

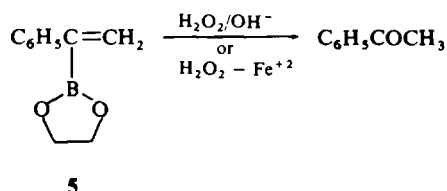
^a Approximately pH1.

Oxidation of ethylene 1-phenylethaneboronate (**4**) with basic hydrogen peroxide produces essentially only 1-phenylethanol. Treatment of **4** with Fenton's reagent produced a number of products which are indicated in Table 3.

TABLE 3. PRODUCTS FORMED FROM ETHYLENE 1-PHENYLETHANEBORONATE (**4**) WITH FENTON'S REAGENT

Product	Yield
Benzaldehyde	8.0
Benzylalcohol	9.7
1-Phenylethanol	30.5
Acetophenone	27.5
Styrene	12.5

Oxidation of ethylene α -styreneboronate (5) with either basic hydrogen peroxide or Fenton's reagent produced high yields of acetophenone and only trace quantities of benzaldehyde.



The products formed in the hydrogen peroxide oxidation of diethylene 1-phenylethane-1,2-bisboronate (6) in 20% sodium hydroxide and in pH 9 buffer, and with Fenton's reagent are tabulated in Table 4. The results obtained by treating 6 with Fenton's reagent varied greatly from run to run (Experimental). This was not observed

TABLE 4. OXIDATION PRODUCTS OF DIETHYLENE 1-PHENYLETHYL-1,2-BISBORONATE (6)

Product	H ₂ O ₂ - 20% NaOH	H ₂ O ₂ (pH 9)	H ₂ O ₂ - Fe ⁺²
Benzaldehyde	12%	55%	19 → 48%
Acetophenone	6%	27%	0 → 43%
1-Phenylethanol	70%	14%	—
2-Phenylethanol	12%	4%	—
Phenylethanediol	present	present	—
Styrene	—	—	9 → 81%

^a Yields of the first four products are normalized for comparison purposes. Total yields of these products averaged 75 → 85%. The yield of phenylethanediol could not be accurately determined, but appeared to be near 10 → 15%.

in the reactions of the other organoboron derivatives with Fenton's reagent. Hydrogen gas was also formed in the reaction of 6 with Fenton's reagent, the yield of which corresponded very closely with the yield of the styrene produced. This is in agreement with our earlier observation.⁴

A series of control experiments were run on the various products formed in the oxidation reactions of 1 through 6 with Fenton's reagent under the same experimental conditions. These results are tabulated in Table 5.

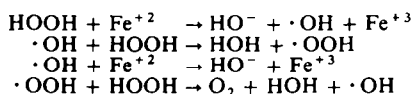
TABLE 5. OXIDATION OF MODEL SYSTEMS WITH FENTON'S REAGENT

Starting material	Product(s)	Yield (%)
Benzyl alcohol	Benzaldehyde	23.8
Styrene	Benzaldehyde	1.2
Ethylbenzene	1-Phenylethanol	7.1
	Acetophenone	3.2
1-Phenylethanol	Acetophenone	15.6

DISCUSSION

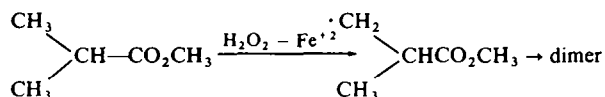
The formation of the abnormal oxidation products from **1** through **6** with basic hydrogen peroxide are undoubtedly the result of radical reactions as indicated by the reactions with Fenton's reagent.⁵ However, before launching into a mechanistic discussion, it is important to consider the nature of Fenton's reagent itself, the known reactions of the radical species present in Fenton's reagent, and the fate of possible intermediates formed by reaction of these radical species with compounds **1** through **6**.

The following sequence of reactions are believed to take place:⁷

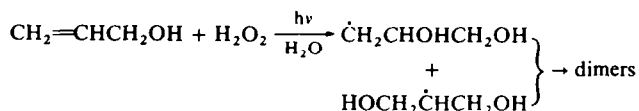


The latter reaction does not appear to be occurring in the reactions with **1** through **6** as no gas evolution is noted.*

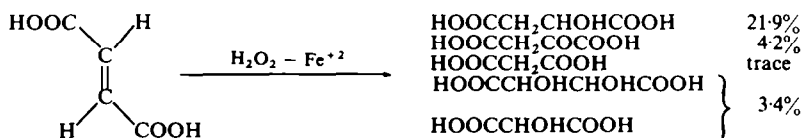
Either, or both the hydroxyl and hydroperoxyl radicals appear to be capable of abstracting hydrogen atoms from organic compounds leading to organic free radical intermediates. Boguslavskaya and Razuvaev⁹ have reported that Fenton's reagent (no attempt will be made to designate the reactive species) is capable of hydrogen atom abstraction as illustrated below, the intermediate organic free radical undergoing dimerization.



The addition of hydroxyl radical to olefins has been proposed by several groups of investigators. Volman and coworkers¹⁰ have proposed that hydroxyl radical adds to allyl alcohol with the resulting isomeric dihydroxypropyl radicals undergoing dimerization.

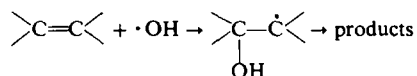


Nofre *et al.*¹¹ have characterized a number of products derived from fumaric acid on treatment with Fenton's reagent.

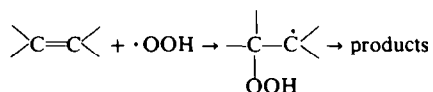


* A similar observation has been made by Boxendale⁸ that oxygen evolution is repressed in the presence of methylacrylate and acrylonitrile.

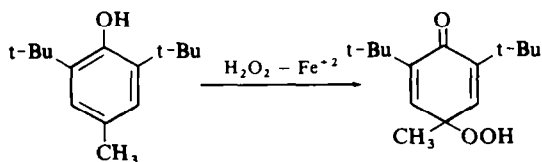
These authors proposed that the reaction proceeded *via* addition of hydroxyl radical to the double bond with further reactions ensuing from the β -hydroxy free radical.



As will be developed in the following discussion, these products can just as easily be formed by addition of hydroperoxyl radical to the double bond followed by subsequent reaction. Evidence for the formation of the hydroperoxyl radical is provided



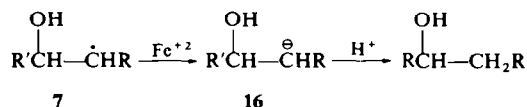
by Coppinger¹² in the isolation of the hydroperoxyl radical adduct of 2,6-di-*t*-butyl-4-methylphenol.



The detection of the presence of the hydroperoxyl radical during the ferrous ion catalyzed decomposition of hydrogen peroxide provides several additional mechanistic pathways, in addition to those outlined in the foregoing paragraphs, for product formation as illustrated in Scheme I. There are several features of Scheme I which are not completely clear and it appears that there is no simple way to clarify these ambiguities.

(1) The formation of the alkyl radical **9** from the hydrocarbon can occur by hydrogen atom abstraction by hydroxyl and/or hydroperoxyl radical. Although we cannot distinguish between these possibilities, this will not be critical in our discussions of the possible mechanisms for product formation with compounds **1** through **6**.

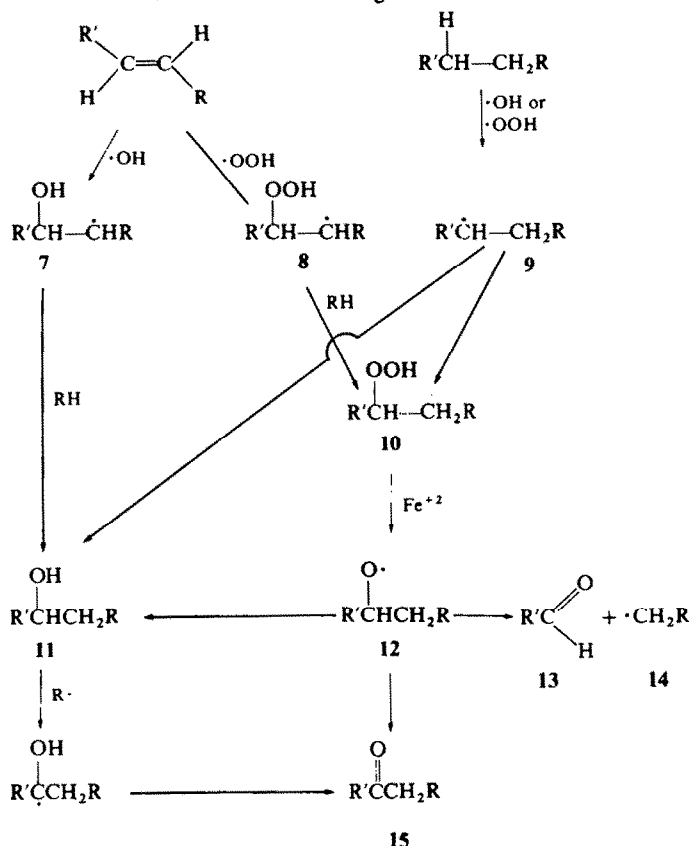
(2) The conversion of the β -hydroxyalkyl radical **7** to alcohol **11**, and the β -hydroperoxyalkyl radical **8** to alkylhydroperoxide **10**, may occur directly by a hydrogen atom abstraction from some species RH, or by a reduction of **7** and **8** to the corresponding carbanions by ferrous ion with subsequent protonation.¹¹ This latter



pathway might be more favorable when such anions are stabilized by the R functional group, for example a carbonyl system or atom with a vacant *p*-orbital such as boron in the present study. Again, there appears to be no way to distinguish between the two possibilities at the present time and conversions such as **7** \rightarrow **11** and **8** \rightarrow **10** in this article will be employed without designation of the pathway involved.

SCHEME 1

Possible Mechanistic Pathways for Product Formation Involving Reactions of Hydrocarbons and Olefins with Fenton's Reagent.



(3) The formation of alcohol **11** may occur *via* two pathways from each starting material: olefin $\rightarrow 7 \rightarrow 11$, or olefin $\rightarrow 8 \rightarrow 10 \rightarrow 12 \rightarrow 11$; and hydrocarbon $\rightarrow 9 \rightarrow 11$, or hydrocarbon $\rightarrow 9 \rightarrow 10 \rightarrow 12 \rightarrow 11$. The pathways *via* alkylhydroperoxide (**10**) appear attractive in that the conversion of **10** \rightarrow **12** is a known reaction¹³ and the conversions of **12** to **11**, **13** and **14**, and **15** also represent known reactions.¹⁴ Furthermore, the observation that considerable C—C bond cleavage occurs in some of our organoboron systems adds further support to the proposed formation of alkylhydroperoxides as reaction intermediates. The competition between pathway **12** \rightarrow **13** + **14** versus **12** \rightarrow **11** and **12** \rightarrow **15** is undoubtedly a function of the ease of formation (stability) of the radical **14**; the more stable **14**, the greater will be the tendency for its formation.

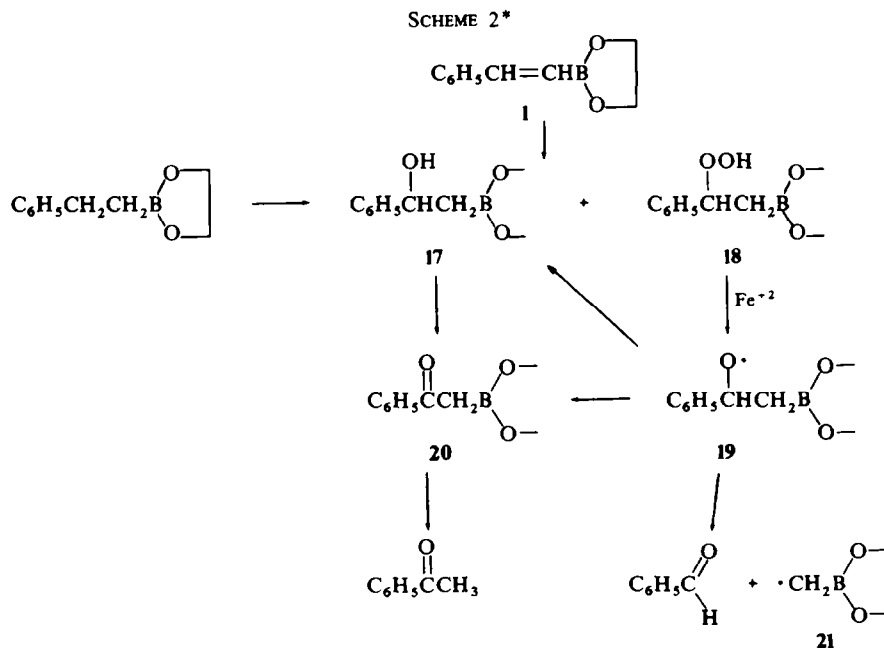
(4) The formation of the ketone **15** may occur directly from **12** or *via* alcohol **11**. Both reaction pathways have been demonstrated to occur.¹⁴

Applying the foregoing to the oxidation results of compounds **1** through **6**, one may write reasonable mechanisms for the formation of practically all of the products.

The reaction of ethylene 2-phenylethylboronate (1) with Fenton's reagent produced mostly 2-phenylethanol along with low yields of benzaldehyde, acetophenone, and phenylacetaldehyde (Table 1). The 2-phenylethanol is the normal oxidation product of 1 with basic hydrogen peroxide. The phenylacetaldehyde, formed in quite low yield, undoubtedly arises by oxidation of the 2-phenylethanol by Fenton's reagent as demonstrated in a control experiment (Table 5). The benzaldehyde and acetophenone represent "abnormal" oxidation products. A similar assessment of the oxidation products of 2 through 6 can be made. Phenylacetaldehyde is the normal oxidation product of ethylene β -styreneboronate 2, and acetophenone and benzaldehyde are the abnormal products. With diethylene 2-phenylethane-1,1-bisboronate (3), phenylacetaldehyde is the normal oxidation product and acetophenone, benzaldehyde and benzyl alcohol are the abnormal products. The formation of 2-phenylethanol occurs by hydrolysis of 3 to give 2-phenylethaneboronic acid followed by oxidation.⁵

Ethylene α -styreneboronate (4) produces only the normal oxidation product acetophenone on treatment with basic hydrogen peroxide and Fenton's reagent. 1-Phenylethanol is the normal oxidation product of ethylene 1-phenylethaneboronate (5); acetophenone, benzaldehyde, and benzyl alcohol comprising the abnormal products. Phenylethane diol is the normal oxidation product of diethylene 1-phenylethane-1,2-bisboronate. 1- and 2-Phenylethanols are formed by hydrolysis of 6 to 1- and 2-phenylethaneboronic acids followed by oxidation.⁴ Acetophenone, benzaldehyde, and styrene comprise the abnormal products.

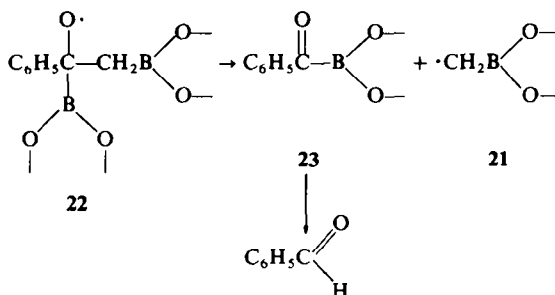
The proposed mechanisms for the formation of acetophenone and benzaldehyde from 1 and 2 are outlined in Scheme 2.



* The ethylene boronate functional group undoubtedly hydrolyzes to the corresponding boronic acid under the experimental conditions. No attempt will be made to specify the functional group bonded to the oxygen of the boronic acid groups.

The α -borylacetophenone intermediate **20** is proposed to undergo a facile hydrolysis to give acetophenone. Tufariello¹⁵ has observed a very facile hydrolysis of the C—B bond of an α -borylester, a system closely related to the present system.

Similar mechanistic schemes can be written for the formation of the oxidation products of **3**, **5** and **6**. The fragmentation of intermediate radical **22**, derived from **6**, produces benzoylboronic acid (**23**) which is proposed to undergo hydrolysis to benzaldehyde. This is consistent with our earlier observation that deuterium is incorporated



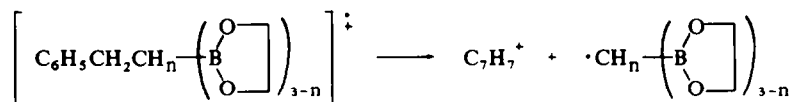
in the benzaldehyde when the oxidation is carried out in deuterium oxide.⁴ The chemistry of systems such as **20** and **23** is under further study in our laboratories.

As in Scheme 1, we are faced with alternate pathways for the formation of some of the products. Differences in product ratios derived from the different substrates allow a qualitative evaluation of their importance. The formation of alcohol **17** and hydroperoxide **18** from **2**, **3**, **5** and **6** occurs *via* the intermediate benzylic radical derived by abstraction of a benzylic H atom. The relative yields of alcohol **17** and hydroperoxide **18** derived from **1** and **2** may be estimated from the yields of acetophenone and benzaldehyde. As the oxidation of 1-phenylethanol with Fenton's reagent gave only 15.6% of acetophenone under similar reaction conditions, it is therefore conceivable that a good portion of the acetophenone from **2** is derived from alcohol **17** *via* **20**. Thus it would appear that hydroxyl and hydroperoxyl radicals react at comparable rates with the intermediate benzylic radical to give alcohol **17** and hydroperoxide **18**. A similar analysis of the reaction of ethylene β -styreneboronate (**2**) with Fenton's reagent (benzaldehyde: acetophenone ratio of 1.66 compared to 0.52 from **1**) indicates that hydroperoxyl radical adds more rapidly to **2** than does hydroxyl radical. (The position of hydroxyl and hydroperoxyl radical attack in **2** is the same as observed for bromine atom attack in the radical hydrobromination of **2**).

A point of great interest is the dramatic increase in the abnormal oxidation products, as well as the change in the benzaldehyde:acetophenone (B:A) ratio as one progresses from ethylbenzene (no abnormal products, B:A = 0) to ethylene 2-phenylethane-boronate (**1**) (~6–7%, B:A = 0.52) to diethylene 2-phenylethane-1,1-bisboronate (**3**) (>41%, B:A = 2.22). The relatively low yield of abnormal oxidation products derived from **1** is readily attributed to a more rapid normal oxidation of **1** to give 2-phenylethanol. As pointed out in the previous paper, diethylene 2-phenylethane-1,1-bisboronate (**3**) is quite nonreactive toward electrophilic substitution of boron and the radical reactions thus predominant. The changes in the B:A ratios are readily

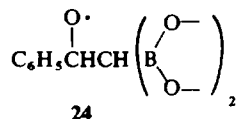
understood if one considers the possible fates of the alkoxy radical **19**. The competition between the three reaction paths for the disappearance of the alkoxy radicals of the general structure **12** (Scheme 1) in the systems involved in this study will depend primarily on the radical stabilizing ability of R in radical **14**, the factors affecting the other two reaction paths remaining essentially constant. Assuming that the ratio of hydroxyl and hydroperoxyl radical reactions with the initially formed benzylic radical remains the same in these systems, one is able to interpret the product ratios in terms of the relative importance of the three modes of reaction of the alkoxy radical **19**. It is apparent that as the number of boron function groups attached to the radical increases from zero for ethylbenzene* to two for diethylene 2-phenylethane-1,1-bisboronate (**3**), the preference for formation of radical cleavage products increases indicating increased stabilization of the radical of type **21**.

Additional evidence for this proposed trend of radical stabilities is derived from the mass spectral cracking patterns of **1** and **3**†. The parent ions derived from ethylbenzene, **1**, and **3** undergo increasingly greater fragmentation according to the equation below as the number of boron atoms on the β -carbon increases; the m/e 91: parent



ion ratio for ethylbenzene ($n = 3$) being 100:30, for ethylene 2-phenylethaneboronate (**1**, $n = 2$) 100:30, and for diethylene 2-phenylethane-1,1-bisboronate (**3**, $n = 1$) no parent ion with the 91 m/e peak representing 26% of the total ion abundance with m/e greater than 40.

The results of the basic hydrogen peroxide oxidation of diethylene 2-phenylethane-1,1-bisboronate (**3**) differ substantially from those obtained in the Fenton's reagent oxidation of **3** (Table 2), and the results depend on the pH of the reaction mixture. At relatively high pH 2-phenylethanol is found as a product, undoubtedly arising by base-catalyzed hydrolysis of **3** to 2-phenylethaneboronic acid followed by oxidation. The benzaldehyde: acetophenone ratio is pH dependent, increasing at higher pH values indicating that the alkoxy radical **24** (or conceivably **19**)



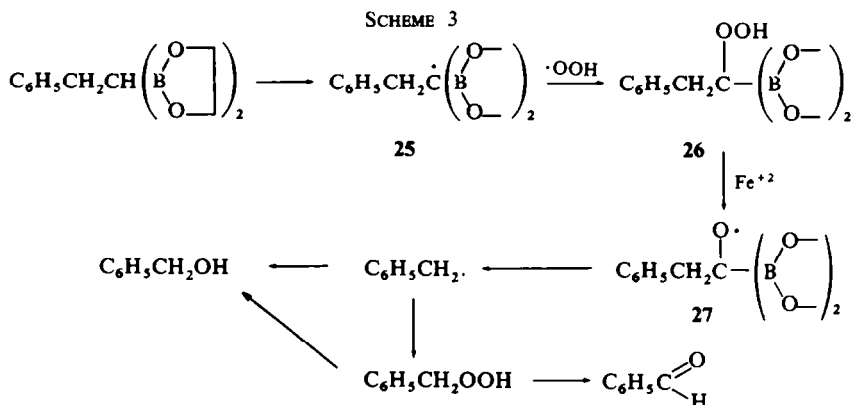
prefers to undergo more extensive C—C bond cleavage at the higher pH values. The pH dependence on the fate of the alkoxy radical is not completely unexpected as the stability of radicals of type **21** would be expected to depend on the degree of

* The ferrous ion catalyzed decomposition of 1-phenylethylhydroperoxide has been shown by Kharash¹⁴ to produce 94.5% acetophenone and 5.5% 1-phenylethanol (the percentages have been normalized).

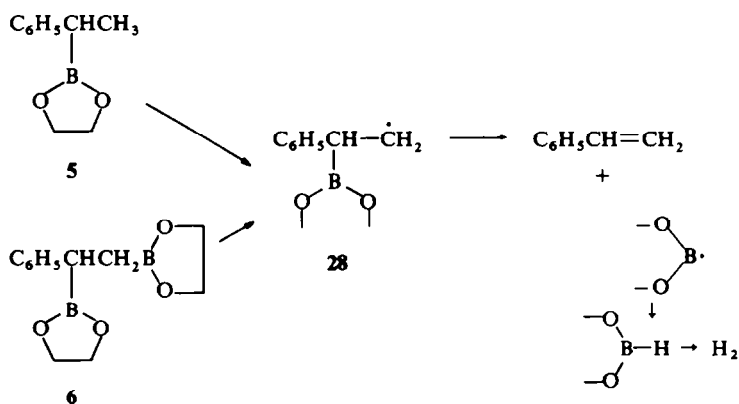
† We wish to thank Prof. T. Kinstle of Iowa State University for recording the mass spectra of compounds **1** through **6**. A detailed discussion of these mass spectra, and those of other related systems will be presented at a later time.

ionization of the boronic acid functional group; the stability apparently increasing at the higher pH values.


Benzyl alcohol is also formed during the oxidation of **3** at the higher pH values. Employing radical fragmentation mechanisms similar to those outlined in Schemes 1 and 2 for cleavage products, and the observation that bora substituted radicals appear to be more readily formed at higher pH values, the following mechanism (Scheme 3) is proposed for the formation of the benzyl alcohol. Abstraction of a *beta*-H atom of **3**, favored by the apparently greater radical stabilizing ability of the boronic acid functional group at high pH, followed by reaction of the intermediate radical **25** with hydroperoxyl radical gives **26**. Decomposition of **26** with ferrous ion leads to the production of the radical (**27**) which fragments to produce the benzyl radical and ultimately benzyl alcohol, and benzyl alcohol or benzaldehyde via the hydroperoxide. A similar scheme may also be used to describe the formation of benzyl alcohol from ethylene 1-phenylethaneboronate (**5**). From the relative reactivities of ethylbenzene, **2**, and **5** described in the previous article,¹ abstraction of a β -hydrogen of **5** with the more reactive species in Fenton's reagent is not inconceivable.



The formation of styrene, and an equivalent amount of hydrogen, from **5** and **6** is depicted below. The formation of hydrogen, or deuterium (D_2) in deuterium oxide from **6**, demands the formation of a >B-H (>B-D) species. It is convenient to



picture this elimination proceeding via radical **28**, derived by β -hydrogen atom

abstraction from **5** or by $\cdot\text{B}$  abstraction from **6**.

SUMMARY

The modes of formation of the anomalous basic hydrogen peroxide oxidation products derived from **3** and **6** have been clarified by comparison with oxidation studies involving compounds **1** through **6** and other model systems with Fenton's reagent. In contrast, compounds **1**, **2**, **4** and **5** undergo normal oxidation reactions with basic hydrogen peroxide. The radical oxidation reactions involving organoboron derivatives become important only when the typical electrophilic substitution, or rearrangement, reactions become less favorable, for example with **3** and **6**, allowing the radical reactions to compete successfully for the substrate.

Important conclusions which may be drawn from this investigation are: (1) Basic solutions of hydrogen peroxide may produce radical reactions involving hydroxyl or hydroperoxyl radicals; (2) Reactions involving Fenton's reagent appear to produce substantial quantities of hydroperoxyl radical which may be more important in determining product formation than hydroxyl radicals. These reactions include additions to olefins and radical combination reactions.

Further investigations will be required to clarify the effect of substituents on boron on the course of the reactions, the role of the phenyl group in determining the reactivity of compounds **1** through **6**, and the chemistry of the intermediates proposed in the oxidation reaction mechanisms.

EXPERIMENTAL

Oxidation with basic hydrogen peroxide. To a soln of the compound, normally 100 to 300 mg, in 5 ml THF at 0° was added a 50% excess of 20% NaOHaq immediately followed by the addition of a 50% excess 30% H₂O₂. The reaction mixtures were stirred at room temp for 1 hr and extracted with several portions ether. The combined extracts were dried over MgSO₄. The extract was analyzed by GLPC on Carbowax 20 M on Chromsorb W Columns employing an internal standard and predetermined response ratios to determine the yields.

Oxidation in pH 8.8 buffered media. A 50% aqueous dioxan 8.8 buffer was prepared by dissolving 0.373 g KCl, 0.310 g boric acid, and 3.9 ml 0.1N NaOH in 100 ml 50% by volume aqueous dioxan. The sample, normally 100 to 150 mg, was dissolved in approximately 50 ml of the buffer and oxidized by the addition of 1 ml 30% H₂O₂. The reaction mixture was extracted and analyzed as described above.

Oxidations employing Fenton's reagent. To a mixture composed of 10 ml freshly prepared 0.1N ferrous ammonium sulfate, 5 ml 0.5N H₂SO₄, and 0.5 ml AcOH cooled to 0° was added approximately 0.0013 mole of the compound to be oxidized. The reaction mixtures were stirred at room temp for 2 hr, extracted with ether and analyzed as described above.

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