acid[13] yielded a mixture of *cis*- and *trans*-2-phenyl-2-butenes from which the pure cis isomer could be obtained by fractional distillation on a spinning-band column. Distillation of 13 g of the same mixture from 0.1 g of *p*-toluenesulfonic acid gave a mixture of 20% cis and 80% trans olefin from which the pure trans olefin was isolated by preparative GLC on the same column used to purify 3-phenyl-1-butene (above).

Elimination Reactions. Solutions 0.06–0.08 M in the *p*-toluenesulfonate and 0.4–0.5 M in base were prepared, and 5-mL samples were sealed in stainless-steel reaction tubes.[14] The tubes were heated in a constant-temperature bath at the temperatures and for the times quoted in Table I. The reaction mixture was added to 10 mL of cold distilled water and the resulting solution extracted with 10 mL of pentane. The pentane solution was dried and analyzed by GLC on a 16 ft × 0.125 in. column of 15% tris(2-cyanoethoxy)propane on Chromosorb W. Retention times increased in the order *trans*-2-phenyl-2-butene < 3-phenyl-1-butene < *cis*-2-phenyl-2-butene.

Registry No. 1, 10545-60-5; 2, 10588-22-4; 3, 15324-90-0; 4, 935-00-2; 5, 934-10-1.

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Novel Oxidation of Tetrahydrofuran to γ-Butyrolactone with Peroxyphosphoric Acid[1]

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Received September 13, 1979

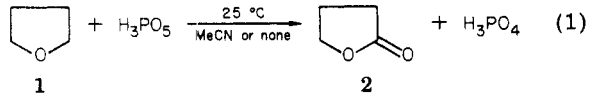
In the course of a kinetic study on the oxidation of *trans*-stilbene with H_3PO_5,[2] we looked for solvents which were miscible with acetonitrile and were not attacked by H_3PO_5. Then we found out that no *trans*-stilbene oxide was obtained on mixing *trans*-stilbene with H_3PO_5 in tetrahydrofuran (THF) in spite of the consumption of H_3PO_5, but another product was formed which was identified as γ-butyrolactone, derived from the solvent THF.

It is known that γ-butyrolactone is obtained by metallic ion-catalyzed decomposition of α-(hydroperoxy)tetrahydrofuran obtained by the autoxidation of THF[3-6] and by the oxidation of THF by RuO_4[7] or $PhSO_2NBr_2$,[8] but there is no report on γ-butyrolactone formation by peracid oxidation of THF.

The present paper reports this novel formation of γ-lactone by the reaction of THF with H_3PO_5. The reaction mechanism will be discussed shortly.

Result and Discussion

The reaction of THF with H_3PO_5 was carried out in MeCN or without solvent at 25 °C. γ-Butyrolactone, which was identified by NMR and GLC analyses, was obtained in 40–45% yield based on decomposed H_3PO_5 (eq 1), assuming H_3PO_5 reacts with equimolar THF.



1 2

(1) Contribution No. 271.
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Table I. Effect of *p*-Benzoquinone (*p*-BQ) on the Yield of γ-Lactone 2 in the Reaction of THF with H_3PO_5 at 25 °C in MeCN

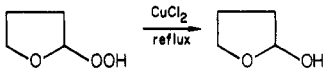
10-[THF]$_0$, M	10-[H_3PO_5]$_0$, M	10-[*p*-BQ]$_0$, M	% decompd H_3PO_5	yield of 2, %
3.0	3.0	0	62.3	41.2
3.0	3.0	3.0	58.7	39.6
6.0	3.0	0	70.4	45.2
6.0	3.0	3.0	64.7	44.7

Table II. Effect of *p*-Benzoquinone (*p*-BQ) on the Pseudo-First-Order Rate Constant in Equation $v = k_{obsd}[H_3PO_5]$ at 25 °C in MeCN[a]

10[*p*-BQ]$_0$, M	$10^5 k_{obsd}$, s^{-1}	10[*p*-BQ]$_0$, M	$10^5 k_{obsd}$, s^{-1}
0	1.48	1.5	1.45
0.6	1.40	3.0	1.37

[a] Initial concentration of THF = 0.67 M, and initial concentration of H_3PO_5 = 0.03 M.

THF was distilled after being refluxed in the presence of $CuCl_2$. This procedure reduces α-hydroperoxide 3 contained in THF to α-hydroxytetrahydrofuran (4), which



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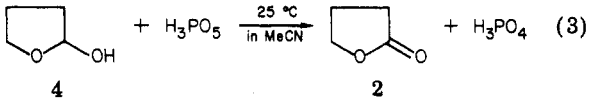
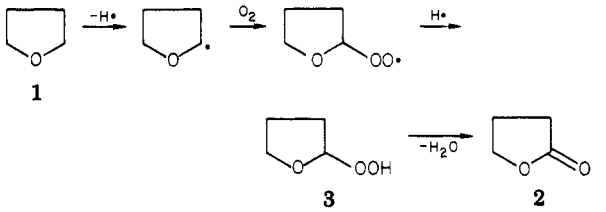


4 2

was easily oxidized with H_3PO_5 to give the γ-lactone quantitatively. However, no 4 was detected by GLC and NMR analyses in THF freshly distilled after treatment with $CuCl_2$. Therefore, THF used in the reaction contains neither 3 nor 4.

The possibility of autoxidation of THF by O_2 (eq 4) was eliminated.



1 3 2

The reaction with H_3PO_5 in two sorts of solution, (a) exposed to the air and (b) deaerated under cooling and then saturated with N_2, gave analogous yields of γ-lactone 2, i.e., 44.1% for a and 42.3% for b. Furthermore, the oxidation in solution b under N_2 bubbling also gave γ-lactone 2 in 41.4% yield. Therefore, the effect of O_2 contained in the solution is negligible.

The effect of *p*-benzoquinone (*p*-BQ) as a radical inhibitor is shown in Tables I and II.

Tables I and II suggest that the addition of *p*-BQ in this system does not affect the yield of 2 or the pseudo-first-order rate constant. These results would exclude the radical mechanism for the formation of 2.

α-Hydroxytetrahydrofuran (4) synthesized alternatively is oxidized quickly by H_3PO_5 to give γ-lactone 2 quantitatively as stated above, where 4 is known to be in equilibrium with γ-hydroxybutanal (5).[9] In fact, even freshly synthesized 4 was in equilibrium with 5 by NMR analysis.

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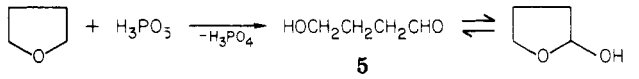
Table III. Effect of Acetic Acid on the Yield[a] of *n*-Butyl Butyrate (7) at 25 °C after 20 h of Reaction[b]

$10[H_3PO_5]_0$, M	$10[CH_3CO_2H]_0$, M	% decompd H_3PO_5	% products: *n*-BuOCO-*n*-Pr (7)	% products: *n*-BuOH	% products: *n*-$BuOCOCH_3$ (8)
0.917		13.3	10.0	38.7	
1.83		13.8	18.5	29.3	
1.83	9.15	12.4	8.4	11.2	23.4
1.83	18.3	11.8	6.4	9.4	25.5
3.67		15.0	22.0	23.8	

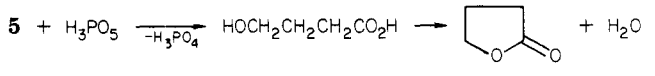
[a] Based on decomposed H_3PO_5. [b] Initial concentration of *n*-$Bu_2O = 1.01 \times 10^{-1}$ M.

Generally, a secondary alcohol is oxidized slower than the corresponding aldehyde, and di-*n*-butyl ether is also oxidized via aldehyde as shown below (eq 6). Therefore, **5** may be a main intermediate in this reaction; i.e., **5** may be more quickly oxidized by H_3PO_5 to give γ-hydroxybutyric acid which is subject to intramolecular esterification to γ-butyrolactone.

In this reaction, the yield of γ-lactone **2** does not exceed 50%. Hence, 2 equiv of H_3PO_5 may be necessary for the oxidation of THF to γ-lactone **2** as shown in eq 5a,b.



(5a)



(5b)

According to eq 5a,b, the yield of γ-lactone **2** should become 80–90% on the basis of the decomposition of 2 mol of H_3PO_5.

The oxidation of THF with peracetic acid (CH_3CO_3H) was conducted under conditions analogous to those with H_3PO_5 (see Experimental Section), but no γ-lactone **2** was detected by NMR and GLC analyses. The reaction of di-*n*-butyl ether **6** with H_3PO_5 at 25 °C for 20 h gave *n*-butyl butyrate (**7**) in 10–22% yield based on decomposed H_3PO_5 (Table III). The rate was slower than that of THF because the consumption of H_3PO_5 was only <15% after 20 h. Therefore, the reactivity of **6** is lower than that of THF. *n*-Butyl butyrate (**7**) would be formed via an intermolecular pathway (eq 6c) rather than an intramolecular

$$\underset{\mathbf{6}}{CH_3CH_2CH_2CH_2OCH_2CH_2CH_2CH_3} \xrightarrow{H_3PO_5} CH_3CH_2CH_2CH_2OH + CH_3CH_2CH_2CHO \quad (6a)$$

$$CH_3CH_2CH_2CHO \xrightarrow{H_3PO_5} CH_3CH_2CH_2CO_2H \quad (6b)$$

$$CH_3CH_2CH_2CH_2OH + CH_3CH_2CH_2CO_2H \rightarrow \underset{\mathbf{7}}{CH_3CH_2CH_2CH_2OCOCH_2CH_2CH_3} + H_2O \quad (6c)$$

$$\mathbf{6} \xrightarrow{H_3PO_5} CH_3CH_2CH_2CH_2OCH(OH)CH_2CH_2CH_3 \quad (7a)$$

$$CH_3CH_2CH_2CH_2OCH(OH)CH_2CH_2CH_3 \xrightarrow{H_3PO_5} \mathbf{7} \quad (7b)$$

one (hemiacetal pathway, eq 7), since the addition of acetic acid results in a high yield of *n*-butyl acetate (**8**) with a decrease of the yield of *n*-butyl butyrate (**7**). Here, both transesterification of *n*-butyl butyrate (**7**) to *n*-butyl acetate (**8**) and esterification via autoxidation did not occur under these conditions.

On the other hand, the reaction of tetrahydropyran with H_3PO_5 gave a trace of the corresponding lactone, and no product was obtained from dioxane. Hence this oxidation seems to be a peculiar reaction of THF with H_3PO_5 to give γ-butyrolactone via intramolecular esterification. Little formation of lactone from tetrahydropyran indicates the lower reactivity of the α-position of the ether oxygen, just like that of dioxane. A lower yield of *n*-butyl butyrate (**7**) than of γ-lactone from THF may be ascribed to the intermolecular esterification (eq 6c).

Experimental Section

Apparatus. GLC analyses were performed on a Yanagimoto gas chromatograph with a FID, Model G 180, using two sorts of columns (PEG 20M and Porapak QS). NMR spectra were recorded on a Hitachi R-24B spectrometer using Me_4Si as an internal standard.

Materials. Acetonitrile was distilled over P_2O_5 (bp 81–82 °C). Peroxyphosphoric acid (H_3PO_5) and peroxyacetic acid (CH_3CO_3H) were prepared by the methods described in our previous papers.[10,11] THF was refluxed in the presence of $CuCl_2$ and was distilled; bp 64–65 °C. α-Hydroxytetrahydrofuran (**4**) was prepared by Meerwein's method:[12] yield 29%, bp 88–89 °C (35 mm); NMR ($CDCl_3$) δ 1.80 (2 H, m, CH_2), 2.01 (2 H, m, CH_2), 3.75 (2 H, m, CH_2), 5.05 (1 H, s, OH), 5.40 (1 H, m, CH). From the NMR spectrum, **4** contained a small amount of 4-hydroxybutanal (**5**) [NMR ($CDCl_3$) δ 9.70 (CHO)]; i.e., **4** is in equilibrium with **5**.[9] Other reagents were of guaranteed reagent grade.

Reaction of THF (1) and H_3PO_5. THF (1, 100 mL) was oxidized with H_3PO_5 (0.30 M) at 25 °C for 2 h. After iodometric estimation of the remaining H_3PO_5, H_3PO_5 and H_3PO_4 were removed by separation with added water. A product was obtained by the removal of THF from the separated THF solution under vacuum and identified as γ-butyrolactone (**2**, 0.84 g, 34%) by NMR [($CDCl_3$) δ 1.70 (2 H, m, CH_2), 2.35 (2 H, m, CH_2), 4.10 (2 H, m, CH_2)] and by GLC in comparison with an authentic sample.

The effect of O_2 on the yield was examined by the same procedure as that stated above, and the yield of γ-lactone **2** was estimated by GLC using biphenyl as an internal standard.

The reaction in MeCN was carried out by using THF (0.05–0.70 M) and H_3PO_5 (0.03–0.50 M), and the yield of γ-lactone **2** was estimated by GLC.

The pseudo-first-order rate constant was measured by iodometry of the consumed H_3PO_5.

Oxidation of Other Ethers with H_3PO_5. Tetrahydropyran (10 mL) and dioxane (10 mL) were oxidized with H_3PO_5 (0.30 M) at 25 °C for 30 h. After the estimation of the consumed H_3PO_5 (below 5%) after 30 h and the removal of H_3PO_5 and H_3PO_4 by the treatment above, their ether solutions were analyzed by GLC. Tetrahydropyran gave a trace of δ-valerolactone, but no product was obtained from dioxane.

Di-*n*-butyl ether (**6**, 10 mL) was oxidized with H_3PO_5 (0.30 M) at 25 °C for 20 h. After iodometric estimation of the remaining H_3PO_5, the reaction solution was analyzed by GLC. In this case, H_3PO_5 and H_3PO_4 were not removed, since *n*-butyl butyrate (**7**) was easily hydrolyzed on addition of water to separate H_3PO_5 and H_3PO_4. In this workup, no contamination by H_3PO_5 was observed during GLC analysis. *n*-Butyl butyrate (**7**) and *n*-butyl alcohol

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were obtained in 18.5 and 22.1% yields based on the consumed H_3PO_5, respectively.

n-Butyl alcohol was trapped by using acetic acid, the yields of *n*-butyl acetate (8), *n*-butyl alcohol, and *n*-butyl butyrate (7) being estimated by GLC (Table III).

Reaction of THF and CH_3CO_3H. THF (100 mL) was treated with CH_3CO_3H (0.18 M) at 25 °C in the presence of 0.15 M H_3PO_4 under conditions analogous to those above or in the absence of H_3PO_4, but no appreciable amount of peracetic acid was decomposed after 30 h, and no product was detected by GLC.

Registry No. 1, 109-99-9; 2, 96-48-0; 4, 5371-52-8; 5, 25714-71-0; 6, 142-96-1; 7, 109-21-7; 8, 123-86-4; *n*-BuOH, 71-36-3; H_3PO_5, 13598-52-2.

^1H and ^{13}C NMR Spectra of Substituted Borylbenzenes

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Received July 26, 1979

In an earlier paper,[2] an analysis, based upon modified CNDO/2 calculations, was presented of BX_2 substituent effects on benzene π orbital energies and atomic charge densities in the series $PhBX'_2$ (X' is F, Cl, OH, and Me). Agreement was found between the results of these calculations and photoelectron ionization energies, as well as UV transition energies of $PhBX_2$ (X is F, Cl, OH, OMe, and X_2 = 9-bicyclononane). No correlation was found between changes in calculated (π or total) charge densities at carbon and reported[2,3] ^1H NMR (60 MHz) chemical shifts of $PhBX_2$ (X is Cl, F, OMe), and it was suggested[2] that the ortho and meta proton assignments[3a] in the NMR spectra of $PhBF_2$ and $PhBCl_2$ should be reversed. We report a redetermination of the ^1H NMR spectra of the series $PhBX_2$ at 100 MHz which confirms our earlier suggestion and corrects the previous misassignments in the ^1H NMR spectra of $PhBF_2$ and $PhBCl_2$.

The ^{13}C aromatic carbon NMR chemical shifts relative to benzene were also determined for each member of the series $PhBX_2$ by proton-decoupled 25.2-MHz FT NMR spectroscopy. In this series, only the ^{13}C NMR spectra of $PhB(OH)_2$ and $PhB(OMe)_2$ have been previously reported by Niedenzu and co-workers.[4] The ortho and meta carbon assignments in the ^{13}C NMR spectra of $PhBCl_2$, $PhBF_2$, and other phenylboranes by Niedenzu are, however, in conflict with later assignments by Brown and co-workers[5] for similar molecules in a series of phenylalkoxy- and aminoboranes. The assignments of Brown were made by off-resonance-decoupled, selectively decoupled, and undecoupled ^{13}C NMR spectroscopy and must be regarded as correct for the molecules studied. In agreement with the results of Brown and co-workers, our results support assignment of the ortho carbon ^{13}C NMR chemical shifts as downfield with respect to those of meta or para carbons for all members of the series $PhBX_2$.

Table I. ^1H and ^{13}C NMR Chemical Shifts (δ) of $PhBX_2$ Relative to Benzene

	δ ortho		δ meta		δ para	
BX	^1H	^{13}C	^1H	^{13}C	^1H	^{13}C
BCl_2[a]	0.75	8.57	0.07	−0.13	0.23	6.76
BF_2[a]	0.49[b]	8.02	0.08	0.05	0.22	5.80
BR_2[g]	0.60	6.33	(0.1)[d]	−0.27	(0.1)[d]	4.46
$B(OH)_2$[c]	0.40	5.91	(0.0)[d]	−0.29	(0.0)[d]	2.38
$B(OMe)_2$[a,e]	0.22	5.08	(−0.1)[d]	−0.64	(−0.1)[d]	1.31
BPh_2[f]		9.9		−1.2		2.7

[a] Solvent $CDCl_3$. [b] J [^{13}C,F (ortho)] = 4.70 Hz. [c] Solvent CD_3OD. [d] Multiplet center. [e] OCH_3 δ^{CH} C 25.48, δ^{CH} H 3.73 (cyclohexane internal reference). [f] Reference 7. [g] R is 9-bicyclononane.

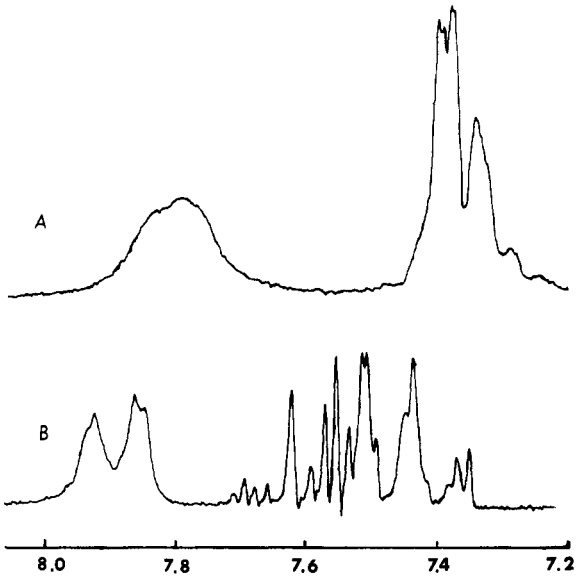

Figure 1. ^1H NMR spectrum at 100 MHz of (a) $PhB(OH)_2$ in CD_3OD and (b) $PhBF_2$ in $CDCl_3$ in parts per million downfield from Me_4Si.

Proton and ^{13}C NMR chemical shifts downfield relative to benzene for the compounds investigated appear in Table I. In the ^1H spectra, the aromatic protons divide into two multiplets of two (low field) and three (high field) protons, each separated by 0.3 to 0.5 ppm. Figure 1 provides ^1H NMR spectra of $PhBF_2$ and $PhB(OH)_2$ as representative. The low-field multiplet of two protons, which is broadened by coupling to boron, is assigned to the ortho protons in each case. Ortho shifts are reported as the average of the two most intense inner lines in the multiplet, a procedure supported by computer analysis of the spectra of $PhBCl_2$ and $PhBF_2$ which were very similar in appearance.

The observed ^1H NMR spectra of $PhBCl_2$ and $PhBF_2$ can be adequately computer similated to extract meta and para ^1H chemical shifts (Table I) by using the following coupling constants (Hz): $J_{2,3} = J_{5,6} = 7.0$, $J_{3,4} = J_{4,5} = 7.5$, $J_{2,4} = J_{4,6} = 1.3$, $J_{3,5} = 1.4$, $J_{3,6} = J_{2,5} = 0.6$. Remaining ^1H NMR spectra of $PhBX_2$ were not subjected to computer analysis because of poor resolution of structure, and combined meta-para ^1H NMR shifts are therefore reported as the center of the high-field multiplet.

Proton-decoupled ^{13}C NMR shifts were assigned on the basis of intensity and an assumed larger downfield shift for ortho than meta carbon, as found for ortho and meta H, and in agreement with Brown and co-workers's assignments in similar molecules.[5]

(1) (a) Department of Chemistry, San Francisco State University, San Francisco, CA 94132. (b) Department of Physiology, California College of Medicine, University of California, Irvine, CA 92717.
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