spectra of several compounds. We thank Mr. Steve M. Bonser who first prepared compound 7 and treated it with potassium *tert*-butoxide.

Registry No. 7, 72866-28-5; 8, 72881-42-6; 9, 1445-69-8; 11, 72866-29-6; 12, 18393-54-9; 19, 24847-86-7; 3,3-(α-hydroxypentamethylene)diaziridine, 4469-71-0; *o*-phthaloyl chloride, 88-95-9; 2-hydroxycyclohexanone, 533-60-8.

Mechanisms of Elimination Reactions. 31. Stereochemistry of Elimination Reactions of 3-Phenyl-2-butyl Tosylates[1]

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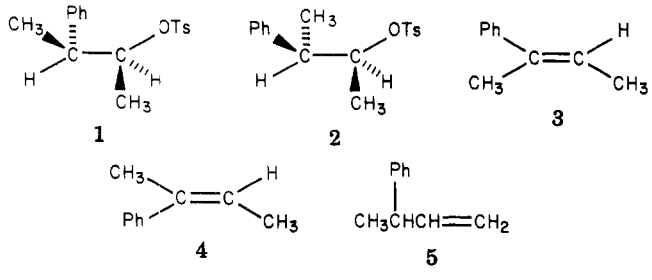
An often-quoted piece of evidence for the anti rule in E2 reactions is the report of Cram[3] that *erythro*-3-phenyl-2-butyl tosylate (1) gives only *cis*-2-phenyl-2-butene (3) and *threo*-3-phenyl-2-butyl tosylate (2) gives only *trans*-2-phenyl-2-butene (4) on treatment with sodium



ethoxide in ethanol, in both cases the products of exclusive anti elimination. The presence of some 3-phenyl-1-butene (5) was deduced from the fact that chiral substrate gave a crude product mixture retaining some optical activity, but none of this olefin was isolated. More recent studies have revealed significant extents of syn elimination in E2 reactions of secondary alkyl tosylates.[4-7]

Because of these results, and because sensitive methods of analysis for minor products were not available at the time of the original work, we felt it advisable to reinvestigate this reaction by using GLC to analyze the product mixtures. The results are given in Table I. There is clearly no detectable syn elimination with 1, either under Cram's[3] conditions or with the stronger base sodium *tert*-butoxide. While small percentages of the product (3) of syn elimination from 2 are found with both base/solvent pairs, the same product is shown to result from isomerization of 5 (previously observed by Cram and Uyeda with *tert*-butoxide[8]). Closer examination of the figures strongly suggests that 3 does result from isomerization rather than

Table I. Product Proportions from E2 Reactions of the Diastereomeric 3-Phenyl-2-butyl Tosylates[a]

		% yield		
reactant	base/solvent	3	4	5
1	EtONa/EtOH[b]	90.9	0	9.1
2		2.7	84.1	13.2
5[d]		18.1	0	81.9
1	*t*-BuONa/*t*-BuOH[c]	56.4	0	43.6
2		7.4	36.3	56.3
5[d]		14.5	0	85.5

[a] Substrate 0.06–0.08 M, base 0.4–0.5 M. [b] Conditions: 4 h at 110 °C and then overnight at 80 °C. [c] Conditions: 5 h at 80 °C. [d] Isomerization of pure 5; 3 and 4 were stable under the reaction conditions.

syn elimination. With sodium ethoxide, the ratio of 3 to 5 is 0.22 in the isomerization and 0.20 in the elimination. The corresponding figures with sodium *tert*-butoxide are 0.17 and 0.13, respectively. The similarity of the ratios strongly suggests that the 3 obtained in the eliminations from 2 arises predominantly or exclusively from isomerization. The upper limit for syn elimination from 2 thus seems to be a few percent and that for syn elimination from 1 much less than 1%.

There are several possible reasons why syn elimination is so unimportant in this system. It is known that simple secondary alkyl tosylates give cis olefin almost entirely by anti elimination, even when there is substantial syn elimination in the formation of the corresponding trans olefins,[7] the difference presumably being due to greater eclipsing interactions in the transition state for syn than for anti elimination. The transition states for syn elimination from 1 and 2 must have methyl–phenyl and methyl–methyl eclipsing, respectively, and are thus sterically analogous to the transition states for the formation of the cis isomers of simple straight-chain alkenes.

It is also possible that the β-phenyl group is less activating toward syn than anti elimination. The trans olefin from the reaction of stereospecifically deuterated 2-chloro-1-phenylpropane-*1-d* with alkoxides in the corresponding alcohols is formed exclusively or nearly exclusively by anti elimination,[9] a case where eclipsing interactions cannot significantly hinder syn elimination. In addition, anti elimination from *cis*-2-phenylcyclopentyl tosylate is 9 times as fast as syn elimination from *trans*-2-phenylcyclopentyl tosylate with potassium *tert*-butoxide in *tert*-butyl alcohol as base.[10] On the other hand, this rate effect could simply reflect steric differences between the reactants, and the Hammett ρ is actually larger for syn than for anti elimination.[10] Thus the experimental evidence is ambiguous on the possibility of an adverse electronic effect of a β-phenyl group on syn elimination.

Experimental Section

***erythro*- and *threo*-3-Phenyl-2-butyl *p*-Toluenesulfonates.** 3-Phenyl-2-butanol was prepared and separated into the pure racemic diastereomers, and the *p*-toluenesulfonates of the diastereomers were prepared by the method of Cram.[11]

3-Phenyl-1-butene was obtained by the method of Cram.[12] It was purified by preparative GLC on an 8 ft × 0.25 in. column of 15% Carbowax 1540 on Chromosorb W (60/80 mesh).

***cis*- and *trans*-2-Phenyl-2-butenes.** The dehydration of methylethylphenylcarbinol by refluxing for 10 h with 4 N sulfuric

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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.

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

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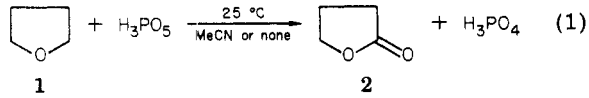
In the course of a kinetic study on the oxidation of *trans*-stilbene with H_3PO_5,[2] we looked for solvents which were miscible with acetonitrile and were not attacked by H_3PO_5. Then we found out that no *trans*-stilbene oxide was obtained on mixing *trans*-stilbene with H_3PO_5 in tetrahydrofuran (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

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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

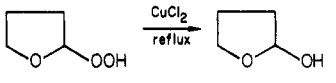
10-[THF]$_0$, M	10-[H_3PO_5]$_0$, M	10-[*p*-BQ]$_0$, M	% decompd H_3PO_5	yield of 2, %
3.0	3.0	0	62.3	41.2
3.0	3.0	3.0	58.7	39.6
6.0	3.0	0	70.4	45.2
6.0	3.0	3.0	64.7	44.7

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]

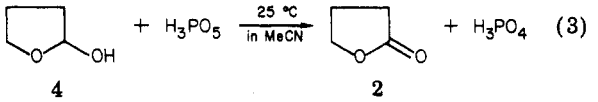
10[*p*-BQ]$_0$, M	$10^5 k_{obsd}$, s^{-1}	10[*p*-BQ]$_0$, M	$10^5 k_{obsd}$, s^{-1}
0	1.48	1.5	1.45
0.6	1.40	3.0	1.37

[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



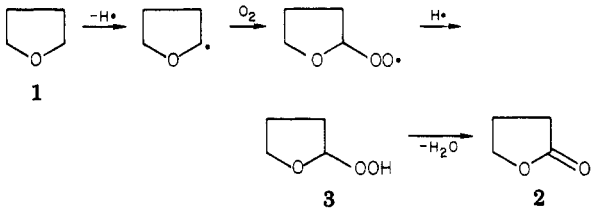
3 4



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.



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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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