Oxidation of Cinnamyl Alcohol with Peracetic Acid in Acidic Solvents[1)]

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Peracetic acid oxidation of cinnamyl alcohol(**1**) in tetrahydrofuran(THF) at room temperature has been found to give phenylacetic acid(**2**), benzaldehyde(**4**) and cinnamyl acetate(**5**) as major products. A probable first-formed intermediate, 2,3-epoxy-3-phenyl-1-propanol(**7**), was detected as its derivative (1-phenyl-1,2,3-propanetriol), and also a probable second intermediate, 1-hydroxy-3-phenyl-2-propanone (**3**), was detected. **3** was found to be converted to **2** by the Baeyer-Villiger reaction. On the other hand, the peracetic acid oxidation of **1** in methanol gave a methanolysis product of oxirane ring, 3-methoxy-3-phenyl-1,2-propanediol (**6a**), a small amount of a rearrangement product and benzaldehyde. The peracid oxidation of **1** in various solvents was also studied. A probable reaction mechanism is discussed.

We have previously reported that peracid oxidation of vitamin A alcohol, $\mathrm{Me_3C_6H_6{-}CH{=}CH{-}CMe{=}CH{-}CH{=}CH{-}CMe{=}CH{-}CH_2OH}$, yielded 11,12-epoxy-vitamin A aldehyde, $\mathrm{Me_3C_6H_6{-}CH{=}CH{-}CMe{=}CH{-}\overset{O}{CH{-}CH}{-}CMe{=}CH{-}CHO}$, *via* oxidation of primary alcohol group to aldehyde as well as epoxidation of an ethylenic bond.[2)] In the present paper, we intended to study the peracetic acid oxidation of cinnamyl alcohol (**1**), which have an α,β-unsaturated alcohol group.

The present study showed that the peracid oxidation of **1** had a behaviour different from that of vitamin A alcohol. In this paper we wish to report the mechanism of peracid oxidation of **1** which was speculated from the products of an assumed intermediary epoxide, 2,3-epoxy-3-phenyl-1-propanol (**7**).

It was reported that the perbenzoic acid oxidation of in $CHCl_3$ at 0 °C gave **7**, which could be converted to phenylacetaldehyde, formaldehyde and 1-hydroxy-3-phenyl-2-propanone (**3**) on pyrolysis in the presence of kieselguhr,[3–5)] but resinous material on pyrolysis in the presence of H_2SO_4 or $ZnCl_2$.[3,4)] The pyrolysis products of **7** and the migratory aptitude of the epoxide rearrangement were studied only in the absence of peracid at high temperature[3,6–8)] and little was known on the peracid oxidation of **1** and the subsequent reactions in solution and at lower temperature.

Also peracid oxidation of α,β-unsaturated secondary alcohol was reported to yield the epoxides and its derivative,[9,10)] but no report is available on the mechanism of formation of these derivatives.

Results and Discussion

Oxidation of cinnamyl alcohol(**1**) with an equivalent of peracetic acid in tetrahydrofuran(THF) and in some solvents containing acetic acid at room temperature gave a distribution of products as shown in Table 1. In addition of products listed in the table, a trace of cinnamaldehyde, PhCH=CHCHO, and significant amounts of unknown products were formed but the expected products, 2,3-epoxy-3-phenylpropanal, $\mathrm{Ph\overset{O}{CH{-}CH}CHO}$(**8**), was not detected. Most of these products were identified by the comparison of IR and NMR spectra and GLC peaks with those of the corresponding authentic specimens.

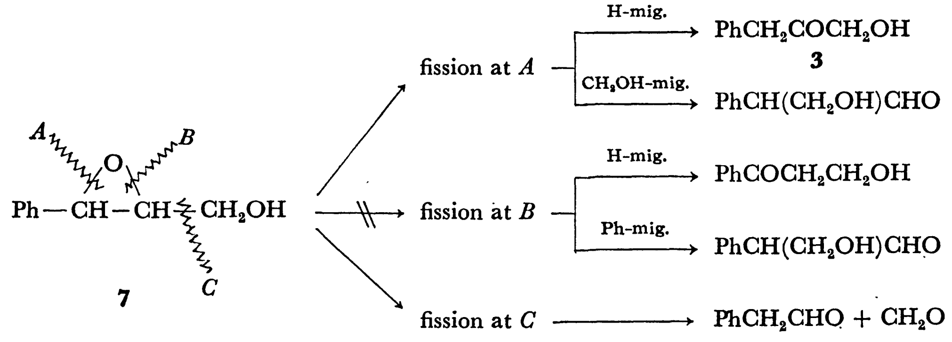
A trace of cinnamaldehyde formed during this oxidation cannot be the precursor to **8**, because the peracetic acid oxidation of cinnamaldehyde did not proceed under these conditions. Furthermore, we observed that **8** was very unstable, thus **8** could not be synthesised by oxidation of cinnamaldehyde by H_2O_2 or *t*-BuOOH even according to the reported procedure in alkaline media[11)] as described in Experimental part. In the case of oxidation of vitamin A alcohol, the steric selectivity of attacking site seems to play an important role,[2)] thus the observed oxidation of unsaturated alcohol to epoxy aldehyde can occur because of the chemical driving force for the formation of its α,β-unsaturated aldehyde in acidic media. Whereas, the peracetic acid oxidation of cinnamyl alcohol (**1**) to **8** is unfavourable because of the

TABLE 1. SOLVENT EFFECT ON THE YIELDS OF PRODUCTS IN THE PERACETIC ACID OXIDATION OF CINNAMYL ALCOHOL (**1**)

Solvent	Reaction time h	Conversion %	Product %					
			2	**3**[b)]	**4**	**5**	**6a**	**6b**
THF	66	65.2	19.2	6.2	16.0	17.0	—	—
Ether	54	61.5	13.9	1.8	14.6	16.3	—	—
Benzene	54	60.3	24.1	7.9	13.4	14.1	—	—
Cyclohexane[a)]	54	70.4	trace	—	4.6	39.7	—	—
CH_2Cl_2	24	75.4	28.9	6.7	15.3	14.3	—	—
Methanol	24	52.7	3.4	—	1.2	5.2	63.5	trace

a) Heterogeneous system. b) The yield of **3** was the value corrected for the amounts of **3** derived from GLC pyrolysis of **7**.

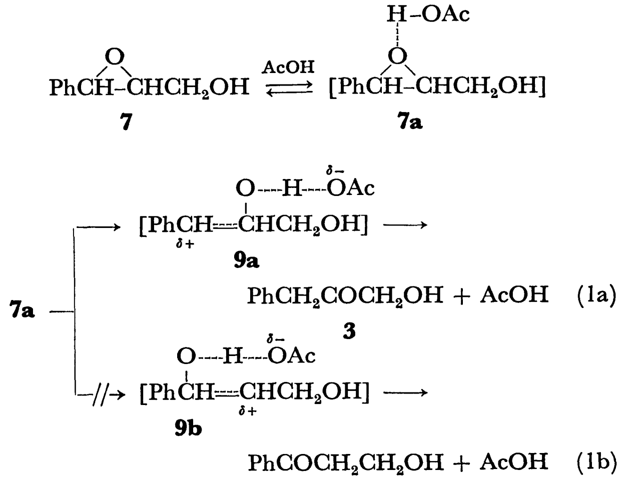
2; $PhCH_2CO_2H$. **3**; $PhCH_2COCH_2OH$. **4**; PhCHO. **5**; $PhCH{=}CHCH_2OAc$. **6a**; PhCH(OMe)-CH(OH)CH_2OH. **6b**; PhCH(OH)CH(OMe)CH_2OH.



Scheme 1.

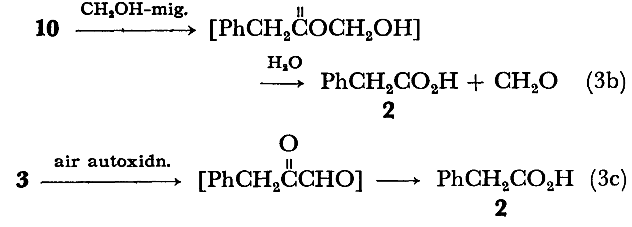
faster ring opening of its intermediate epoxide **7** as discussed below.

1-Hydroxy-3-phenyl-2-propanone (**3**) should be a rearrangement product of the initially formed 2,3-epoxy-3-phenyl-1-propanol (**7**) from **1** as shown in Eq. (1a). The epoxide (**7**) may afford by fissions at *A* and *B* three isomers, and by fission at *C*, products of cleavage at C–C as shown in Scheme 1, but actually the catalytic pyrolysis of **7** was reported to give phenylacetaldehyde, formaldehyde and **3**, which may be products of radical reactions.[3,4] Also our pyrolysis of alternatively synthesised **7** at 200—250 °C at the injection temperature of GLC yielded phenylacetaldehyde (25%) and **3** (29%) and unknown products. On the other hand, during the column chromatography with silica gel ($SiO_2 \cdot xH_2O$), **7** was completely changed to give 1-phenyl-1,2,3-propanetriol, PhCH(OH)CH(OH)CH₂OH, and no phenylacetaldehyde and **3** was detected by GLC. The present peracetic acid oxidation of **1** gave **3** and a little phenylacetaldehyde, which were identified by GLC, but 1-phenylpropane-1,2,3-triol was obtained instead of phenylacetaldehyde by the column chromatography with silica gel. The above fact suggests that **7** is a primary intermediate formed in this oxidation and that **7** is converted to **3** by the following ionic path (Eq. 1a) which involves no radical species.



On account of the more resonance delocalization of the positive charge in **9a**, the pathway (Eq. 1a) *via* **9a** leading to **3** should be favoured rather than the pathway (Eq. 1b) *via* **9b** leading to β-hydroxypropiophenone.

The authentic **3**, which was prepared alternatively,[4,12] gave phenylacetic acid (**2**) on the peracetic acid oxidation under similar conditions. Hence, **3** may be an intermediate in the formation of **2** from **1**. Three paths from **3** (Eqs. 3a—c) are conceivable for this oxidation, but the Baeyer-Villiger reaction of Eq. 3a is negligible because of the formation of little benzyl alcohol which is fairly stable under these conditions as evidenced in Experimental part. Further, the autoxidation of **3**(Eq. 3c) is less probable, because peracetic acid is necessary for this reaction forming **2** which proceeds even under N₂. Hence, **2** is probably formed *via* Eq. 3b alone, where the preferential migration of methylol group of **10** occurs. The Taft σ* values are 0.225 for benzyl group and 0.555 for hydroxymethyl group.[13] In



$$\underset{\mathbf{3}}{PhCH_2\overset{O}{\overset{\|}{C}}CH_2OH} \xrightarrow[AcOOH]{\text{B-V reaction}} \underset{\mathbf{10}}{[PhCH_2-\underset{OOAc}{\overset{OH}{C}}-CH_2OH]} \quad (2)$$

$$\mathbf{10} \xrightarrow{PhCH_2\text{-mig.}} [PhCH_2O\overset{O}{\overset{\|}{C}}CH_2OH] \xrightarrow{H_2O} PhCH_2OH + HOCH_2CO_2H \quad (3a)$$

$$\mathbf{10} \xrightarrow{CH_2OH\text{-mig.}} [PhCH_2\overset{O}{\overset{\|}{C}}OCH_2OH] \xrightarrow{H_2O} \underset{\mathbf{2}}{PhCH_2CO_2H} + CH_2O \quad (3b)$$

$$\mathbf{3} \xrightarrow{\text{air autoxidn.}} [PhCH_2\overset{O}{\overset{\|}{C}}CHO] \longrightarrow \underset{\mathbf{2}}{PhCH_2CO_2H} \quad (3c)$$

most Baeyer-Villiger reactions, a more electron-releasing group tends to migrate preferentially, but in this case the more electron-attracting hydroxymethyl group must migrate. This migration of methylol group may be due to the formation of hydrogen bonding which facilitates O–O fission in the transition state of migration as shown in **11**. The similar migration of an electron-attracting phenyl group was reported for acetophenone, where

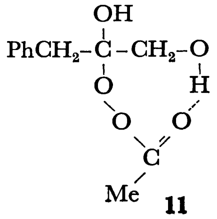


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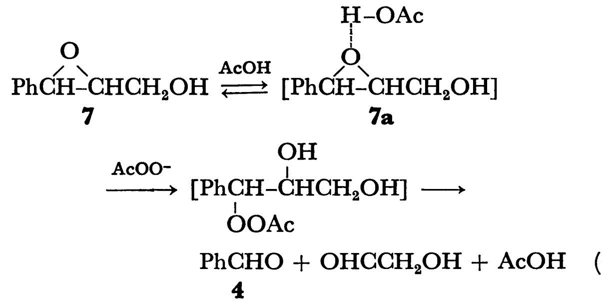
Table 2. Effect of molar ratio of reactants ($PhCH{=}CHCH_2OH$: AcOOH)

Solvent	Mole ratio[a]	Reaction time h	Conversion %	Product % **2**	**3**[b]	**4**	**5**
THF	1:1	66	65.2	19.2	6.2	16.0	17.0
THF	1:2	35	75.4	38.5	5.2	5.3	14.0
Ether	1:1	54	61.5	13.9	1.8	14.6	16.3
Ether	1:2	24	78.6	29.7	4.3	8.7	16.8
Benzene	1:1	54	60.3	24.1	7.9	13.2	14.1
Benzene	1:2	24	73.5	32.4	10.5	10.2	13.2

a) Ratio of cinnamyl alcohol (**1**) and peracetic acid. b) The value for **3** was determined in the same way as Table 1.

bridged phenonium ion assists the migration.[14]

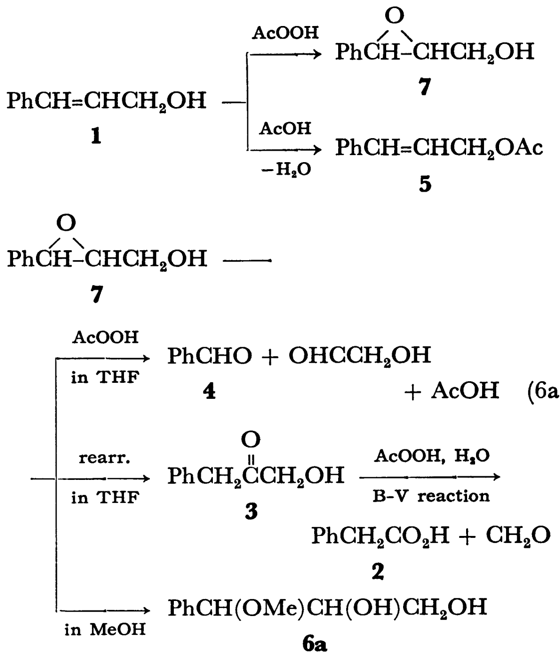
The formation of benzaldehyde (**4**) can also be explained by assuming the H-bonded neutral intermediate **7a**, which is cleaved to give **4** by the addition of peracetic acid to its oxirane ring (Eq. 4) in view of the acid catalysis as will be discussed below. The similar mechanism was reported for the peracetic acid oxidation of ketene.[15]



(4)

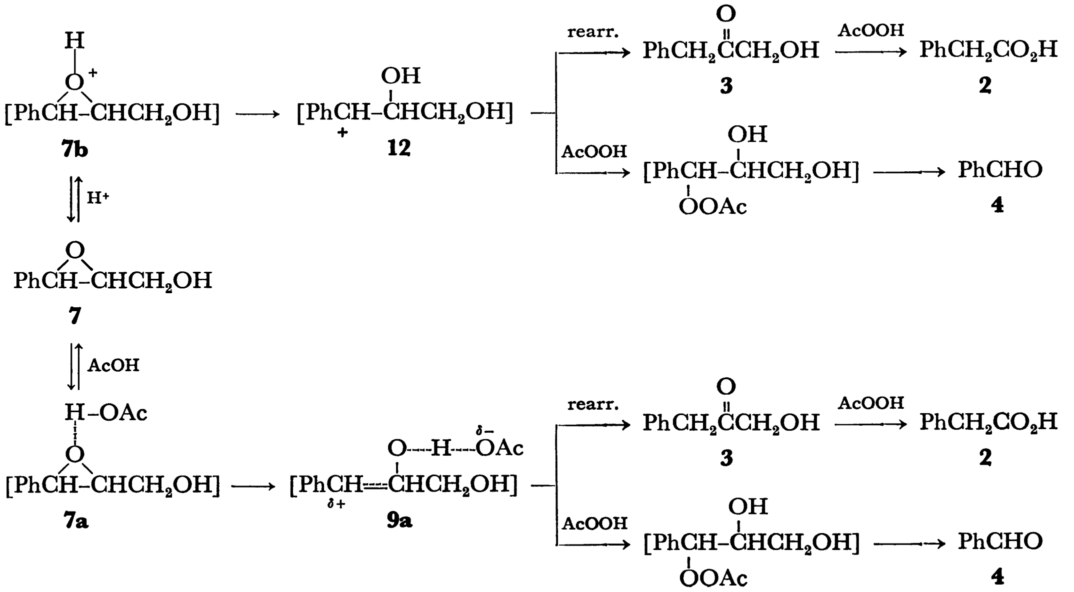
Observed products and pathways in various solvents for the oxidation of **1** are shown in Scheme 2. The structure of **6a** was supported by comparison with 1,3-dimethoxy-1-phenyl-2-propanol (**14**) which was prepared by peracid oxidation of cinnamyl methyl ether (**13**) in MeOH.

The yield of phenylacetic acid (**2**) from **1** increases with increasing amount of peracetic acid, while the yield of benzaldehyde (**4**) decreases (Table 2). On the other hand, when a small amount of mineral acid is added to a mixture of **7** and peracetic acid, the yield ratio [**4**]/[**2**] increases significantly. The above facts may be explained as follows: (i) In the presence of mineral acid, benzaldehyde (**4**) should be obtained as a major product *via* **12** (Eq. 7b), because the greater electro-



(5a) (5b) (6a)=(4) (6b) (6c)

Scheme 2.

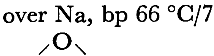


(7a) (7b) (8a) (8b)

philicity of **12** than that of **7a** accelerates an attack of nucleophiles on **12** and thus favours this addition (Eq. 7b) rather than the rearrangement (Eq. 7a). (ii) In the absence of mineral acid, the precursor of **2**, $PhCH_2COCH_2OH$(**3**), is probably formed as a main product via neutral intermediate **7a** (Eq. 8a), because the carbonium ion from **7a**, if formed, is very unstable and hence the rearrangement (Eq. 8a) is preferred to an attack of nucleophiles ($AcOO^-$, AcOOH) on **9a**. The decrease of the yield of **4** with increasing amount of peracid seems to be curious, but the increase would accelerate the Baeyer-Villiger reaction (Eq. 8a) more than the C–C cleavage (Eq. 8b), which does not involve peracid in the rate-determining step. The increase of acidity on addition of mineral acid promotes the formation of **7b** and increases the yield of **4** by the acceleration of an attack of peracid on **12**. Whereas, in the absence of mineral acid, there is formed no **7b** but H-bonded **7a**, which is much weaker electrophile and thus the rate of Eq. (8a) going to **3** is much faster than the rate of Eq. (8b) going to **4**, and then the increase of concentration of peracid increases the ratio of [**2**]/[**4**].

Experimental

Mps were measured by a Yanagimoto micro-melting point apparatus and they were corrected. IR spectra were measured by a Perkin-Elmer Model 337 grating infrared spectrophotometer. GLC analysis was carried out by a Yanagimoto gas chromatograph with FID, Model GCG-550F, employing two sorts of 2 m×2.5 mm columns(one of which was packed with 2.5% PEG-20 M on Chamelite CS of 80—100 mesh and another packed with 13% DEGS on Chromosorb W of 80—100 mesh), using N_2 as a carrier gas. NMR spectra were recorded by a Japan Electron Optic Laboratory Co., C60 HL NMR instrument. The yield of products are listed in Table 1.

Materials. Peracetic acid was prepared by the reaction of Ac_2O (205 g) with 60% aq. H_2O_2 (50 g) added with concd H_2SO_4 (0.5 ml) at 35—40 °C.16) The peracid concentration was 3.0—3.1 M in average. THF was purified by distillation over Na, bp 66 °C/760 Torr. 2,3-Epoxy-3-phenyl-1-propanol,  $PhCH\overset{O}{-}CHCH_2OH$ (**7**), was obtained by the oxidation of cinnamyl alcohol (**1**) (0.105 mol) with perbenzoic acid (0.105 mol) in $CHCl_3$ at 0 °C in a yield of 38%: bp 117.5—118.5 °C/1.5 Torr (lit,17) 117—118 °C/1.5 Torr), IR (liquid film): 3450—3350, 2920, 2860, 1240, 1025, 880, 750, and 700 cm^{-1}; NMR (CCl_4): δ 3.17 (1H, m, 2-H), 3.65 (1H, s, OH), 3.80 (1H, d, J=6 Hz, 3-H), 3.88 (2H, d, J=3 Hz, 1-H), and 7.40 (5H, s, aromatic). 1-Hydroxy-3-phenyl-2-propanone, $PhCH_2COCH_2OH$ (**3**), was synthesised by the reaction of $HOCH_2CN$ (19.7 g) with $PhCH_2MgCl$ in ether and recrystallized from ethanol-petroleum ether,4,12) in a yield of 5% based on the used nitrile, mp 49.5—50.5 °C (lit,4) mp 47—48 °C), IR (KBr disk): 3450—3350, 1720, 750, and 695 cm^{-1}; NMR ($CDCl_3$): δ 3.08 (1H, s, OH), 3.35 (2H, s, 3-H), 4.18 (2H, s, 1-H), and 7.17 (5H, s, aromatic). Cinnamyl methyl ether, $PhCH=CHCH_2OMe$ (**13**), was obtained by the reaction of cinnamyl alcohol (**1**) (25 g) with Me_2SO_4 and $NaNH_2$ in ether in a yield of 78%, bp 115—117 °C/20 Torr (lit,18) 111—112.5 °C/15 Torr), IR (liquid film): 2815, 965, 742, and 690 cm^{-1}; NMR (CCl_4): δ 3.26 (3H, s, OMe), 3.97 (2H, d, J=7 Hz, 1-H), 6.10 (1H, m, 2-H), 6.55 (1H, d, J=16 Hz, 3-H), and 7.20 (5H, s, aromatic). Cinnamyl acetate, $PhCH=CHCH_2OAc$ (**5**), was prepared by the acetylation of **1** with Ac_2O, (68%), bp 104—106 °C/3 Torr (lit,19) 141 °C/18 Torr).

Oxidation of Cinnamyl Alcohol (1). Product Isolation. For the reaction of **1** with peracetic acid, **1** (4.33×10^{-2} mol) was treated with peracetic acid (4.31×10^{-2} mol) in THF (100 ml) at room temperature. The produced solution was condensed under vacuum (50 °C at 30 Torr), and the residue was chromatographed on a 60×2 cm column slurry packed with silica gel (benzene and benzene–ethyl acetate). The first substance eluted was benzaldehyde (**4**) and the second was cinnamyl acetate (**5**). The third was colourless crystals, 1-hydroxy-3-phenyl-2-propanone (**3**), and the fourth was recovered **1** and the fifth was colorless crystals, phenylacetic acid (**2**), mp and mmp 77—78 °C. The sixth was a colourless liquid, which was identified to be 1-phenyl-1,2,3-propanetriol, IR (liquid film): 3400—3300, 2920, 2860, 1460, 1100, 1025, 760, and 695 cm^{-1}; NMR ($CDCl_3$): δ 3.30 (1H, m, 2-H), 3.58 (2H, d, 1-H), 4.25 (3H, s, OH), 4.62 (1H, d, 3-H), and 7.25 (5H, s, aromatic).

Oxidation of 1 in Methanol. Product Isolation. The similar oxidation of **1** in MeOH and the similar work up gave products which were chromatographed through a 60×2 cm column of silica gel and developed by the gradient method of benzene–ethyl acetate. The first eluted substance was benzaldehyde (**4**) (trace). The second one was cinnamyl acetate (**5**) and the third was recovered **1** and the fourth was phenylacetic acid (**2**). The fifth was 3-methoxy-3-phenyl-1,2-propanediol (**6a**) which was identified by IR and NMR spectra, IR (liquid film): 3450—3350, 2820, 1200, 760, and 700 cm^{-1}; NMR (CCl_4): δ 3.06 (3H, s, OMe), 3.47 (2H, s, 1-H), 3.58 (1H, m, 2-H), 3.89 (2H, s, OH), 4.00 (1H, d, J=7 Hz, 3-H), and 7.20 (5H, s, aromatic). Found: C, 66.21; H, 7.74%. Calcd for $C_{10}H_{14}O_3$: C, 65.91; H, 7.74%. The sixth was 2-methoxy-1-phenyl-1,3-propanediol (**6b**) which was identified by IR and NMR spectra, IR (liquid film): 3450—3400, 2815, 1210, 760, and 700 cm^{-1}; NMR (CCl_4): δ 3.15 (3H, s, OMe), 3.30 (2H, d, 1-H), 3.66 (1H, m, 2-H), 3.83 (2H, s, OH), 4.19 (1H, d, 3-H), and 7.30 (5H, s, aromatic).

The peracetic acid oxidation of cinnamyl methyl ether (**13**) in MeOH affords 1,3-dimethoxy-1-phenyl-2-propanol (**14**). The comparison of NMR spectra of $PhCH(OMe)CH(OH)CH_2OH$ (**6a**) with those of $PhCH(OH)CH(OMe)CH_2OH$ (**6b**) and **14** confirms the structure of **6a** and **6b**.

In addition, the structure of **6a** was assured by the structure of product (**15**) by H_2SO_4-catalysed dehydration of **6a**; *i.e.*, **15** was identified to be 1-methoxy-1-phenyl-2-propanone, PhCH(OMe)COMe, IR (liquid film): 1715, 755, and 700 cm^{-1}; NMR (CCl_4): δ 2.05 (3H, s, 3-H), 3.35 (3H, s, OMe), 4.48 (1H, s, 1-H), and 7.27 (5H, s, aromatic).

Oxidation of Cinnamyl Methyl Ether (13) in Methanol. The similar oxidation of **13** and the similar work up afforded 1,3-dimethoxy-1-phenyl-2-propanol (**14**), which was identified by IR and NMR spectra, IR (liquid film): 3450—3400, 2820, 1200, 1140, 755, and 695 cm^{-1}; NMR (CCl_4): δ 2.60 (1H, s, OH), 3.16 (3H, s, 3-OMe), 3.27 (3H, s, 1-OMe), 3.30 (2H, d, J=7 Hz, 1-H), 3.76 (1H, m, 2-H), 4.08 (1H, d, J=7 Hz, 3-H), and 7.22 (5H, s, aromatic).

Oxidation of 1-Hydroxy-3-phenyl-2-propanone (3). Two THF solutions of **3**, one of which contained peracetic acid but the other no peracid, were warmed to 20 °C for 24 h and the resulting solutions were analysed similarly by GLC. In this experiment, the former gave phenylacetic acid (**2**) but the latter did not. Also two THF solutions of **3** and peracetic acid, one of which was filled with air and the other filled with N_2 after deaerated under -78 °C, were warmed to 20 °C for 24 h and the products were analysed similarly. Both of them gave **2** in a good yield. Therefore, **2** was formed from the reaction of **3** with peracetic acid and no autoxidation occurs during the reaction.

Pyrolysis of 2,3-Epoxy-3-phenyl-1-propanol (7). **7** was pyrolysed at 200—250 °C at the injection temperature of GLC. Phenylacetaldehyde and **3** were obtained in yields of 25 and 29%, respectively, together with two unknown products. In the present pyrolysis, neither phenylacetic acid (**2**) nor benzaldehyde (**4**) was formed. Further, phenylacetaldehyde was not oxidised to form **2** during this pyrolysis.

Column Chromatography of 2,3-Epoxy-3-phenyl-1-propanol (7). **7** was chromatographed on a 60×2 cm column slurry packed with silica gel. A large portion of the substance eluted with benzene–ethyl acetate (50: 50) was a colourless liquid and it was identified to be 1-phenyl-1,2,3-propanetriol by IR and NMR spectra. In this column chromatography **7** was not recovered and a small amount of unknown material was obtained. Further, neither phenylacetaldehyde nor **3** was obtained.

Oxidation of 2,3-Epoxy-3-phenyl-1-propanol (7). **7** was oxidised similarly with peracetic acid in THF at room temperature for 24 h and the formation of **2** and **4** established by GLC, since the pyrolysis of **7** at 200—250 °C gave neither **2** nor **4** thus their contamination could be avoided. By the reaction with an equivalent of peracetic acid **7** yielded **2** and **4** in yields of 16 and 12%, respectively. Whereas the reaction with two equivalents of peracid gave **2** and **4** in yields of 24 and 13%, respectively. On addition of a small amount of mineral acid, the peracid oxidation of **7** gave **2** (8%) and **4** (32%).

Oxidation of Benzyl Alcohol in THF. Benzyl alcohol was treated with peracetic acid in THF at room temperature by a work up similar to the oxidation of **1**, the resulting products were identified by GLC using two columns by comparing those of authentic samples. The products and their yields were shown in Table 3.

TABLE 3. THE PERACETIC ACID OXIDATION OF BENZYL ALCOHOL IN THF

Reaction time h	Conversion %	Product %		
		PhCHO (**4**)	$PhCO_2H$	$PhCH_2OAc$
24	23.8	8.8 (1.5)[a]	2.4	88.7
48	34.0	10.3 (1.7)[a]	2.5	87.2

a) Yield by autoxidation.

Oxidation of Cinnamaldehyde. Cinnamaldehyde was oxidised with method (1) H_2O_2 in aq. MeOH at pH 8—8.5 and method (2) *t*-BuOOH in MeOH at pH 10.5±0.2, where pH was controlled with a glass electrode pH meter. The reaction solution was condensed under N_2 *in vacuo* and distilled. In both methods 1 and 2, a considerable amount of cinnamaldehyde was recovered and unknown products were obtained. Further, an attempt to oxidise cinnamaldehyde with peracetic acid in THF under conditions similar to that for **1** gave mostly recovered starting material.

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