Reaction of Styrene Glycol with Aqueous Acids

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Although Zincke[1] reported in 1882 that, when treated with aqueous acid, styrene glycol yielded phenylacetaldehyde (I), together with higher boiling materials, there have been few investigations to examine the utility of the procedure for the synthesis of I, except that Emerson[2] has reported a vapor phase isomerization of styrene glycol to I in a yield of 74%. This reaction is a well-known pinacolic rearrangement and it may be a possible synthetic route for I. As styrene glycol[2] is easily prepared from styrene, we undertook to explore the procedure to clarify the course of reaction and to find the most suitable conditions for the preparation of I.

1) Th. Zincke, *Ann.*, **216**, 295 (1882).
2) W. S. Emerson, *J. Am. Chem. Soc.*, **67**, 516 (1945).

Results and Discussion

Effect of Reaction Conditions.—As Zincke's paper was concerned chiefly with the structure of the higher boiling material and did not disclose any optimum conditions for obtaining I, we first examined the effect of reaction conditions upon the yield of I, varying the kind of acids, the acid concentrations and the

Table I. Effects of kind and concentration of acids

Reaction time: 2 hr.

Acid			Product		
			Phenylacet-aldehyde	Higher fraction**	
Kind	Concn.	H_0*			
	mol./l.		%	%	n_D^{25}
H_2SO_4	1.00	−0.25	2.3	36.8[a]	1.5691
HCl	1.09		3.5	44.9	1.5670
H_3PO_4	3.06		2.9	34.9[a]	1.5698
H_2SO_4	2.33	−1.00	18.7	69.0	1.5740
HCl	2.89		12.9	67.6	1.5798
H_3PO_4	5.99		17.3	71.9[b]	1.5728
H_2SO_4	3.79	−1.75	12.9	73.4	1.5820
HCl	4.57		5.8	53.2[c]	1.6150
H_3PO_4	7.85		14.4	76.3	1.5818

* H_0 values were quoted from M. Z. Paul and F. A. Long, *Chem. Revs.*, **57**, 12 (1957).

** Products a and b were combined and redistilled and analyzed for elemental composition.

Table II. Effect of reaction time*

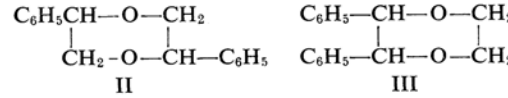
Aqueous acid: 2.24 mol./l. sulfuric acid

Time	Product		
	Phenylacet-aldehyde	Higher fraction	
hr.	%	%	n_D^{25}
1.0	11.5	73.4	1.5682
1.5	15.8	70.5	1.5689
2.0	18.7	69.0	1.5740
2.5	17.3	63.3	1.5776
3.0	17.3	66.2	1.5782
5.0	14.4	50.4	1.5925

* Mixtures of styrene glycol (10 g.) and the aqueous acid (15 ml.) were refluxed for the specified periods.

reaction times. The results are summarized in Tables I and II.

These results reveal that the yield of I in the simple treatment was relatively low but that a higher boiling material was formed in an appreciable quantity; however, severe conditions, prolonged reaction periods, or treatment with more concentrated acid solutions lowered the yields of the higher boiling material. It was also noticed that, under the more severe conditions, the refractive indices of the higher boiling materials were higher and that the intensity of their infrared absorptions at 1730 and 1698 cm^{-1} were stronger. Especially, the product c (indicated in Table I) was found at 1130 cm^{-1} to lack the C–O–C absorption which appeared in the others. These observations seemed to indicate that another type of by-product was formed under the more severe conditions, especially on treatment with an aqueous hydrochloric acid. The higher boiling fractions, with a lower refractive index (product a and b in Table I), were combined and redistilled. The results of the elemental analysis of the redistilled product (Found: C, 80.43; H, 6.80%: hereafter named "dimer A") coincided well with the composition of phenylacetaldehyde dimer ($C_{16}H_{16}O_2$), to which Zincke assigned either structure II or III and which he considered as an intermediate to I.



II III

As Zincke pointed out that dimer A also afforded I on treatment with aqueous acid, dimer A was treated with aqueous sulfuric acid repeatedly in order to confirm the formation of I. The results are shown in Table III.

Table III. Product ratios with repeated treatment

Reaction time: 2 hr.

Aqueous acid: 3.0 mol./l. sulfuric acid

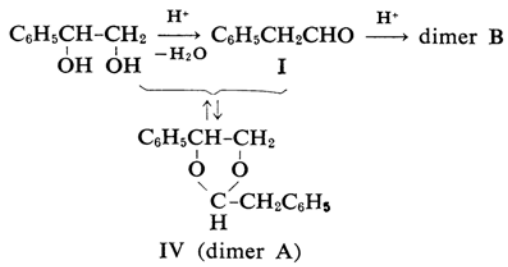
No.	Phenylacet-aldehyde	Higher fraction recovered	
	%	%	n_D^{25}
1	13.6	80.3	1.5772
2*	14.0	70.0	1.5900
3	13.3	76.7	1.5960

* The recovered dimer A in No. 1 (n_D^{25} 1.5772) was used as the reactant in experiment No. 2, and so on.

The results show that, in each run, the ratios of I to the higher boiling fraction were kept nearly constant, but that the refractive indices of the recovered dimer A increased gradually in this case, too. These results seemed strongly to support the hypotheses that dimer A was not a simple intermediate but was in equilibrium with I and that any device to remove I from the reaction mixture would increase the yield. A preliminary experiment was made, in which styrene glycol was treated with acid in methanol and in ethanol instead of in water in order to remove I in the form of the acetals, but the products isolated were neither the expected acetals nor dimer A respectively. In another attempt, the reaction mixture obtained from styrene glycol with aqueous acid was steam-distilled; this procedure seemed to be promising because I was isolated in a 31% yield.

Structure of Dimer A.—If such an equilibrium between dimer A and I existed, we could expect that I would give a similar equilibrium mixture in the treatment of I with an acid solution. After being refluxed for two hours

with aqueous acid, I gave a product which was found to consist of recovered I (18%) and of a higher boiling material. The higher boiling material showed a boiling range similar to that of dimer A but a somewhat higher refractive index. The infrared spectrum of the latter (hereafter named "dimer B") revealed that the product thus obtained was different from dimer A but was identical with the product c in Table I. In the reaction with aqueous acid, dimer A did not give I and was recovered unchanged in a 90% yield. These results lead us to the presumption that another structure of dimer A, one which can account for its molecular formula ($C_{16}H_{16}O_2$) and for its infrared absorption behavior, should be sought. Among others[3], the structure of 2-benzyl-4-phenyl-1, 3-dioxorane (IV) could well interpret the observed results, especially that dimer A was hydrolyzed easily in acidic conditions and that both styrene glycol and I were necessary for the formation of dimer A. The acetal IV was prepared in a yield of 94% by the reaction of I and styrene glycol in benzene in the presence of monochloroacetic acid as a catalyst. The product was proved to be identical with dimer A by its infrared spectrum and yielded 18% of I and 70% of the starting material when treated with aqueous sulfuric acid, but the latter was proved to be contaminated with a small amount of dimer B by the presence of a weak absorption in its carbonyl range and by its higher refractive index. Thus we have concluded that dimer A was 2-benzyl-4-phenyl-1, 3-dioxorane and that the equilibrium mixture of I, styrene glycol and IV is rapidly formed in the reaction of the glycol with an aqueous acid under suitable conditions, while I gradually changed to dimer B. The course of the reaction may be represented by the following scheme;



IV (dimer A)

Preparation of Phenylacetaldehyde. — Based upon the above-mentioned results, the following procedure was used for the preparation of I. A mixture of styrene glycol and of an aqueous acid was refluxed for one hour; steam was then introduced immediately into the reaction mixture to distill out the I, avoiding the dimerization resulting from prolonged contact with the acid. The volume of the reaction mixture was kept almost constant during the course of the steam distillation by applying a controlled external heating. By this technique we realized a significantly higher yield (as much as 70%) of I, as is summarized in Table IV.

TABLE IV. PREPARATION OF PHENYLACETALDEHYDE

No.	Materials	Acid		Yield of phenylacetaldehyde %
		Kind	Concn. mol./l.	
1	Styrene glycol	H_2SO_4	2.24	31.3*
2	Styrene glycol	H_2SO_4	1.01	62.2
3	Styrene glycol	H_2SO_4	1.78	70.2
4	Styrene glycol	H_2SO_4	2.29	63.3
5	Styrene glycol	H_2SO_4	3.49	56.4
6	Dimer A	H_2SO_4	2.23	66.7
7	Styrene glycol	H_3PO_4	5.03	70.2
8	Styrene glycol	H_3PO_4	5.96	57.5

* Steam distillation was performed without external heating.

Experimental

Styrene Glycol. — Styrene glycol was prepared from styrene by the method of Emerson[2] through styrene chlorohydrin; it appeared as white needles; m. p., 67.0~67.5°C.

Reaction of Styrene Glycol with Aqueous Acid. —A mixture of styrene glycol (10 g.) and aqueous acid (150 ml.) was refluxed for two hours. The reaction mixture was then cooled and extracted with ether (50 ml.×3), and the combined extract was washed with a 5% sodium carbonate solution and water and dried over anhydrous sodium sulfate. The ether was distilled off, and the residue was vacuum-distilled to yield: 1. phenylacetaldehyde (b. p. 56.0~58.0°C/5 mmHg); 2. a higher boiling fraction (b. p. 150~157°C/5 mmHg). The yields of these fractions under a variety of conditions are shown in Tables I and II. Redistillation of the combined fraction 1 gave pure phenylacetaldehyde, b. p. 57.0~57.5°C/5 mmHg, n_D^{25} 1.5319, semicarbazone, m. p. 150~151°C. The higher boiling fractions a and b indicated in Table I were combined and redistilled; b. p., 157~158°C/5 mmHg, n_D^{25} 1.5697.

Found: C, 80.42; H, 6.80. Calcd. for $C_{16}H_{16}O_2$: C, 80.00; H, 6.70%.

Reaction of Phenylacetaldehyde with Aqueous Acid.—A mixture of phenylacetaldehyde (5 g.) and 2.42 mol./l. aqueous sulfuric acid (100 ml.) was refluxed for two hours, and the reaction mixture was treated as above to give: 1. phenylacetaldehyde, 0.9 g. (18%) (b. p. 55.5~58.0°C/5 mmHg); 2. a higher boiling fraction, 3.5 g. (70%) (b. p. 158~161°C/5 mmHg, n_D^{25} 1.5970). The latter showed strong absorptions at 1730 and 1698 cm^{-1} but lacked

3) L. A. Bryan, W. M. Smedley and R. K. Summerbell (ibid., 72, 2206 (1950)) have reported that 2, 5-diphenyl-1, 4-dioxane (II) was a solid with a m. p. of 121~122 and of 173°C (cis and trans forms respectively).

them in the 1150~1100 cm^{-1} region, and treatment with an aqueous sulfuric acid gave only the recovered material in a yield of 90%.

2-Benzyl-4-phenyl-1, 3-dioxorane (IV). — A mixture of styrene glycol (5 g.), phenylacetaldehyde dimethylacetal (6 g.), and monochloroacetic acid (4 g.) in 50 ml. of benzene was refluxed for two hours. Thirty milliliters of benzene was distilled off from the reaction mixture, and the residue was neutralized with a 5% sodium carbonate solution, washed with water, and dried over anhydrous sodium sulfate. Distillation under vacuum gave 8.3 g. (94%) of 2-benzyl-4-phenyl-1,3-dioxorane; b. p., 187~188°C/14 mmHg, n_D^{25} 1.5669. Treatment of the compound with 2.42 mol./l. aqueous sulfuric acid gave an 18% yield of phenylacetaldehyde and a 70% yield of dimer A; b. p., 177~182°C/12mmHg, n_D^{25} 1.5675.

Preparation of Phenylacetaldehyde.—A mixture of styrene glycol (10 g.) and 1.78 mol./l. aqueous sulfuric acid (150 ml.) was refluxed for one hour. The reaction mixture was then immediately steam-distilled under external heating of the flask so that the volume of the content was kept constant. The distillate was saturated with sodium chloride and extracted with ether (50 ml.×3). The combined extract was washed with a 10% sodium bicarbonate solution and water and dried over anhydrous sodium sulfate. The ether was distilled off, and the residue was vacuum-distilled to give 6.1 g. (70.2%) of phenylacetaldehyde. The results under other conditions are given in Table IV.

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