which at that pressure boils at 77°. Upon distilling *o*-vinylphenol from the polymerized product a temperature approximating that given by Fries and Fickewirth is noted.[8]

(2) **3,5,1¹,1²-Tetrabromo-2-hydroxy-ethylbenzene.**—*o*-Vinylphenol, as prepared above in a chloroform solution, was treated with an excess of bromine with cooling. After the action had subsided, the hydrogen bromide, excess bromine, and chloroform were driven off with heat and the remaining solid purified by recrystallization from benzene. The final product melted at 105°, which is in agreement with the literature.

(3) ***o*-Vinylphenoxyacetic Acid.**—Molar quantities of *o*-vinylphenol, as prepared above, and bromoacetic acid were allowed to stand at room temperature in an alkaline solution for a few hours. The solution was then acidified and the resulting product purified by recrystallization from benzene or dilute alcohol. Prisms melting at 137° were obtained. This also was in agreement with the literature.

(4) **(β-Hydroxy-ethyl)-phenyl Ether.**—Molar quantities of potassium phenoxide and ethylene chlorohydrin were heated at 150° for six hours, and after cooling and filtering the liquid was distilled in vacuo. The fraction boiling at 163–167° at 80 mm. was retained as being the desired phenoxy glycol.

(5) ***o*-Vinylphenol from (β-Hydroxy-ethyl)-phenyl Ether.**—A molar quantity of the phenoxy glycol was allowed to stand for one week at room temperature with a fifth molar quantity of concentrated sulfuric acid. The product was washed with water and distilled in vacuo. *o*-Vinylphenol with the same boiling point as previously given was obtained; it formed the same bromine and acetic acid derivatives, proving that the compounds prepared by the two different methods were identical.

Summary

1. Ethylene oxide reacts with phenol in the cold in the presence of concentrated sulfuric acid to yield an ortho substituted phenol.

2. A probable mechanism for the above reaction has been advanced and reasons substantiating it have been given.

3. Two new methods for the preparation of *o*-vinylphenol have been discussed.

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NOTES

The Optical Activity of Cystine Preparations Used for Animal Experimentation.—Marston and Robertson[1] have recently expressed the opinion that much of the confusion in the literature dealing with cystine metabolism might have been avoided by determining the optical activity of the preparations used and have severely criticized certain studies on this account.

For several years we have been using cystine, prepared from human hair, in animal feeding experiments. Most of our preparations, as well as a number of student preparations subsequently reprecipitated by the author,

[8] Fries and Fickewirth, *Ber.*, **41**, 370 (1908).

[1] Marston and Robertson, "The Utilization of Sulfur by Animals," Commonwealth of Australia, Council for Scientific and Industrial Research, Melbourne, **1928**, Bulletin No. 39, 51 pp.

have been tested for their optical activity. All of these preparations were made for use in animal experimentation, and not for the determination of precise physical and chemical constants. It occurred to the writer that this information might furnish a rough index of the validity of Marston and Robertson's criticisms.

The method of isolation was essentially that outlined by Morrow.[2] The isoelectric precipitations were controlled with Congo red and litmus papers. The student preparations had been precipitated only once from the more or less successfully decolorized solutions, and varied considerably in color and tyrosine content. These preparations were subsequently reprecipitated by the author.

After drying, 1 g. of each of the above preparations was made up to 100 ml. in *N* hydrochloric acid, analyzed for sulfur and polarized at 21°. The accompanying table shows the results obtained.

Sample	S, %	$[\alpha]_D^{21}$	Remarks
158	26.02	−212.3°	Author's preparation
159	26.02	−212.3°	Student preparation
160	26.34	−210.4°	Student preparation
161	25.91	−208.4°	Student preparation
162	26.14	−207.4°	Student preparation
163	26.53	−185.9°	Student preparation
164	26.40	−210.0°	Student preparation
177	26.48	−216.6°	Author's preparation

It is obvious that the variations in specific rotation cannot be explained on the basis of sulfur content. It is highly probable that any of these samples, with the exception of No. 163, is suitable for animal feeding unless it is assumed that inactive cystine is highly toxic. Subsequent treatment of Sample No. 163 indicated that the above variations in specific rotation are partly due to the prolonged washing of certain samples with hot water in order to remove the tyrosine present.

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p-Cymene Studies. XIV. p-Cymylhydrazine-2.—This note is an extension of a paper by Wheeler and Thomas [THIS JOURNAL, **51**, 3135 (1929)]. Additional salts such as the acetate, oxalate, lactate and benzoate and a condensation product with m-nitrobenzaldehyde have been prepared. Unstable products were obtained with formaldehyde, acetalde-

[2] Morrow, "Biochemical Laboratory Methods," John Wiley and Sons, Inc., New York, 1927, p. 140.

hyde, propional, heptaldehyde, chloral, furfural, *o*-chlorobenzaldehyde, 2,4-dichlorobenzaldehyde, anisaldehyde, ethyl acetoacetate, mesityl oxide, cyclohexanone, carvone and benzoylacetone. The products were reddish, viscous oils which did not crystallize at −30°. No reaction seemed to take place with *p*-hydroxybenzaldehyde, piperonal, vanillin and camphor. *p*-Cymylhydrazine cannot therefore be regarded as a good reagent for the carbonyl group.

Experimental.—The frequent appearance of tar, causing varying yields of cymylhydrazine, led to the observation that the acid concentration in the reduction process is very important. The proper acid concentration was obtained by running the sulfur dioxide into the sodium hydroxide solution until it was neutral and then continuing the passage of the gas for a period equal to one-tenth of the time required for neutralization. The free base did not change color in well-stoppered bottles.

TABLE I

PREPARATIONAL DATA

	Salt	Crystal form	Solvent	M. p., °C.	Action with H_2O
1	Acetate	Needles	Chloroform	63–64	Unstable
2	Lactate	Plates	Dil. CH_3OH	134.5	Stable
3	Oxalate	Plates	Ether-alcohol	167	Unstable
4	Benzoate	Needles	Ether-gasolene	72.5	Unstable

TABLE II

ANALYTICAL DATA

	Formula	Calculated for, %		Found, %
1	$C_{12}H_{20}O_2N_2$	CH_3COOH	26.8	27.1
2	$C_{18}H_{28}O_3N_2$	N	11.03	11.44
3	$C_{12}H_{18}O_4N_2$	$(COOH)_2$	21.50	21.53
4	$C_{17}H_{22}O_2N_2$	C_6H_5COOH	42.66	42.71

***m*-Nitrobenzaldehyde-*p*-cymylhydrazine-2,** $C_{10}H_{13}NHN{:}CHC_6H_4NO_2$.—Two grams of the aldehyde was dissolved in a very little petroleum ether–alcohol (1–1) and mixed with 5 g. of cymylhydrazine in 5 cc. of petroleum ether. A bright red precipitate formed at once. The product crystallizes beautifully from glacial acetic acid, alcohol or benzene, hot solutions on cooling giving abundant yields of rectangular prisms which melt at 143°. The crystals are very rich red, though yellow by transmitted light. Ether or acetone solutions may be precipitated by heptane. The compound is stable toward hot water.

Anal. Calcd. for $C_{17}H_{19}O_2N_3$: N, 14.14. Found: 14.23.

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Homochromanone.[1,2]—Since phenoxyacetic and β-phenoxypropionic acids can be converted by loss of water into coumaranone[3] and chromanone,[4] respectively, it seemed likely that homochromanone could be obtained in a similar manner from γ-phenoxybutyric acid. It was found in this investigation that γ-phenoxybutyric acid did yield homochromanone, although, as might have been expected, the formation of the 7-membered ring did not take place as smoothly as that of the 6-membered ring in chromanone. In fact, the yields were so poor that proper purification of the product was impossible due to the small quantity obtained.

Attempts to dehydrate γ-phenoxybutyric acid with phosphorus pentachloride and with thionyl chloride were unsuccessful. Treatment of the acid with thionyl chloride and then with anhydrous aluminum chloride yielded no homochromanone. It was found that the best results were obtained by dehydrating the acid in small portions (1 g.) with phosphorus pentoxide.

Although no pure homochromanone was obtained, the semicarbazone and oxime were prepared and purified.

Homochromanone.—One gram of γ-phenoxybutyric acid dissolved in 15 cc. of benzene was treated with 1 g. of phosphorus pentoxide following the method described by one of us[4a] for the preparation of chromanone. On evaporation of the benzene a few drops of a lemon-yellow, highly refracting oil remained. Attempts to induce crystallization were unsuccessful, and even after combining the product from several runs, not enough was obtained to carry out a distillation. The oil was readily soluble in ether, benzene, petroleum ether and alcohol. A drop dissolved in concd. sulfuric acid gave a red solution on warming.

Semicarbazone.—This was prepared in the same manner as chromanone semicarbazone. It crystallizes from alcohol in white needles, m.p. 228–229° (uncorr.).

Anal. (Kjeldahl). Subs., 0.0980, 0.2231: HCl (0.0969 *N*), 14, 31.04 cc. Calcd. for $C_{11}H_{13}O_2N_3$: N, 19.2. Found: 19.4, 18.9.

Oxime.—This was prepared in the same manner as chromanone oxime. It crystallizes from petroleum ether in white plates, m. p. 99°.

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[1] Presented at the Cincinnati meeting of the American Chemical Society, September, 1930.

[2] This paper is taken from a portion of a thesis submitted by Lucile Anderson in partial fulfilment of the requirements for the degree of Master of Science.

[3] Stoermer and Bartsch, *Ber.*, **33**, 3175 (1900).

[4] (a) Powell, THIS JOURNAL, **45**, 2708 (1923); (b) Arndt and Källner, *Ber.*, **57B**, 202 (1924).