found possible to replace but one of the two halogen atoms with an OR group (where R is either an alkyl or an aryl radical). The structure of the resulting compounds has been determined and shows that the halogen attached to the carbon atom at position 4 is more reactive than the halogen atom on carbon atom 2. Recrystallization of dichloroquinazoline from toluene or toluene plus petroleum ether yields a very pure product; these solvents are superior to benzene (which had been previously used in the preparation) because of the greater temperature coefficient of solubility. The following new compounds have been prepared: 2-chloro-4-methoxyquinazoline, 2-chloro-4-ethoxyquinazoline, 2-chloro-4-phenoxyquinazoline and 2-chloro-4-resorcinoxyquinazoline.

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THE PREPARATION OF CERTAIN GAMMA-LACTONES

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Gamma-butyrolactone was prepared by a method which involves (1) the condensation of the sodium salt of ethyl malonate with β-chloro-ethylvinyl ether to form ethyl vinyloxyethylmalonate,[1] (2) saponification of the ester, (3) liberation of the free acid with simultaneous hydrolysis and liberation of acetaldehyde to form β-hydroxyethylmalonic acid, (4) pyrogenic decomposition to the lactone of γ-hydroxybutyric acid. The alpha-substituted ethyl and propyl butyrolactones were prepared in the same manner from the corresponding alkyl malonic esters.

Fittig and Chanlarow[2] prepared the α-ethyl derivative by hydrolysis of ethyl β-hydroxyethylacetoacetate. The unsubstituted lactone has been prepared by a variety of methods.[3]

It is interesting to note that in Fittig's description of α-ethyl butyrolactone he stated that a clear, approximately saturated water solution of the lactone on warming in the hand became clouded and remained so when placed in hot water until a temperature between 80–90° was reached, whereupon the second phase disappeared to reappear upon slight lowering of the temperature. When cooled more strongly, the solution again became clear. We have repeated Fittig's experiment with the same result. So far as the authors are aware, this is the first mention in the literature of a

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[1] Cretcher, Koch and Pittenger, This Journal, **47**, 1173 (1925).

[2] Fittig and Chanlarow, *Ann.*, **226**, 327 (1884).

[3] (a) Frühling, *Monatsh.*, **3**, 700 (1882); (b) Michael, *Ber.*, **34**, 4053 (1901); (c) Henry, *Bull. soc. chim.*, [2] **45**, 341 (1886); (d) Bentley, Haworth and Perkin, *J. Chem. Soc.*, **69**, 168 (1896); (e) Willstätter, *Ber.*, **35**, 619 (1902); (f) Fittig and Roder, *Ann.*, **227**, 23 (1885); (g) Marvel and Birkhimer, This Journal, **51**, 260 (1929).

system having both upper and lower consolute points. This fact has been overlooked by those who have investigated closed solubility curves.[4]

The present authors have found that the system α-propyl-γ-butyrolactone–water has no determinable lower consolute temperature because of the separation of water in the solid phase before the lower critical temperature is reached.

Experimental Part

Preparation of γ-Butyrolactone.—44.5 g. of ethyl vinyloxyethylmalonate was added to a solution of 43 g. of potassium hydroxide in 35 cc. of water. The mixture was slowly warmed, with continual agitation, in a water-bath. At about 30° the saponification took place, the temperature going spontaneously to the boiling point of alcohol. After the vigorous reaction was over, the solution was heated on a water-bath for thirty minutes. After cooling 140 cc. of 1:1 hydrochloric acid was added and the solution evaporated to dryness under reduced pressure. The solid mass was cooled and extracted several times with anhydrous ether. The ether was removed by distillation and the distilling flask placed in such a position that the side-tube was inclined slightly upward. A short air condenser was attached to the side-tube and the flask was provided with a thermometer immersed in the solution. Water was removed by cautious heating over a direct flame.

The temperature was raised to 180° to decompose the dibasic acid and the product was then distilled. The yield of lactone boiling at 201–205° was 72% of the theoretical.

Brucine Salt of γ-Butyrolacetone.—The brucine salt of the unsubstituted hydroxybutyric acid offered no difficulties in purification. The salts of the ethyl and propyl substituted acids were not obtained in pure condition and will not be described.

The brucine salt was prepared by heating a water solution of the lactone with an excess of the alkaloid. The excess brucine was extracted with chloroform, the solution filtered through "Nuchar" and evaporated to dryness under reduced pressure. The salt was twice dissolved in 95% alcohol, cooled and precipitated with ether. It was then dried to constant weight, *in vacuo*, over phosphorus pentoxide. The compound softened at 80° and melted at 147–148°. It is very hygroscopic.

Anal. Calcd. for $C_{27}H_{34}O_7N_2$: N, 5.62. Found: N, 588, 562.

Optical rotation. 0.2579 g. in 10.08 cc. of aqueous solution in a 1-dm. tube gave $\alpha = -0.69°$; $[\alpha]^{25}_{D}$ $-26.97°$.

Sodium γ-Hydroxybutyrate.—It was stated by Marvel and Birkhimer[3g] that on neutralization of the lactone of γ-hydroxybutyric acid with sodium hydroxide a 40% yield of the sodium salt was obtained. In order to determine, if possible, the cause of their low yield of salt, we neutralized the lactone, with results as follows: the calculated amount of *N* sodium hydroxide was added to a hot aqueous solution of 1.509 g. of the lactone. The ring was easily opened, as the pink color due to a drop of phenolphthalein disappeared after several minutes. The solution was evaporated under reduced pressure to dryness and the residue dissolved in hot alcohol. On cooling part of the salt crystallized. The precipitation was completed by addition of ether. The product, dried over phosphorus pentoxide, weighed 1.960 g., corresponding to a yield of 89% of the theoretical.

Anal. Subs., 0.1644: Na_2SO_4, 0.0930. Calcd. for $C_4H_7O_3Na$: Na, 18.27. Found: Na, 18.32.

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[4] *Cf.* Cox, Nelson and Cretcher, THIS JOURNAL, **49**, 1080 (1927), for references to the literature of this subject.

When an excess of alkali was used for neutralization of the lactone a substance was formed which was not the sodium salt of the hydroxy acid. This substance was insoluble in alcohol or water.

α-Ethyl γ-Butyrolactone.—This compound was prepared from ethyl, ethylvinyloxyethyl malonate[5] in the same manner as γ-butyrolactone except that the saponification was conducted in alcoholic solution. From 12 g. of the malonic ester 2.8 g. of product was obtained boiling at 214–218°. The yield was 59% of the theoretical.

α-Propyl-γ-butyrolactone was prepared as above from ethyl propylvinyloxyethyl malonate.[5] The product boiled at 230–235°; d_4^{25} 1.008. The yield was 63% of the theoretical.

Anal. Calcd. for $C_7H_{12}O_2$: C, 65.57; H, 9.45. Found: C, 65.23; H, 9.34.

Neutralization equivalent. Calcd.: 128.1. Found: 127.8.

Summary

A method is described for the preparation of γ-butyrolactone and its α-alkyl derivatives.

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[CONTRIBUTION NO. 68 FROM THE COBB CHEMICAL LABORATORY OF THE UNIVERSITY OF VIRGINIA]

SYNTHESES IN THE PHENANTHRENE SERIES. I. ACETYLPHENANTHRENES[1]

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The preparation of 9-acetylphenanthrene was described by Willgerodt and Albert[2] in 1911. These authors obtained the substance by the Friedel–Crafts reaction, and describe it as fluorescent leaflets of melting point 123°. Analysis and the formation of an oxime and a phenylhydrazone showed the compound to be a phenanthryl methyl ketone. Oxidation with chromic acid led exclusively to 9,10-phenanthrenequinone, showing that the acetyl group occupied the 9-position on the phenanthrene nucleus. The authors do not mention the yields obtained, but from their description it is to be gathered that the ketone is very difficult to obtain in a pure state because of accompanying oils and tarry material.

In attempting to prepare 9-acetylphenanthrene according to Willgerodt's directions, we have obtained results differing considerably from those mentioned above. Acetylation of phenanthrene with acetyl chloride and aluminum chloride in carbon disulfide solution, under Willgerodt's conditions, gave a small amount of crystalline material, together with resinous products and a considerable quantity of a thin oil. From the oil a small quantity of a ketone could be isolated as the semicarbazone; the oil dis-

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[5] Cretcher, Koch and Pittenger, THIS JOURNAL, **47**, 3083 (1925).

[1] These researches have been supported by the Committee on Drug Addiction of the National Research Council.

[2] Willgerodt and Albert, *J. prakt. Chem.*, [2] **84**, 383 (1911).