tives show a slight decrease as the molecular weight increases, although less of the *sec.*-amyl derivative is required to produce anesthesia than of the *sec.*-butyl or the *sec.*-hexyl derivatives.

The writers wish to express their appreciation to Dr. G. H. A. Clowes, Director of the Lilly Research Laboratories, for his suggestions.

Summary

1. The following new esters of diethylmalonate have been prepared and described: diethylcarbinyl, cyclopentyl, *n*-butyl-allyl, β-hydroxyethyl-ethyl, diethyl-carbinyl-ethyl, isopropylmethylcarbinyl-ethyl, cyclopentyl-ethyl, *n*-butylmethylcarbinyl-ethyl, di-*n*-propylcarbinyl-ethyl, phenyl-ethyl-ethyl and *n*-heptyl-ethyl.

2. The following new barbituric acids have been prepared and described: cyclopentyl, cyclopentyl-ethyl, *n*-butyl-methylcarbinyl-ethyl, propylmethylcarbinyl-allyl, diethylcarbinyl-allyl, and cyclopentyl-allyl barbituric acids.

3. No marked difference was found in the ratio, M. L. D./M. E. D. of the various isomeric amyl-ethyl or allyl barbituric acids. The ratio obtained for the amyl group was, however, double that obtained for diethyl or phenyl-ethylbarbituric acid. The secondary isomers usually were effective at a much lower dose than were the primary.

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[CONTRIBUTION FROM THE LABORATORIUM FUER CHEMISCHE TECHNOLOGIE DER UNIVERSITAET WIEN, VIENNA, AUSTRIA, AND NORTHWESTERN UNIVERSITY MEDICAL SCHOOL, DEPARTMENT OF RESEARCH BACTERIOLOGY, CHICAGO, ILLINOIS]

TWO ISOMERIC QUINONEDITHIOGLYCOLIC ACIDS

BY E. GEBAUER-FUELNEGG AND HELENE JARSCH

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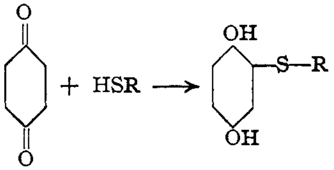
In the course of some work on the formation and properties of a variety of thioindigoid derivatives, the preparation of a 1,4-benzoquinone-2,5-dithioglycolic acid was attempted.

Usually the arylthioglycolic acids are prepared by alkaline condensation of the corresponding mercaptan with monochloro-acetic acid. As to the method of preparing the quinonedithioglycolic acids a general procedure was given by German Patent 175,070. According to this patent, *p*-quinones are found to react with substances represented by the general formula RSH (R representing an acid radical) as indicated by the equation



This reaction is said to proceed further when a second mole of quinone oxidizes the hydroquinone-monothio derivative to the corresponding quinone. A third and fourth RS group is said to be introduced by this method with primary formation of the corresponding hydroquinone derivatives by repeating the reaction.

The patent mentioned a variety of substances to be used as RSH. However, no reference could be found for the reaction with thioglycolic acid, which apparently is of possible value. In fact, the reaction did not proceed, as we found, in the way indicated by the general equation given, since under all circumstances tested the reaction product consisted chiefly of two isomeric 1,4-benzoquinonedithioglycolic acids, which were separated by their different solubilities in ether.

Upon treatment of the two isomers with dehydrating agents, they behave differently. The one which forms the main part of the reaction yields finally an intensely violet substance if added to an excess of chlorosulfonic acid. It dyes cotton (vat dye) as well as wool (acid dye) a greenish-blue color. The fact that condensation actually occurred makes it most likely that the isomer in question is the 1,4-benzoquinone-2,5-dithioglycolic acid (2,6-substitution is unlikely but possible).

The second isomer upon treatment in the above manner yielded no colored substance. Its structure therefore is given as the 1,4-benzoquinone-2,3-dithioglycolic acid.

The dual behavior of the thioindigoid dye prepared from the 2,5-isomer as noted above possibly gives a clue as to the structure of the dye obtained, even though it was not obtained in a sufficient degree of purity to insure reliable analysis. It will be discussed elsewhere.

The 1,4-benzoquinone-2,5-(2,6?)-dithioglycolic acid was found to exist in two modifications: brown needles (from ether by precipitation with ligroin below 30–40°) and a red powder m. p. 171 (from other solvents at elevated temperatures). The two modifications can be converted into each other and crystallized from water in deep violet, sometimes nearly black, needles containing one mole of water; the water of crystallization is lost at 50–60° with formation of the intensely red colored modification mentioned above.

Experiments

Preparation and Behavior of the Two Isomeric 1,4-Benzoquinone-dithioglycolic Acids.[1]—After a number of preliminary experiments varying the relative amounts of the components, temperature of the reaction and solvents to be used, the following procedure was finally adopted for the preparation and isolation of the two isomeric quinone dithioglycolic acids. Ten grams of quinone were dissolved in 100 cc. of chloroform and 8.6 g. of thioglycolic acid dissolved in 100 cc. of chloroform was added. The reaction mixture first turned greenish-black (quinhydrone) but began to deposit a red precipitate

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[1] The preliminary experiments were carried out with H. A. Beatty.

after thirty-six hours. After seventy hours the mixture was filtered and dried in a vacuum. Upon extraction with ether for twenty-four hours in a Soxhlet apparatus, a red residue was left. This residue was then extracted with benzene several times to insure its freedom from hydroquinone and repeatedly recrystallized from water. Finally violet (black) needles were obtained melting at 205° (const.). The figures obtained by the analysis correspond well with the values for a 1,4-benzoquinonedithioglycolic acid.

Anal. Subs., 5.205 mg.: CO_2, 7.904 mg.; H_2O, 1.461 mg. Subs., 0.1016: $BaSO_4$, 0.1597. Calcd. for $C_{10}H_8O_6S_2$: C, 41.64; H, 2.80, S, 22.26. Found: C, 41.42; H, 3.14; S, 21.59.

The ether extract was evaporated to dryness and extracted with benzene in a Soxhlet apparatus. The extraction was stopped when all of the hydroquinone present was dissolved. The residue finally gave, on repeated recrystallization from water, violet (black) needles which melted at 171° and analyzed well for 1,4-benzoquinonedithioglycolic acid plus one mole of water.

Anal. Subs., 5.181 mg.: CO_2, 7.591 mg.; H_2O, 1.578 mg. Calcd. for $C_{10}H_8O_6S_2 \cdot H_2O$: C, 39.19; H, 3.29. Found: C, 39.96; H, 3.41.

The water of crystallization is lost at about 60° with the formation of a bright red substance. Its formation is also noticeable when the melting point is determined. These red needles analyze well for a water-free quinonedithioglycolic acid.

Anal. Subs., 5.301 mg.: CO_2, 8.066 mg.; H_2O, 1.606 mg. Calcd. for $C_{10}H_8O_6S_2$: C, 41.66; H, 2.80. Found: C, 41.50; H, 3.39. Subs., 0.0155: after drying in a vacuum of 13 mm. to constant weight, 0.0145; diff., 0.0010. Calcd. for $C_{10}H_8O_6S_2 \cdot H_2O$: H_2O, 5.89. Found: H_2O, 6.45.

Upon the recrystallization from water of both isomers an appreciable amount of substance is lost, the mother liquors become brown and contain decomposition products of the original acid. These mother liquors, upon acidification, dye wool a clear and fast brown color; the substances found have not been investigated.

The hydrated and water-free modifications are interconvertible. Both forms dissolve in ether giving an orange-red solution and are precipitated from such solutions in the form of brown needles by an excess of ligroin. These needles apparently represent a second water-free modification (containing no solvent of crystallization). It is stable only at low temperatures, since it was found that when the ligroin precipitation is carried out at 40° the red modification is obtained immediately. The brown modification upon recrystallization from water also yields the violet (black) needles containing one mole of water.

The two isomeric quinonedithioglycolic acids described are the main products of the reaction. There are, however, other substances formed and found in the various extracts and mother liquors. Their isolation has not yet been attempted due to the comparatively small amounts formed.

The 1,4-benzoquinonedithioglycolic acid, m. p. 205°, was treated in the usual manner with chlorosulfonic acid but was found not to condense. The acid, therefore, is most likely the 1,4-benzoquinone-2,3-dithioglycolic acid.

The second isomer, m. p. 171°, condensed readily upon heating with an excess of chlorosulfonic acid for twelve hours at 50–70°. The thioindigoid dye was isolated. This isomer therefore represents a 1,4-benzoquinone-2,5(2,6?)-dithioglycolic acid.

Summary

Two isomeric benzoquinonedithioglycolic acids have been prepared. Their structures are given and their properties described. Upon condensa-

tion with chlorosulfonic acid the 1,4-benzoquinone-2,5-(2,6?)-dithioglycolic acid forms a thioindigoid dye.

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[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE JOHNS HOPKINS UNIVERSITY]

THE EFFECT OF DISSOCIATED WATER VAPOR ON CERTAIN VEGETABLE OILS

BY G. I. LAVIN AND E. EMMET REID

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Introduction

Bonhoeffer[1] has shown that atomic hydrogen will attack the double bond in a straight-chain compound like oleic acid. Watermann and Bertram[2] found that active hydrogen (dried) caused the oleic acid to undergo a polymerization along with the hydrogenation. Wood[3] has conducted some experiments with cottonseed oil and atomic hydrogen and obtained a white solid. In a recent paper Urey and Lavin[4] have shown that water vapor dissociated in a discharge tube is an energetic reducing agent and it is the purpose of this note to describe some experiments carried out with dissociated water vapor and cottonseed oil.

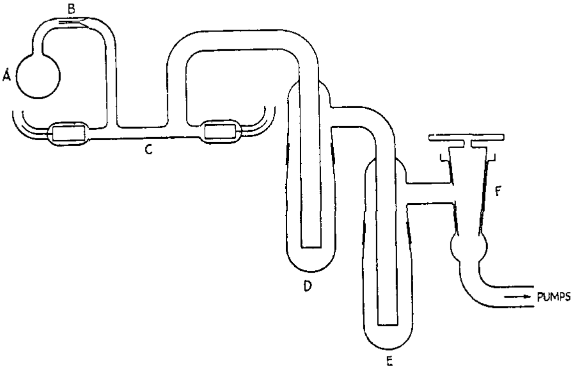

Fig. 1.—Apparatus for treatment of oils with dissociated water vapor.

Apparatus.—The apparatus used is shown in the accompanying diagram. It consists essentially of a source of water vapor A, a capillary B, discharge tube C and traps E and F.

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[1] Bonhoeffer, *Z. physik Chem.*, **113**, 199 (1924).

[2] Watermann and Bertram, *Chem. Umschau Fette, Oele, Wachseu. Harze*, **34**, 255 (1927).

[3] Private communication.

[4] Urey and Lavin, THIS JOURNAL, **51**, 3290 (1929).