XXXVII.—*Phenolcitraconein*.

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SOME years ago, one of us (F.G.P.), in conjunction with J. T. Hewitt, obtained in the preparation of citraconfluorescein a very small quantity of a by-product. This compound appeared, from the results of its analysis and from its properties, as far as they could be ascertained, to be a dihydroxybenzoylcrotonic acid, $C_6H_3(OH)_2 \cdot CO \cdot C_3H_4 \cdot CO_2H$. Lack of material and pressure of other work at the time prevented further examination of the acid.

Citraconic anhydride is now being condensed with various phenols in the hope that, by the decomposition of the resulting substances, acids of the above type may be obtained and characterised. In this preliminary communication, the preparation and properties of the simple phenolcitraconein are described.

EXPERIMENTAL.

This substance was prepared by heating at 120° 20 grams of freshly distilled phenol, 10 grams of citraconic anhydride, and 10 grams of freshly fused zinc chloride. A current of dry hydrogen chloride was passed through the mixture for half an hour, after which the mixture was heated for a further six hours at 120° (compare Copisarow, T., 1920, 117, 209). The melt was then heated with very dilute hydrochloric acid, filtered, washed, and finally extracted by means of a 3 per cent. solution of sodium

hydroxide. The red solution thus obtained was precipitated by the addition of dilute hydrochloric acid, when the citraconein was obtained as a brown precipitate. This was collected, washed, dissolved in alcohol, and reprecipitated by the careful addition of water. It separated as a light brown powder, m. p. 159—161°, readily soluble in alcohol, ether, and chloroform (Found: C=72.22; H=5.11. $C_{17}H_{14}O_4$ requires C=72.34; H=4.96 per cent.).

Phenolcitraconein dissolves readily in aqueous solutions of the alkali hydroxides, yielding red solutions, which are fainter in colour than similar solutions of phenolphthalein. The colour of the alkaline solution is discharged by the addition of acids or by the use of an excess of alkali. In the latter case, however, the colour reappears on acidification, even if the alkaline solution has been previously boiled.

The *potassium* salt was obtained as a "scale" by dissolving the citraconein in the calculated amount of potassium hydroxide, previously dissolved in water, and concentrating the red solution (Found: K=21.97. $C_{17}H_{12}O_4K_2$ requires K=21.78 per cent.).

A *tetrabromo*-derivative, $C_{17}H_{10}O_4Br_4$, was obtained when a solution of bromine in glacial acetic acid was gradually added to a solution of the citraconein in the same solvent. The mixed solutions were heated on the water-bath for half an hour, and then poured into water, when an orange-yellow precipitate was obtained. This was collected, washed, and dried in the usual manner. It was soluble in ether, chloroform, and benzene, and melted at 189° (Found: Br=53.30. $C_{17}H_{10}O_4Br_4$ requires Br=53.51 per cent.).

The *diacetyl* derivative was obtained by heating 5 grams of the citraconein with 20 grams of acetic anhydride and 5 grams of sodium acetate for two hours. The mixture was then poured into dilute alcohol, and the whole digested on the water-bath until the excess of acetic anhydride was destroyed. The solid was collected, washed, boiled a second time with water, and finally crystallised from alcohol, from which it separated as a very light brown, micro-crystalline powder melting at 134° (Found: C=68.73; H=5.11. $C_{21}H_{18}O_6$ requires C=68.85; H=4.91 per cent.).

The *dibenzoyl* derivative was prepared by the Schotten-Baumann method. The crude product was dissolved in acetone, and the solution filtered into an excess of benzene, when the dibenzoate separated as a nearly colourless precipitate melting at 99° (Found: C=75.45; H=4.63. $C_{31}H_{22}O_6$ requires C=75.92; H=4.69 per cent.).

The *dimethyl ether*, $C_{19}H_{18}O_4$, was prepared by dissolving 5.6

grams of the citraconein in the calculated quantity of potassium hydroxide, previously dissolved in aqueous methyl alcohol, and adding 5 grams of methyl sulphate. The mixture was heated on the water-bath for two hours, and then faintly acidified. The brown solid obtained was collected, washed, dissolved in alcohol, and the solution poured into water, when the ether separated as a brown powder melting at 135° (Found: $C=73.46$; $H=5.62$. $C_{19}H_{18}O_4$ requires $C=73.54$; $H=5.80$ per cent.).

The *diethyl ether*, $C_{21}H_{22}O_4$, was prepared by dissolving the citraconein in a solution of the calculated amount of potassium hydroxide, adding 6.2 grams of ethyl iodide, and heating the whole under reflux for two hours on the water-bath. The solution was poured into water, the precipitate collected, washed, and dried. The substance is soluble in ether, chloroform, and acetic acid, and melts at 132° (Found: $C=74.31$; $H=6.49$. $C_{21}H_{22}O_4$ requires $C=74.55$; $H=6.50$ per cent.).

A *fluoran* derivative of citraconic anhydride was prepared by heating 4.3 grams of *p*-cresol with 2.2 grams of the anhydride and 3 grams of zinc chloride, and treating the product as described

under the citraconein. It is a light grey solid, m. p. $128-129^{\circ}$, which is insoluble in the alkali hydroxides, but dissolves readily in alcohol (Found: $C=77.95$; $H=5.64$. $C_{19}H_{16}O_3$ requires $C=78.08$; $H=5.47$ per cent.).

In conclusion, we desire to express our thanks to the firm of Messrs. Thos. Morson and Son for placing the necessary citraconic anhydride at our disposal.

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