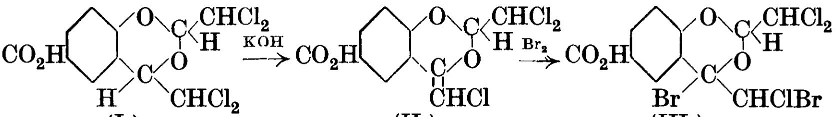
CCXXXIII.—*The Condensation of Dichloroacetaldehyde with* p-*Hydroxybenzoic Acid.*

By Frederick Daniel Chattaway and Larkin Hundley Farinholt.

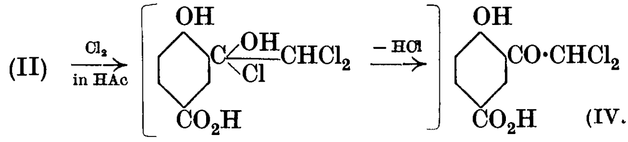
It has been shown (Chattaway, J., 1926, 2720; Chattaway and Calvet y Prats, J., 1927, 685; 1928, 1088, 2915; Chattaway and Morris, J., 1927, 2013) that certain para-substituted phenols react with chloral in the presence of concentrated sulphuric acid to form the benzdioxin ring. In a similar manner the condensation of dichloroacetaldehyde with *p*-nitrophenol and phenol-*p*-sulphonic acid has been accomplished (Chattaway and Morris, J., 1928, 3241), also with the formation of substituted benzdioxins. That this appears to be a general reaction between phenols and aldehydes which can be kept in contact with concentrated sulphuric acid for some time without decomposition is further shown by the condensation of *p*-hydroxybenzoic acid with dichloroacetaldehyde.

In the presence of concentrated sulphuric acid, two molecules of dichloroacetaldehyde condense with one molecule of *p*-hydroxybenzoic acid with the loss of one water molecule to form 6-*carboxy*-2 : 4-*bisdichloromethyl*-1 : 3-*benzdioxin* (I). This acid is a colourless well-crystallised compound which yields similarly constituted *esters*, *acid chloride*, *amide*, and *anilide* without the rupture of the heterocyclic ring. Alcoholic potash removes one molecule of hydrogen chloride from the 4-dichloromethyl group, giving an unsaturated product (II) which combines readily with bromine (III).



(I.) (II.) (III.)

The action of chlorine, even in the absence of sunlight, upon the unsaturated compound (II) does not form a substance analogous to that obtained with bromine, but breaks down the dioxin ring and produces ωω-dichloro-5-carboxy-2-hydroxyacetophenone (compare Chattaway and Calvet y Prats, J., 1927, 691), which must be produced by hydrolysis, addition of chlorine, and the splitting off of a molecule of hydrogen chloride, thus :



(IV.)

This establishes the constitution of the original unsaturated acid and shows that the double bond must occur at the 4- and not at the 2-position.

The corresponding *ester* is not formed when 6-*carboxy*-2-*dichloromethyl*-4-*chloromethylene*-1 : 3-*benzdioxin* (II) is refluxed in ethyl alcohol saturated with hydrogen chloride. It is easily obtained, however, by treating the ester of 6-carboxy-2 : 4-bisdichloromethyl-1 : 3-benzdioxin with the calculated amount of alcoholic potassium hydroxide.

EXPERIMENTAL.

6-*Carboxy*-2 : 4-*bisdichloromethyl*-1 : 3-*benzdioxin* (I).—To a solution of *p*-hydroxybenzoic acid (13·8 g.; 1 mol.) in 125 c.c. of concentrated sulphuric acid, dichloroacetaldehyde alcoholate,

$$CHCl_2\cdot CH(OH)\cdot OEt$$

(31·9 g.; 2 mols.) was slowly added, with vigorous stirring and cooling to about 5°. The liquid was kept at room temperature for 2 hours, becoming slightly brown, and was then poured over crushed ice. 6-*Carboxy*-2 : 4-*bisdichloromethyl*-1 : 3-*benzdioxin*, which separated as a grey viscous mass, was heated for several hours on a water-bath with excess of water and repeatedly crushed; it then became solid and granular (yield, 14·5 g.). It is insoluble in water, easily soluble in alcohol, acetic acid, ether and aqueous alkaline solutions, and sparingly soluble in light petroleum. The compound is best crystallised from a mixture of 2 parts of acetic acid and 1 part of water, in which it is moderately easily soluble, and separates in minute colourless plates, m. p. 181—183° (Found : C, 38·0; H, 2·4; Cl, 40·9. $C_{11}H_8O_4Cl_4$ requires C, 38·2; H, 2·3; Cl, 41·0%).

When the acid was gently heated with an excess of phosphorus pentachloride, the *acid chloride* was formed as a yellow semi-solid which was scraped into a mixture of ice and water and extracted with ether. The solution was dried over calcium chloride for 10 minutes, and on concentration the acid chloride separated as colourless flattened prisms, which were recrystallised from light petroleum–

ether; m. p. 110° (Found: Cl, 48·5. $C_{11}H_7O_3Cl_5$ requires Cl, 48·65%).

The *amide* was obtained by gently heating the acid chloride with a mixture of concentrated ammonia solution and alcohol in equal parts and pouring the solution into water. The oily liquid obtained solidified on standing; it was extremely soluble in alcohol, from which it crystallised in minute six-sided prisms, m. p. 177° (Found: Cl, 41·2. $C_{11}H_9O_3NCl_4$ requires Cl, 41·1%).

When the acid chloride was heated with aniline, and the product treated with dilute hydrochloric acid, the *anilide* was obtained. It separated from alcohol, in which it was very soluble, in tufts of flattened prisms, m. p. 145° (Found: Cl, 33·7. $C_{17}H_{13}O_3NCl_4$ requires Cl, 33·7%).

When the acid chloride was boiled with ethyl alcohol, or when an alcoholic solution of the acid saturated with hydrogen chloride was heated for 8—10 hours in a sealed tube at 100°, the corresponding *ethyl* ester was formed. It crystallised from alcohol, in which it was very soluble, in colourless, compact, six-sided prisms, m. p. 114—115° (Found: Cl, 38·2. $C_{13}H_{12}O_4Cl_4$ requires 37·9%).

The *methyl* ester, obtained in like manner by boiling the acid chloride with methyl alcohol, separated from alcohol in colourless flattened prisms, m. p. 113° (Found: Cl, 39·6. $C_{12}H_{10}O_4Cl_4$ requires Cl, 39·4%).

6-*Carboxy*-2-*dichloromethyl*-4-*chloromethylene*-1 : 3-*benzdioxin* (II).—To a solution of potassium hydroxide (23 g.; 8 mols.) in 200 c.c. of alcohol kept at about 70°, 6-carboxy-2 : 4-bisdichloromethyl-1 : 3-benzdioxin (14 g.; 1 mol.) was gradually added. Potassium chloride soon separated and when no further action took place, water was added to the mixture and the clear solution was poured into dilute hydrochloric acid. After 1 hour, an easily filterable, white solid, 6-*carboxy*-2-*dichloromethyl*-4-*chloromethylene*-1 : 3-*benzdioxin*, was obtained which crystallised from alcohol, in which it was extremely soluble, in clusters of colourless flattened prisms (10 g.), m. p. 183° (Found: Cl, 34·5. $C_{11}H_7O_4Cl_3$ requires Cl, 34·4%).

This compound was also prepared by hydrolysis of 6-carbethoxy-2 : 4-bisdichloromethyl-1 : 3-benzdioxin with hot aqueous sodium hydroxide and precipitation with dilute hydrochloric acid.

To a solution of 6-carboxy-2-dichloromethyl-4-chloromethylene-1 : 3-benzdioxin (II) in acetic acid, bromine was gradually added until the colour persisted. On careful addition of water 4-*bromo*-6-*carboxy*-2-*dichloromethyl*-4-*chlorobromomethyl*-1 : 3-*benzdioxin* (III) separated as a yellow crystalline solid. It crystallised from light petroleum (b. p. 60—80°) in clusters of long, slender, pale yellow prisms, m. p. 116° (Found : Br, 33·9. $C_{11}H_7O_4Cl_3Br_2$ requires Br, 34·1%).

6-*Carbethoxy*-2-*dichloromethyl*-4-*chloromethylene*-1 : 3-*benzdioxin*.—To a solution of 6-carbethoxy-2 : 4-bisdichloromethyl-1 : 3-benzdioxin (18 g.; 1 mol.) in 100 c.c. of alcohol was added an alcoholic solution of potassium hydroxide (2·8 g.; 1 mol.), and the mixture heated to about 50°. Potassium chloride separated, water was added, and the resulting solid *ester* was washed with dilute sodium hydroxide solution. It crystallised from alcohol in clusters of colourless, slender, flattened prisms, m. p. 102° (Found : Cl, 31·7. $C_{13}H_9O_4Cl_3$ requires Cl, 31·6%).

On treatment of this ester with hot aqueous sodium hydroxide, the unsaturated acid (II) was obtained by hydrolysis.

Action of Chlorine on 6-*Carboxy*-2-*dichloromethyl*-4-*chloromethylene*-1 : 3-*benzdioxin* (II) *and the Formation of* ωω-*Dichloro*-5-*carboxy*-2-*hydroxyacetophenone* (IV).—Chlorine was passed through a solution of 10 g. of the unsaturated acid (II) in 150 c.c. of glacial acetic acid in the dark, heat being evolved. When the solution was saturated with chlorine, it was poured into cold water. The white precipitate obtained crystallised from alcohol–water in thin plates, m. p. 163—165°, in every way identical with ωω-dichloro-5-carboxy-2-hydroxyacetophenone (Chattaway and Calvet y Prats, *loc. cit.*) (Found : Cl, 28·7. Calc. for $C_9H_6O_4Cl_2$: Cl, 28·5%).

The osazone, prepared by boiling an alcoholic solution of the acetophenone with excess of phenylhydrazine, agreed with that prepared by Chattaway and Calvet y Prats (*loc. cit.*) in every particular.

THE QUEEN'S COLLEGE LABORATORY,
OXFORD.

[*Received, May 7th,* 1931.]