

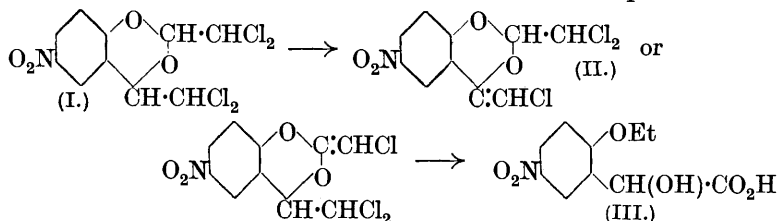
CCCCXXXI.—*The Condensation of Dichloroacetaldehyde with Phenols.*

By FREDERICK DANIEL CHATTAWAY and ALEXANDER ALLAN MORRIS.

THE new type of condensation between phenols and aldehydes leading to the formation of the dioxin ring (J., 1926, 2720; 1927, 685, 2013; this vol., p. 1088) is not confined to chloral, but appears to be a general reaction of those aldehydes which can be kept in contact with concentrated sulphuric acid for some time without decomposition. Dichloroacetaldehyde, for example, reacts with *p*-nitrophenol and phenol-*p*-sulphonic acid even more readily than chloral itself.

Thus with *p*-nitrophenol two molecules of the aldehyde condense with loss of one molecule of water, the final product being 6-*nitro*-2:4-*bisdichloromethyl*-1:3-*benzdioxin* (I). No hydroxyl group is present in the molecule, since the compound does not dissolve in dilute alkali solution and can be recrystallised unchanged from boiling acetic anhydride. It contains the nitro-group unchanged, since this can be reduced to an amino-group which can be acetylated or diazotised and replaced, the dioxin ring remaining unbroken during these reactions.

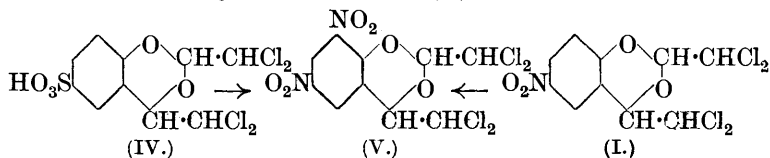
When the benzdioxin (I) is acted upon by alcoholic potash at 50—60°, one molecule of hydrogen chloride is removed from one of the $\text{CH}\cdot\text{CHCl}_2$ groups with formation of 6-*nitro*-2(or 4)-*dichloromethyl*-4(or 2)-*chloromethylene*-1:3-*benzdioxin* (II). If the temperature is not controlled, reaction proceeds further with the formation of 5-*nitro*-2-ethoxymandelic acid (III) as the final product, a reaction which establishes the constitution of the compound.



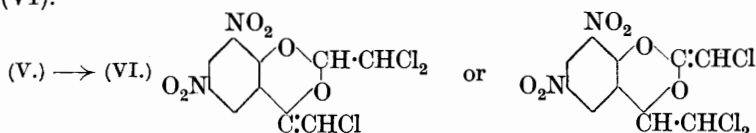
Similarly, dichloroacetaldehyde condenses with phenol-*p*-sulphonic acid, yielding 2:4-*bisdichloromethyl*-1:3-*benzdioxin*-6-*sulphonic acid* (IV). This compound behaves as a normal sulphonic acid. It is a colourless solid with no definite melting point and crystallises with one molecule of water. This molecule of water is probably attached to the sulphonic residue, since the ammonium salt is obtained in the anhydrous condition.

When acted upon by phosphorus pentachloride, the sulphonic acid yields a *sulphonyl chloride*. This with methyl and ethyl alcohols yields *esters*, with ammonia a *sulphonamide*, and with aniline a *sulphonanilide*.

The constitution of the sulphonic acid is similar to that of the condensation product (I), yielded by *p*-nitrophenol and dichloroacetaldehyde, since both compounds on nitration yield 6:8-*dinitro*-2:4-*bisdichloromethyl*-1:3-*benzdioxin* (V).



When acted upon by alcoholic potash, the dinitro-compound (V) loses one molecule of hydrogen chloride with formation of 6:8-dinitro-2(or 4)-dichloromethyl-4(or 2)-chloromethylene-1:3-benzdioxin (VI).



The further action of alcoholic potash causes profound decomposition.

EXPERIMENTAL.

6-Nitro-2:4-bisdichloromethyl-1:3-benzdioxin (I).—Dichloroacetaldehyde alcoholate (70 g.; 2 mols.) was added slowly with shaking to a well-cooled solution of *p*-nitrophenol (30 g.; 1 mol.) in 300 c.c. of concentrated sulphuric acid. The solution became warm and fumes of hydrogen chloride were given off while a viscid, yellow solid slowly separated on the surface. The mixture was kept at the ordinary temperature for 4 hours with occasional shaking and then poured over crushed ice. The viscid, brown solid obtained was freed from sulphuric acid by repeated washing with hot water and dissolved in boiling alcohol, in which it was readily soluble. On cooling, 6-nitro-2:4-bisdichloromethyl-1:3-benzdioxin separated. It was freed from a little unchanged *p*-nitrophenol by washing with warm dilute ammonia and hot water and recrystallised several times from boiling alcohol, in which it was very soluble, separating in pale yellow, flattened, rhombohedral plates (23 g.), m. p. 113.5° (Found: C, 35.0; H, 2.1; N, 4.1; Cl, 41.2; *M*, cryoscopic in benzene, 352, 357. $\text{C}_{10}\text{H}_7\text{O}_4\text{NCl}_4$ requires C, 34.6; H, 2.0; N, 4.0; Cl, 40.9%; *M*, 347).

6-Nitro-2(or 4)-dichloromethyl-4(or 2)-chloromethylene-1:3-benzdioxin (II).—6-Nitro-2:4-bisdichloromethyl-1:3-benzdioxin (20 g.; 1 mol.) was gradually added to a solution of potassium hydroxide (24 g.; 7 mols.) in 250 c.c. of alcohol kept at 50–60° by frequent cooling. The dark brown solution was then nearly neutralised with hydrochloric acid, the alcohol distilled off in steam, and the viscid, brown residue crystallised several times from alcohol and finally from chloroform–light petroleum. The 6-nitro-2(or 4)-dichloromethyl-4(or 2)-chloromethylene-1:3-benzdioxin thus obtained separated from boiling alcohol, in which it was easily soluble, in slender, very pale yellow prisms, m. p. 108° (Found: C, 38.9; H, 2.0; N, 4.7; Cl, 34.2. $\text{C}_{10}\text{H}_6\text{O}_4\text{NCl}_3$ requires C, 38.6; H, 1.9; N, 4.5; Cl, 34.3%). Although apparently unsaturated, the compound does not form an addition product with bromine.

5-Nitro-2-ethoxymandelic Acid (III).—A vigorous reaction took place when 25 g. (1 mol.) of the nitro-compound (I) were added gradually to a hot solution of 30 g. (7 mols.) of potassium hydroxide in 250 c.c. of alcohol, the temperature rising and the solution darkening. The solution was gently boiled for 15 minutes and then nearly neutralised with hydrochloric acid and the alcohol was distilled off in steam. From the filtered solution, strongly acidified with hydrochloric acid, ether extracted 5-nitro-2-ethoxymandelic acid (5 g.), m. p. 138° after crystallising from hot water (compare Chattaway, J., 1926, 2724) (Found : C, 49·7; H, 4·65; N, 5·8. Calc. for $C_{10}H_{11}O_6N$: C, 49·8; H, 4·6; N, 5·8%). The acetyl derivative formed rhombic plates, m. p. 147° (compare Chattaway, *loc. cit.*).

6-Amino-2 : 4-bisdichloromethyl-1 : 3-benzdioxin.—Iron filings (15 g.; 3 mols.) were added in small quantities to a hot solution of 30 g. (1 mol.) of the nitro-compound (I) in 250 c.c. of alcohol containing 66 c.c. (7 mols.) of 33% hydrochloric acid. The hot green solution was filtered, the alcohol removed partly by distillation and finally by evaporation on the water-bath, 100 c.c. of cold water were added to the solid residue to dissolve the iron salts, and on filtration the *hydrochloride* of 6-amino-2 : 4-bisdichloromethyl-1 : 3-benzdioxin was left as a crystalline mass of small, colourless prisms (30 g.). After recrystallisation from boiling dilute hydrochloric acid, in which it was easily soluble, it melted and decomposed at about 210° (Found : Cl, 50·1. $C_{10}H_9O_2NCl_4 \cdot HCl$ requires Cl, 50·2%).

On warming the hydrochloride with a dilute solution of sodium carbonate, 6-amino-2 : 4-bisdichloromethyl-1 : 3-benzdioxin was liberated as a colourless solid, readily soluble in boiling dilute alcohol, from which it separated in thin, colourless, lustrous plates, m. p. 108·5—109·5° (Found : Cl, 44·8. $C_{10}H_9O_2NCl_4$ requires Cl, 44·75%).

6-Acetamido-2 : 4-bisdichloromethyl-1 : 3-benzdioxin was formed with evolution of heat when the base was heated for a few minutes with acetic anhydride (slightly more than 1 equiv.), and the 6-*diacetamido*-derivative was formed when the base (2 g.) was boiled for 5 minutes with acetic anhydride (10 c.c.) and one drop of concentrated sulphuric acid. They separated from boiling dilute alcohol, the former in small compact prisms, m. p. 149—150° (Found : Cl, 39·5. $C_{12}H_{11}O_3NCl_4$ requires Cl, 39·5%), and the latter in small plates, m. p. 145° (Found : Cl, 35·35. $C_{14}H_{13}O_4NCl_4$ requires Cl, 35·4%).

A solution of 2 : 4-bisdichloromethyl-1 : 3-benzdioxin-6-diazonium chloride was formed when nitrous fumes were passed into a solution of 15 g. of the preceding hydrochloride in 50 c.c. of alcohol, through which a little dry hydrogen chloride had been passed, cooled to -6°. On addition of bromine dissolved in a saturated solution of potassium

bromide, 2 : 4-*bisdichloromethyl*-1 : 3-*benzdioxin*-6-*diazonium perbromide* separated as a canary-yellow solid. The perbromide is remarkably stable and crystallises unchanged from warm acetic acid, containing a little free bromine, in small, compact, orange prisms which decompose with brisk evolution of bromine at 128—129° (Found : Cl + Br, 67·1. $C_{10}H_7O_2N_2Cl_4Br_3$ requires Cl + Br, 67·1%).

When boiled for some time with acetic acid, the perbromide decomposes with evolution of bromine, and from the concentrated cooled solution, 6-*bromo*-2 : 4-*bisdichloromethyl*-1 : 3-*benzdioxin* separates in small, colourless, lustrous plates, m. p. 91·5° (Found : Cl + Br, 58·1. $C_{10}H_7O_2Cl_4Br$ requires Cl + Br, 58·2%).

2 : 4-*Bisdichloromethyl*-1 : 3-*benzdioxin*-6-*sulphonic Acid* (IV).—To a well-cooled solution of 30 g. of phenol (1 mol.) in 300 c.c. of concentrated sulphuric acid, 102 g. of dichloroacetaldehyde alcoholate (2 mols.) were added slowly with stirring. After remaining at the ordinary temperature for 6 hours with occasional stirring, the mixture was poured over 150 g. of ice. The *sulphonic acid*, which separated as a white solid, was recrystallised from hot, dilute hydrochloric acid (yield, 40 g.), dried on the water-bath, and dissolved in boiling chloroform, in which it was only very moderately soluble; on addition of low-boiling petroleum it separated in minute, colourless prisms containing $1H_2O$, m. p. 150—155° (decomp.) (Found : C, 30·0; H, 2·5; S, 8·2; Cl, 35·6. $C_{10}H_8O_5Cl_4S, H_2O$ requires C, 30·0; H, 2·5; S, 8·0; Cl, 35·5%).

The monohydrated acid is very soluble in water, acetic acid, alcohol, and ether, and very sparingly soluble in benzene. When heated at 105—110°, it slowly decomposes. It forms an anhydrous *ammonium* salt, which separates from a dilute solution of ammonia in extremely small, colourless prisms (Found : N, 3·5; S, 8·4; Cl, 35·6. $C_{10}H_{11}O_5NCl_4S$ requires N, 3·5; S, 8·05; Cl, 35·55%).

6 : 8-*Dinitro*-2 : 4-*bisdichloromethyl*-1 : 3-*benzdioxin* (V).—To 20 g. of the monohydrated acid suspended in 40 c.c. of concentrated sulphuric acid, a mixture of 40 c.c. of nitric acid (*d* 1·5) and 40 c.c. of nitric acid (*d* 1·41) was added slowly with shaking. Heat was evolved and an emulsion of oily drops was formed. After vigorous shaking for 10 minutes the emulsion was poured into a mixture of ice and water; a semi-solid mass then separated which solidified on cooling. This was crushed and washed with warm water, dried on the water-bath, and dissolved in alcohol, in which it was easily soluble and from which it separated in small, compact, slightly yellow prisms, m. p. 133·5—134·5° (Found : N, 7·1; Cl, 36·2. $C_{10}H_6O_6N_2Cl_4$ requires N, 7·15; Cl, 36·2%).

6 : 8-*Dinitro*-2 : 4-*bisdichloromethyl*-1 : 3-*benzdioxin* identical with

the above compound in every way was obtained when 6-nitro-2 : 4-bisdichloromethyl-1 : 3-benzdioxin (I) was nitrated in the same manner. Unlike the analogously constituted 6 : 8-dinitro-2 : 4-bistrichloromethyl-1 : 3-benzdioxin (compare Chattaway and Morris, J., 1927, 2013), it does not form polymorphic modifications.

6 : 8-Dinitro-2-(or 4)-dichloromethyl-4(or 2)-chloromethylene-1 : 3-benzdioxin (VI).—Potassium hydroxide (1.5 g.; 1 mol.), dissolved in 10 c.c. of alcohol, was added to a hot solution of 10 g. of the preceding dinitro-compound (1 mol.) in 100 c.c. of alcohol. An immediate rose-red colour was developed which quickly changed to brown. The mixture was gently warmed on the water-bath for a few minutes, a little water added, and the alcohol distilled off in steam; a viscid, reddish-brown solid then separated. By repeated crystallisation from small quantities of alcohol, 6 : 8-dinitro-2(or 4)-dichloromethyl-4(or 2)-chloromethylene-1 : 3-benzdioxin was obtained in well-formed, yellow rhombohedra, m. p. 144° (Found : C, 34.3; H, 1.4; N, 7.95; Cl, 29.8. $C_{10}H_5O_6N_2Cl_3$ requires C, 33.8; H, 1.4; N, 7.9; Cl, 29.9%). Like 6-nitro-2(or 4)-dichloromethyl-4(or 2)-chloromethylene-1 : 3-benzdioxin (II), it does not form an addition product with bromine.

2 : 4-Bisdichloromethyl-1 : 3-benzdioxin-6-sulphonyl Chloride.—The monohydrated acid (24 g.) and powdered phosphorus pentachloride (50 g.) were mixed and warmed on a water-bath for a few minutes, a brown oil being formed. This was poured slowly over ice. The *sulphonyl chloride*, which separated as a colourless solid, was dissolved in ether, from which, on addition of low-boiling petroleum, it separated in small, lustrous, colourless prisms, m. p. 105—106° (Found : Cl, 43.85. $C_{10}H_7O_4Cl_5S$ requires Cl, 44.3%).

When boiled with any alcohol, it reacts readily and yields the corresponding alkyl sulphonate. *Methyl 2 : 4-bisdichloromethyl-1 : 3-benzdioxin-6-sulphonate* separates from boiling methyl alcohol in lustrous flattened prisms, m. p. 110—111.5° (Found : Cl, 36.0. $C_{11}H_{10}O_5Cl_4S$ requires Cl, 35.8%), and the *ethyl ester* from boiling ethyl alcohol in small, compact prisms, m. p. 148—149.5° (Found : Cl, 34.6. $C_{12}H_{12}O_5Cl_4S$ requires Cl, 34.6%).

The sulphonyl chloride also reacts readily with ammonia and with aniline in boiling alcohol to form the *sulphonamide* and the *sulphonanilide*, which separate from boiling dilute alcohol in small, silvery prisms, m. p. 175.5° (Found : Cl, 37.0. $C_{10}H_9O_4NCl_4S$ requires Cl, 37.2%), and in small, colourless prisms, m. p. 166—167° (Found : N, 3.15; Cl, 30.9. $C_{16}H_{13}O_4NCl_4S$ requires N, 3.1; Cl, 31.0%), respectively.