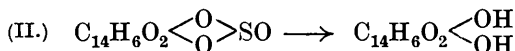
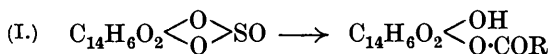


LXXIV.—*Aromatic Thionyl and Chlorothionyl Derivatives. Part I. Thionylpyrocatechol and Dichlorothionylquinol.*

By ALBERT GREEN.

THIS paper is the first of a series in which it is proposed to deal primarily with the thionyl and the chlorothionyl compounds of hydroxybenzenes and, in particular, to study quantitatively their decomposition by weak organic acids, with a view to apply the information obtained to the more complex anthraquinone derivatives (J., 1924, 125, 1450; 1926, 2198).

In the anthraquinone series two types of decomposition have been observed: one, which will be termed the *acyl decomposition*, is undergone by thionylalizarin, which is quantitatively converted by such acids into the 2-acyl derivative (I); the other type, the *hydroxylic decomposition*, is exemplified by thionylhystazarin, which reverts entirely to the hydroxy-compound (II). 2:3-Thionyl-anthragallol represents an intermediate case and gives a mixture of anthragallol and a monoacyl derivative.



Repetition of the method employed by Anschütz and Posth (*Ber.*, 1894, 27, 2752) in the preparation of thionylpyrocatechol ("catechol sulphite") showed that the solid by-products mentioned by them form the greater part of the yield. A method of preparation resembling that used by Richter (*Ber.*, 1916, 49, 2339) in the preparation of some thionyl derivatives of monohydric phenols was adopted.

Thionylpyrocatechol is much more stable to moisture than thionylalizarin, but after exposure to the air for 6 days it reverts completely to the hydroxy-compound. It reacts very slowly with acetic acid or acetic anhydride, even when heated under pressure at 180°, but the addition of a trace of pyridine to the boiling acid solution results in its complete conversion into *monoacetylpyrocatechol*. This compound affords a means of obtaining mixed diacyl derivatives, one of which, *acetylbenzoylpyrocatechol*, is described. With acetic anhydride and a little pyridine, thionylpyrocatechol gives diacetylpyrocatechol in quantitative yield.

Attempts to prepare a chlorothionyl derivative of quinol in the

presence of solvents gave stable, complex products which were analysed but not further investigated. Eventually *dichlorothionylquinol* was obtained as extremely unstable, white crystals which could be preserved only under thionyl chloride; when kept in sealed tubes for 2 days, they liquefied and considerable pressure was developed. In the air the dichlorothionyl compound fumed copiously and was rapidly converted into quinol; with boiling acetic acid or acetic anhydride it formed diacetylquinol in theoretical yield. *p*-Benzoquinone was recognised among the products of its complex auto-decomposition.

The acyl decomposition of dichlorothionylquinol was unexpected, since, in the conversion of 1 : 2-thionyl-7-chlorothionylanthrapurpurin (*loc. cit.*, p. 2198) into a monoacetyl anthrapurpurin by acetic acid, the evidence points to the replacement of the chlorothionyl group by hydrogen.

Attempts to prepare thionyl and chlorothionyl derivatives of resorcinol yielded stable, high melting, insoluble products which analyses showed to be very complex. Richter (*loc. cit.*, p. 2345) states that he obtained the "sulphites" of several phenols including resorcinol, but he gives neither descriptions of the compounds nor analytical data. The author has carried out many preparations under various conditions, and has carefully repeated Richter's method several times, without obtaining such a compound. If indeed a simple derivative is obtainable, resorcinol would be expected to give a dichlorothionyl rather than a thionyl compound.

#### EXPERIMENTAL.

*Thionylpyrocatechol*,  $C_6H_4 \left\langle \begin{smallmatrix} O \\ O \end{smallmatrix} \right\rangle SO$ .—To a cooled solution ( $10^\circ$ ) of 30 g. (1 mol.) of pyrocatechol in 150 c.c. of dry carbon disulphide and 43.0 c.c. (2 mols.) of pyridine, were added, with continuous stirring, 20.3 c.c. (1 mol.) of freshly-distilled thionyl chloride in 80 c.c. of dry carbon disulphide. After standing at  $10^\circ$  for 30 minutes, the mixture was boiled on the water-bath for a similar time. While still warm, the faintly yellow carbon disulphide solution was decanted from the syrupy layer of pyridine hydrochloride, which was washed several times with small quantities of the warm solvent. The carbon disulphide solution and washings were concentrated on the water-bath, and the last traces of the solvent were removed in a vacuum over paraffin wax. Thionylpyrocatechol (41 g.) was thus obtained as a faintly yellow, mobile liquid, b. p.  $137-138^\circ/105$  mm. (Found: S, iodometrically as sulphur dioxide in the solution in aqueous sodium hydroxide, 20.3, 20.4. Calc.: S, 20.5%).

*Decomposition with acetic acid.* (A) A solution of thionylpyrocatechol in acetic acid, after boiling for 12 hours, still contained unchanged sulphite. This was shown by stirring the solution into water and washing the insoluble portion thoroughly; the alkaline solution of this decolorised acidified iodine solution.

(B) *Monoacetylpyrocatechol*,  $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{OAc}$ . A solution of 16 g. of thionylpyrocatechol in 40 c.c. of glacial acetic acid and 3 drops of pyridine was boiled for 6 hours; evolution of sulphur dioxide was then no longer appreciable. The *monoacetyl* derivative was obtained by fractional distillation as a colourless, viscous liquid (14 g.), b. p. 189—191°/102 mm. In a freezing mixture, it set to a felted mass of thin, white plates, which, after draining on a porous tile, melted at 57—58°, were soluble in cold water, and gave a bottle-green colour with ferric chloride (Found : C, 63.0; H, 5.3;  $\text{CH}_3\cdot\text{CO}$ , 28.0.  $\text{C}_8\text{H}_8\text{O}_3$  requires C, 63.2; H, 5.3;  $\text{CH}_3\cdot\text{CO}$ , 28.3%).

*Acetylbenzoylpyrocatechol*,  $\text{OAc}\cdot\text{C}_6\text{H}_4\cdot\text{OBz}$ . A solution of 7.0 g. (1 mol.) of monoacetylpyrocatechol in 10 c.c. of pyridine was treated with 5.5 c.c. (1 mol.) of benzoyl chloride, and after warming slightly, was stirred into cold dilute hydrochloric acid. The oily precipitate was separated, washed thoroughly with cold water, and taken up in ether. *Acetylbenzoylpyrocatechol* was obtained from the dried ethereal solution as a thick syrup (11 g.) which slowly solidified in fine, white needles, m. p. 78°. After recrystallisation from light petroleum-acetone it showed the same melting point (Found : C, 70.1; H, 4.7;  $\text{CH}_3\cdot\text{CO}$ , 16.7.  $\text{C}_{15}\text{H}_{12}\text{O}_4$  requires C, 70.3; H, 4.7;  $\text{CH}_3\cdot\text{CO}$ , 16.8%). The substance is easily soluble in the cold in the common organic solvents except light petroleum, insoluble in water, and its alcoholic solution gives no colour with ferric chloride.

*Diacetylpyrocatechol.* Thionylpyrocatechol (5. g.) in acetic anhydride (15 c.c.) containing one drop of pyridine was boiled until sulphur dioxide was no longer evolved (40 minutes). The solution, when stirred into cold water, gave a white solid (6.5 g.), which crystallised from rectified spirits in short, white rods melting at 64° alone and when mixed with pure diacetylpyrocatechol (Found :  $\text{CH}_3\cdot\text{CO}$ , 44.3. Calc. :  $\text{CH}_3\cdot\text{CO}$ , 44.3%).

*Dichlorothionylquinol*,  $\text{C}_6\text{H}_4(\text{O}\cdot\text{SOCl})_2$ .—Ice-cold thionyl chloride (200 c.c.) was added slowly to a mixture of quinol (40 g.) and pyridine (3 drops) contained in a flask fitted with a ground-in reflux condenser. Reaction commenced in the cold with evolution of hydrogen chloride, and was allowed to proceed at 15° for 2 hours; a dark orange-coloured solution had then been formed, This was boiled on the water-bath for 3 hours, concentrated to about 120 c.c., and kept dry.

The small, white crystals (about 30 g.) which separated were filtered off as required, and rapidly washed with dry benzene and absolute ether. They melted at  $75^{\circ}$  to a pale orange liquid (Found : C, 26.6, 26.4; H, 1.6, 1.7; \* S, 23.2, 23.3; Cl, 25.7, 25.7.  $C_6H_4O_4Cl_2S_2$  requires C, 26.2; H, 1.5; S, 23.3; Cl, 25.8%). By decomposition by the moisture of the air, followed by drying in a vacuum over sulphuric acid, 3.0026 g. of dichlorothionylquinol gave 1.1990 g. of quinol (theory requires 1.2010 g.), and 1.1240 g. yielded 0.4482 g. (theory requires 0.4496 g.). These products melted at  $169^{\circ}$  either alone or when mixed with pure quinol.

*Dichlorothionylquinol* fumes copiously in the air, and becomes yellow within one minute. It reacts violently with water and with aqueous and alcoholic solutions of potassium hydroxide. Even when stored in a dry atmosphere at room temperature, it decomposed to a complex mixture in which free sulphur was recognised.

*Thermal decomposition.* Dichlorothionylquinol was heated gradually from  $70^{\circ}$  to  $150^{\circ}$ . Decomposition commenced at about  $95^{\circ}$ . The sublimes were collected and yielded the characteristic yellow needles of *p*-benzoquinone, which was recognised by its odour and m. p. ( $116^{\circ}$ , either alone or mixed with an authentic specimen). A small quantity of white, feathery crystals, m. p.  $135^{\circ}$ , which sublimed at a higher temperature than the quinone were not obtained in sufficient amount for analysis. The residue in the tube yielded no recognisable substance.

*Decomposition with acetic acid.* A solution of 4.0 g. of dichlorothionylquinol in 10 c.c. of glacial acetic acid was boiled for 15 minutes; hydrogen chloride and sulphur dioxide were then no longer perceptible at the mouth of the flask. When cold, the solution deposited 1.8 g. of lustrous, white plates of diacetylquinol (0.8 g. also was obtained by stirring the filtrate into water), m. p.  $122^{\circ}$ , alone and when mixed with the pure substance (Found :  $CH_3\cdot CO$ , 44.4. Calc. :  $CH_3\cdot CO$ , 44.3%).

*Decomposition with acetic anhydride.* The red solution of 2 g. of the dichlorothionyl compound in 5 c.c. of acetic anhydride, when boiled rapidly, became pale orange and evolved hydrogen chloride and sulphur dioxide very vigorously. After 8 minutes, the solution was cooled, and deposited white plates (0.8 g.) of diacetylquinol which, alone or mixed with an authentic specimen, melted at  $123^{\circ}$  (Found :  $CH_3\cdot CO$ , 44.1. Calc. :  $CH_3\cdot CO$ , 44.3%).

\* Owing to the unstable nature of the compound, better analyses for carbon and hydrogen were not obtained, although both lead chromate and silver gauze were used in the combustion tubes. Satisfactory results for sulphur and chlorine were given by the Carius method.

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