

XLV.—*The Chlorination of Phloroglucol.*

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I HAVE continued my researches (Trans., 1883, 205) in collaboration with Messrs. Cross and Bevan, on the chlorination of the trihydric phenols, confining my attention chiefly to phloroglucol. It is now some years since Hlasiwetz showed that the action of the halogen, in presence of water, is to resolve this compound into dichloroacetic acid (*Annalen*, **155**, 120). He made no attempt to study this decomposition in the successive stages through which it might, with our present knowledge, be presumed to pass, for the reason doubtless that phloroglucol was not then recognised as a phenol. This being now established, the formation of a substituted chlorinated derivative, as a distinct phase of the reaction, preceding the disruption of the benzene-ring, is a well-grounded assumption; and, indeed, the description of the course of the decomposition, given by Hlasiwetz, contains indications of its passing through such a phase. The proof that the reaction actually takes place in this way is the chief result which I have to record, and I shall therefore state at the outset the conditions under which phloroglucol is converted into a trichloro-derivative, $C_6Cl_3(OH)_3$. This compound is obtained by chlorinating the phenol suspended in carbon tetrachloride, in a vessel surrounded by a freezing mixture. Even under these conditions, however, great care must be taken to prevent local heating, as the trichloro-derivative is rapidly resolved, by the action of the chlorine, into acetic derivatives, and that at comparatively low temperatures. For this reason also it is necessary to arrest the reaction before the liquid becomes saturated with the gas. The following are the details of an experiment. About 13 grams of the anhydrous phenol having been finely powdered, and made into a cream with CCl_4 , was introduced into a test-tube of large size, which was plunged into a freezing mixture of ice and salt. A rapid stream of dry chlorine was passed into the fluid mixture, which was stirred from time to time, the passage of the gas being continued for about two hours. At this time, the contents of the tube appeared but little changed, the suspended solid having only a slightly yellower colour than the original phenol. Secondary decomposition had already set in, as was shown by the brisk effervescence of the contents of the tube. The solid was therefore rapidly filtered off, and well washed upon the filter with carbon tetrachloride. I obtained thus 18 grams of the crude product, which still contained some quantity of undecom-

posed phloroglucol. This was easily separated from the chloro-derivative by taking advantage of its much greater solubility in alcohol and water. Finally I obtained the pure trichloro-compound, by crystallisation from its hot aqueous and alcoholic solutions, in the form of slender needles. The identity of the compound, in regard to its empirical composition, was established by the following analytical determinations:—

(a.) Crystallised from water.

0.4130 gram lost 0.0777 exposed 48 hours in a vacuum over H_2SO_4 .
 0.3530 „ „ 0.0700 heated at 100° till the weight was constant.

(b.) Crystallised from alcohol of 0.815 sp. gr.

0.3518 gram lost 0.0655 exposed 48 hours in a vacuum over H_2SO_4 .

	(a.)		(b.)	Calculated.
				$\text{C}_6\text{Cl}_3(\text{OH})_3, 3\text{H}_2\text{O}$.
H_2O	18.8	19.7	18.6	19.0

The substance sublimes slowly at 100° , hence the excess of the loss at this temperature. The anhydrous compound melts at 136° (uncorr.); it sublimes freely at a somewhat lower temperature.

0.2232 gram of the anhydrous substance burnt in a stream of oxygen with the usual precautions gave 0.2512 CO_2 and 0.0367 H_2O .

0.1230 gram gave 0.2328 AgCl .

		Calculated.
		$\text{C}_6\text{Cl}_3(\text{OH})_3$.
C	30.7	31.3
H	1.8	1.3
Cl	46.7	46.2

The compound is almost insoluble in water and in benzene in the cold, but is taken up in some quantity on heating. It is more soluble in alcohol, and crystallises in large transparent needles on the slow evaporation of the solvent. It dissolves in hot concentrated hydrochloric acid, crystallising out on cooling in fine needles. It is decomposed on warming with dilute nitric acid with formation of oxalic acid. It is dissolved without change by concentrated sulphuric acid on gentle warming; but on continuing to heat, hydrogen chloride is evolved, and the solution assumes a deep sage-green colour; on pouring this solution into water, a brown resinous substance is precipitated. It is dissolved by alkaline solutions, and is precipitated unchanged on acidifying. The alkaline solution develops a purple colour on standing.

The original solution, filtered from the crude product, was found to contain traces only of chloracetic acids.

Having thus established that the chlorination of the phenol precedes its resolution under the continued action of the gas, it remained to study the latter under the conditions adopted in the preparation of the trichloro-derivative. The latter was therefore suspended in carbon tetrachloride, and a current of dry chlorine was passed through the liquid, the temperature being maintained at 10° . Rapid decomposition ensued, evidenced by a brisk effervescence and the disappearance of the solid. The solution was found to contain a mixture of chloraldehydes and chloracetic acids, trichloroacetic acid being the chief product.

The action of chlorine on phloroglucol takes place, therefore, in the two stages thus described; the action is limited to the first, *i.e.*, the chlorination of the phenol, at very low temperatures only, and in absence of water: indeed, even when all precautions are observed, it was found impossible altogether to prevent the secondary decomposition. In my earlier attempts, notwithstanding that carbon tetrachloride was used as the distributing medium, and was kept at a low temperature by the employment of a freezing mixture, I repeatedly failed to obtain the derivative above described; on the other hand, I obtained the chloraldehydes and chloracetic acids in large proportion. The only insoluble product formed in such cases was a resinous body from which a crystalline substance was isolated by several recrystallisations from alcohol. It was obtained, but only in minute quantity, in the form of lustrous cubes.* On analysis it was found to contain 47.2 per cent. chlorine. Not only in this respect, but in many of its reactions it resembled the trichloro-compound above described; at the same time its crystalline form and high melting point (above 250°) prove it to be distinct. I am endeavouring to obtain this substance in sufficient quantity to be able to establish its composition.

It might be objected that no evidence has been afforded that the trichloro-compound above described is in reality trichloro-phloroglucol, and the fact that its melting point, 136° , lies so much lower than that of the phenol, 220° , would appear to throw doubt on its identity. On the other hand, the close analogy which it has with the well-known tribromo-derivative, even also in regard to its low melting point—which for the anhydrous tribromophloroglucol I have observed at 148° (uncorr.)—must be regarded in the meantime as establishing for it the simple relationship to the original phenol. At the same time, it is my intention in the course of these researches, by the determination of molecular volumes and in other ways, to obtain such evidence

* The quantity of this resinous precipitate varied from 25 to 30 per cent. of the weight of the phenol taken. It was analysed on two occasions, after precipitation by acid from solution in dilute potash. These preparations contained 48.4 and 46.4 per cent. Cl respectively.

as may be brought to bear on the problems of the constitutional relationships of the derivatives of this group of phenols.

The history of phloroglucol sufficiently proves that it occupies a position which is in many respects anomalous. Hlasiwetz and Habermann (*loc. cit.*) regarded the results of their study of the action of chlorine on this compound as sufficiently demonstrative that phloroglucol is not a phenol, nor, indeed, an aromatic compound at all. The later investigations of Benedikt (*ibid.*, 189) of the exhaustive bromination of phloroglucol, and of Barth and Schreder (*Ber.*, **12**, 503), who succeeded in obtaining this compound as the chief product of the fusion of resorcinol with sodium hydroxide, have however established the contrary, and phloroglucol is now regarded as a trihydroxybenzene. This view is confirmed by the results above detailed. Still its relationships are in many respects anomalous, and afford at least suggestions of a closer connection between the great groups of the aromatic compounds and the carbohydrates than has yet been brought to light. It is from this point of view that this work was undertaken and is being prosecuted.

I wish to express my sense of obligation to Professor Ramsay and the authorities of University College, Bristol, and to Mr. R. E. H. Goffin and the authorities of the United Westminster Schools for the privilege of occupying the laboratories of these institutions for the purposes of this research.
