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Derivatives of Trichlorolactic Acid

I. The Reactions of Trichlorolactic Acid with Phosphorus Pentachloride and Thionyl Chloride

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In a paper by R. Anschütz and A. Haslam [1] it was reported that α,β,β,β-tetrachloropropionyl chloride is the main product of the reaction between β,β,β-trichlorolactic acid and phosphorus pentachloride:

$$CCl_3CHOHCO_2H + 2\ PCl_5 \rightarrow CCl_3CHClCOCl + 2\ POCl_3 + 2\ HCl \qquad (1)$$

The boiling point given for the chloride, 140—142°/12 mm, appeared to us to be too high. Böeseken [2], who later used the same method, obtained the boiling point 150°/18 mm. For comparison it may be noted that pentachloropropionyl chloride has a much lower boiling point, 91—92°/12 mm[3], although the reverse should be true.

It has been even more surprising to note that Anschütz and Haslam state that the α-chlorine in tetrachloropropionyl chloride is very reactive. According to these authors, the chloride is readily hydrolyzed to trichlorolactic acid and in alcoholic solution forms the ethyl ester of α-ethoxy-β,β,β-trichloropropionic acid. These reactions do not seem possible; all other known α,β,β,β-halogenated propionic acids are stable to water [4].

These suspicions led us to renew the experiments of Anschütz and Haslam. After careful fractionation a reaction product was obtained that evidently was identical with that described by Anschütz and Haslam since its hydrolysis gave trichlorolactic acid, but the compound had a different density and above all, its analysis gave different results. The compound contained phosphorus and both the analytical data and the physical and chemical properties prove that the reaction between phosphorus pentachloride and trichlorolactic acid leads to the formation of β,β,β-trichlorolactyl chloride dichlorophosphate:

$$CCl_3CHOHCO_2H + PCl_5 \rightarrow CCl_3CH(OPOCl_2)COCl + 2\ HCl \qquad (1')$$

The analytical data of Anschütz and Haslam differ considerably from those of the product of this reaction, but their data must be in error or their compound must have been impure. Table 1 allows a comparison of the average analytical data.

Table 1. Comparison of analytical data.

Element	Calculated		Found	
	C_3HOCl_5	$C_3HO_3PCl_6$	A & H	L & R
C	15.63	10.96	15.45	
H	0.43	0.31	0.68	
Cl	76.96	64.71	77.22	64.45
P		9.42		9.34

The structure we propose for the compound is consistent with the fact that the products of the hydrolysis of the compound were identified as trichlorolactic, phosphoric and hydrochloric acids. In addition the amount of liberated hydrochloric acid determined by argentometric titration corresponded to half the amount of the total chlorine in the compound. On the other hand, when dissolved in alcohol, the compound did not yield the ethyl ester of α-ethoxy-β,β,β-trichloropropionic acid as Anschütz and Haslam have reported, but the triethyl ester of β,β,β-trichlorolactic acid dihydrogen phosphate. This reaction has been confirmed by Leimu and Kivisaari [5].

The action of thionyl chloride on trichlorolactic acid was also studied. The reaction yielded β,β,β-trichlorolactic acid chlorosulphite:

$$CCl_3CHOHCO_2H + SOCl_2 \rightarrow CCl_3CH(OSOCl)CO_2H + HCl \tag{2}$$

Several attempts were made to replace the chlorosulphite group with chlorine using methods earlier employed in corresponding exchange reactions[6, 7], but the experiments were unsuccessful.

It is, however, possible to prepare α,β,β,β-tetrachloropropionic acid and its chloride starting from β,β-dichloroacrylic acid. This synthesis is described elsewhere [8].

The described reactions of trichlorolactic acid are analogous with the reactions of several other hydroxyacids. Hydroxyarylcarboxylic and hydroxyarylsulphonic acids react in general with phosphorus pentachloride in the same manner as trichlorolactic acid [9]. Thionyl chloride reacts similarly with certain other aliphatic hydroxycarboxylic acids as with trichlorolactic acid [10].

The reaction of salicylic acid with phosphorus pentachloride L. Anschütz [11] has explained to occur *via* the intermediate $C_6H_4(OPCl_4)CO_2H$ which yields the compound $C_6H_4(OPOCl_2)COCl$ by a transfer of chlorine and elimination of hydrogen chloride. A similar mechanism is possible for the reaction between trichlorolactic acid and phosphorus pentachloride:

$$\begin{gathered} CCl_3CHOHCO_2H + PCl_5 \rightarrow CCl_3CH(OPCl_4)CO_2H + HCl \\ CCl_3CH(OPCl_4)CO_2H \rightarrow CCl_3CH(OPOCl_2)COCl + HCl \end{gathered} \tag{3}$$

It should be noted that the second stage may also involve the interaction of two molecules by a more complex mechanism.

An alternative mechanism is that phosphorus pentachloride first reacts with the carboxyl group and the phosphorus oxychloride formed reacts with the hydroxyl group to yield the final reaction product:

$$\begin{array}{c} CCl_3CHOHCO_2H + PCl_5 \rightarrow CCl_3CHOHCOCl + POCl_3 + HCl \\ CCl_3CHOHCOCl + POCl_3 \rightarrow CCl_3CH(OPOCl_2)COCl + HCl \end{array} \qquad (3')$$

A decision between these two mechanisms is rendered difficult by the fact that the reaction proceeds only partly according to Eq.(1′) to give trichlorolactyl chloride dichlorophosphate and hydrogen chloride. Considerable amounts of phosphorus oxychloride and other byproducts with higher boiling points than that of the main fraction are formed, but the isolation of the latter by distillation is difficult. Phosphorus oxychloride is shown as one of the reaction products in Eq. (1) and as an intermediate compound in Eq. (3′). The occurrence of reaction (1) is questionable since tetrachloropropionyl chloride was not detected among the reaction products. The presence of phosphorus oxychloride among the final products of the reaction may be explained by assuming that another reaction takes place instead of the second stage of reaction (3′), *i. e.* the trichlorolactyl chloride formed in the first stage does not react with phosphorus oxychloride but, for example, with itself with the formation of a di- or polymeric lactide, or with phosphorus pentachloride whereupon the compound $CCl_3CH(OPCl_4)COCl$ is formed. This latter compound, the chloride of the acid formed as an intermediate in reaction (3), may also be produced by the reaction of this intermediate with phosphorus pentachloride, the latter changing into phosphorus oxychloride. The acid $CCl_3CH(OPCl_4)CO_2H$ or its chloride may also react with the α-hydroxyl group of trichlorolactic acid to form a compound containing two trichlorolactic acid residues linked together by the chlorophosphate residue. The elucidation of these different possibilities may require further investigation.

The literature contains numerous investigations which deal with the reactions between organic hydroxycompounds and phosphorus and other non-metal halides but the opinions presented are not concordant with each other in all respects [12]. In only a few of these studies has it been considered to what extent the structure of the hydroxycompound favours the fission of the carbon-oxygen bond in preference to the oxygen-hydrogen bond [13]. It may be noted, however, that among the simple alcohols the tertiary alcohols exhibit the smallest tendency to retain carbon-oxygen bonds and in general they yield the corresponding alkyl halides [13, 14]. These are followed by secondary alcohols which usually give higher yields of alkyl halides than the primary alcohols [13, 15]. β-Chloroethanol [16] and the phenols [13, 17] favour oxygen-hydrogen bond fission and yield ester halides (compounds which are both halides and esters of inorganic acids). These observations can be explained by the fact that an increase in the electronegativity of the carbon atom to which the hydroxyl group is attached strengthens the bond between carbon and oxygen. Accordingly, the formation of ester chlorides as the only detectable products of the reaction of trichlorolactic acid with phosphorus pentachloride and thionyl chloride is readily understood when it is noted that both the trichloromethyl and carboxyl groups increase the electrophilic properties of the adjacent carbon atom carrying the hydroxyl group.

EXPERIMENTAL

The reaction between trichlorolactic acid and phosphorus pentachloride. Trichlorolactic acid was prepared from chloral hydrate by the cyanohydrin synthesis developed by Kölln [18]. The samples of phosphorus pentachloride used in some of the experiments were commercial products from different manufacturers, whereas the chloride used in other experiments was prepared from pure phosphorus trichloride and chlorine. In accordance with Anschütz and Haslam [1] one mole of trichlorolactic acid and 2 moles of phosphorus pentachloride were heated together for 5—6 hours on an oil bath, first slowly to 70° and then to 120—130°. The phosphorus oxychloride was distilled from the reaction product either under normal pressure or, more advantageously, under reduced pressure, after which the residue was fractionated under reduced pressure. The main fraction obtained after the removal of the phosphorus oxychloride was found to contain phosphorus. The yield from the fractionation was 40—45 % of the theoretical and boiled at 120—140°/10 mm. The distillate was a yellow liquid. The residue, a dark viscous syrupy mass, was fairly large. In a few cases it was possible to distill from the residue a fraction with a higher boiling point than that of the main fraction. The main fraction was redistilled from a Claisen flask two or three times at a pressure of 1—2 mm, whereupon its weight diminished by one half. It boiled at 101—102°/2 mm and had only a very slight yellow colour. When the synthesis was begun with equimolar quantities of trichlorolactic acid and phosphorus pentachloride in accordance with Eq. (1′), the fractionation was more difficult and the yield of the pure compound poor. An even smaller yield of the pure compound was obtained when trichlorolactic acid was first allowed to react with an equimolar amount of phosphorus oxychloride after which an equimolar amount of phosphorus pentachloride was added to the reaction mixture.

To determine the composition of the isolated compound, analyses were conducted for total chlorine, phosphorus, chlorine liberated by hydrolysis, and the molecular weight was determined cryoscopically (benzene). Parallel determinations were performed on the same and different preparations. β,β,β-Trichlorolactyl chloride dichlorophosphate is a viscous fluid slightly yellow in colour, the latter presumably due to impurities. Qualitative tests showed that the compound decomposed in water to trichlorolactic acid, phosphoric acid and hydrogen chloride. Its density at 20° was 1.7682 (d_4^{20}).

Calc. for $C_3HO_3PCl_6$ (329): Cl 64.71, P 9.42, Cl/2 32.36, Mol.wt. 328.8
Found » » 64.94, » 9.32, » 32.42, » » 340.2
» » » 64.22, » 9.13, » 33.42
» » » 64.20, » 9.21, » 32.36
» » » 64.44, » 9.70, » 31.92

The reaction of trichlorolactic acid with thionyl chloride. An excess of thionyl chloride was added to the trichlorolactic acid and the mixture refluxed on an oil bath during five days. Forty grams of trichlorolactic acid yielded 30 grams of a substance boiling at 107—109°/8 mm. When fractionated it boiled at 110°/10 mm. The compound, trichlorolactic acid chlorosulphite, was a colourless liquid of pungent odour which gradually solidified on standing. It dissolved in water with the formation of trichlorolactic acid, sulphur dioxide and hydrogen chloride.

$C_3H_2O_4SCl_4$ (276): Calc. for Cl 51.40, S 11.62
Found » » 51.22, » 11.50

Attempts to transform β,β,β-trichlorolactic acid chlorosulphite into tetrachloropropionic acid or its chloride [6, 7] (in collaboration with P. Niemi). Several experiments were performed in which the relative amounts of thionyl chloride and trichlorolactic acid were varied. When the reaction had continued several days, a few drops of pyridine were added to the reaction mixture the temperature of which was then gradually increased to 110° during several hours. It was not possible to extract α,β,β,β-tetrachloropropionic acid from the reaction mixture with petroleum ether.

Five grams of ethyl trichlorolactate prepared according to Pinner [19] were heated on an oil bath at 80° with thionyl chloride (1.8—3 ml) and pyridine (6 drops) for several days. On distillation under reduced pressure the ester was obtained unchanged, but no ester of tetrachloropropionic acid.

Thirty-five grams of trichlorolactic acid chlorosulphite (0.13 mole) and 54 grams of phosphorus pentachloride (0.26 mole) were heated three days at 130°. The excess of phosphorus pentachloride was filtered off on a glass filter and the filtrate fractionated under reduced pressure. Seven grams of a substance boiling at 115—117°/10—12 mm were obtained. It was found to contain phosphorus and yielded 29.1 per cent hydrolyzable chlorine. In a second experiment the amount of phosphorus pentachloride was reduced to one half of the above. The reaction product was divided into three fractions on distillation; all three fractions gave qualitative reactions for phosphorus and sulphur. The percentages of hydrolyzable chlorine were 26.7, 26.8 and 27.6. It is probable that the products of these reactions were mixtures of trichlorolactyl chloride dichlorophosphate and trichlorolactyl chloride chlorosulphite, $CCl_3CH(OSOCl)COCl$, since the two compounds liberate 32.4 and 24.1 % chlorine, respectively, on hydrolysis.

SUMMARY

The reaction between β,β,β-trichlorolactic acid and phosphorus pentachloride does not yield, as assumed previously, α,β,β,β-tetrachloropropionyl chloride, but gives β,β,β-trichlorolactyl chloride dichlorophosphate. Thionyl chloride reacts with trichlorolactic acid to give β,β,β-trichlorolactic acid chlorosulphite. The chlorosulphite-group in the latter compound could not be replaced by chlorine.

REFERENCES

1. Anschütz, R. and Haslam, A. *Ann.* **253** (1889) 132.
2. Böeseken, J. *Rec. trav. chim.* **32** (1913) 7.
3. Leimu, R. *Ann. Univ. Turkuensis* **A IV : 3** (1935) 74.
4. Mabery, C. F. and Weber, H. C. *Am. Chem. J.* **4** (1882) 104; Mabery, C. F. and Robinson, F. C. *ibid.* **5** (1883) 251; Mabery, C. F. and Lloyd, R. *ibid.* **6** (1884) 157; Mabery, C. F. *ibid.* **9** (1887) 1; according to *Ber.* **15** (1882) 1756, **16** (1883) 2919, **17** (1884) Ref. 475, **20** (1887) Ref. 364.
5. Leimu, R. and Kivisaari, S. *Acta Chem. Scand.* **8** (1954) 596.
6. Darzens, G. *Compt. rend.* **152** (1911) 1314; *Chem. Zentr.* **1911 : II** 74; Gerrard, W. *J. Chem. Soc.* **1939** 99; Gerrard and French, K. H. V. *Nature* **159** (1947) 263; Libermann, D. *ibid.* **160** (1947) 903.
7. Carré, P. and Libermann, D. *Compt. rend.* **195** (1932) 1080; *Chem. Zentr.* **1933 : I** 927.
8. Leimu, R. and Ronkainen, P. *Suomen Kemistilehti* **26 B** (1953) 31.
9. Kosolapoff, G. M. *Organophosphorus Compounds*, John Wiley & Sons, Inc. New York 1950, pp. 219, 243—4.
10. Blaise, E. E. and Montagne *Compt. rend.* **174** (1922) 1173, 1553; *Chem. Zentr.* **1922 : III** 1287, **1923 : I** 818.
11. Anschütz, L. *Ann.* **439** (1924) 271.
12. E.g. Kenyon, J., Phillips, H. and Taylor, F. M. H. *J. Chem. Soc.* **1931** 382; Hückel, W. and Pietrzok, H. *Ann.* **540** (1939) 250; Hückel, W. *ibid.* **540** (1939) 274; Gerrard, W. *J. Chem. Soc.* **1940** 218, 1464; **1944** 85; **1945** 106; **1946** 741; Berlak, M. C. and Gerrard, W. *ibid.* **1949** 2309; French, K. H. V. and Gerrard, W. *ibid.* **1949** 3326; Gerrard. W., Nechvatal, A. and Wilson, B. M. *ibid.* **1950** 2088; Bissinger, W. E. and Kung, F. E. *J. Am. Chem. Soc.* **69** (1947) 2158. *Cf.* also Kosolapoff, G. M. *op. cit.*, p. 213.
13. *E. g.* Carré, P. *Compt. rend.* **194** (1932) 1835; **196** (1933) 1806; *Chem. Zentr.* **1932 : II** 1155; **1933 : II** 1009.
14. *E. g.* Rodd, E. H. *Chemistry of Carbon Compounds* I A, Elsevier Publishing Company, Amsterdam 1951, p. 330.
15. Kosolapoff, G. M. *op. cit.*, pp. 211, 212.
16. Renshaw, R. R. and Hopkins, C. Y. *J. Am. Chem. Soc.* **51** (1929) 953; Kosolapoff, G. M. *op. cit.*, p. 241.
17. Bissinger, W. E. and Kung, F. E. *J. Am. Chem. Soc.* **70** (1948) 2664; Kosolapoff, G. M. *op. cit.*, p. 243.
18. Kölln, H. *Ann.* **416** (1918) 231.
19. Pinner, A. *Ber.* **18** (1885) 754.

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