

CCXI.—*The Action of Phosphorus Pentachloride on Homophthalic Acid.*

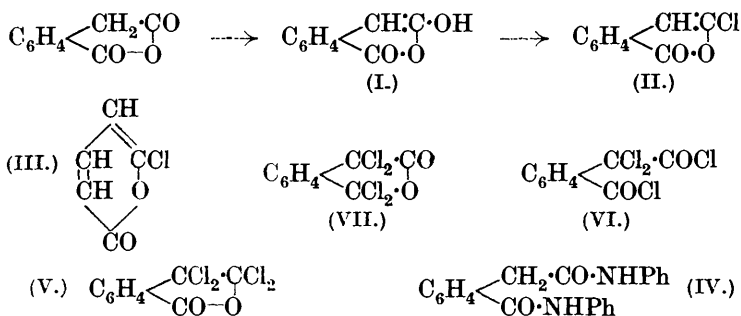
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WITH a view to study the relationship of the three possible forms of homophthalyl chloride, the reaction of phosphorus pentachloride with homophthalic acid has been investigated: instead of homophthalyl chloride, however, 3-chloroisocoumarin (II) and 3:3:4:4-tetrachloro-3:4-dihydroisocoumarin (V) were formed. Neither phosphorus pentachloride nor thionyl chloride seems capable of converting homophthalic acid or its anhydride into homophthalyl chloride, which is still unknown.

The explanation of the production of (II) is to be found in the existence of homophthalic anhydride in the enolic form (I). Dieckmann (*Ber.*, 1914, **47**, 1428) has shown that some of the reactions of homophthalic anhydride, and the production of a yellow colour

during hydrolysis (*ibid.*, p. 1435), can be explained by means of this formula, and a proof of the existence of (I) in solution is now given. The existence of (I) and its conversion into (II) show the great resemblance of homophthalic to glutaconic anhydride, which can be converted into its chlorine derivative (III) (Bland and Thorpe, *J.*, 1912, **101**, 864).

The constitution of 3-chloroisocoumarin is shown by its conversion into homophthalic acid by alkaline hydrolysis, and also by its conversion into a compound which is not homophthalanil (Dieckmann, *loc. cit.*, p. 1434), and is probably *homophthalanilide* (IV). 3-Chloroisocoumarin is much less reactive towards non-alkaline solutions than a true acid chloride and it distils in steam almost unchanged. The formula (II) does not, however, represent some of its properties, for despite its "unsaturated" character it is stable towards some non-alkaline oxidising and reducing agents and is not attacked by bromine in benzene. In some respects the lack of activity shows that the double bond is of "aromatic" character.



Excess of phosphorus pentachloride converts homophthalic acid into an isomeride of dichlorohomophthalyl chloride (VI) which has none of the characteristic properties of an acid chloride and is changed by hydrolysis into phthalonic acid. It is probably 3 : 3 : 4 : 4-tetrachloro-3 : 4-dihydroisocoumarin (V), because of the three possible formulæ (V, VI and VII), (VI) and (VII) are analogous to the two forms of phthalyl chloride and are therefore improbable.

EXPERIMENTAL.

Homophthalic Acid.—The best method of preparing homophthalic acid is by the reduction of phthalonic acid after the method of Graebe and Trumpy (*Ber.*, 1898, **31**, 375; Dieckmann and Meiser, *Ber.*, 1908, **41**, 3258, Anm. 1), now that this acid is easily accessible (von Braun, *Ber.*, 1923, **56**, 2333). The following conditions give phthalonic acid, containing less than 0.5% of phthalic acid, in yields up to 82%

calculated on the permanganate used. Tetrahydronaphthalene (250 g.) is vigorously stirred in 12 l. of gently boiling water while powdered potassium permanganate (2000 g.) is introduced in 5 to 10 g. lots during about 8 hours; tetrahydronaphthalene vapour is apt to escape, and the process is finished when the permanganate no longer causes a vigorous reaction. Von Braun does not state the proportion of water to the permanganate or tetrahydronaphthalene used, and our experience is that a small quantity of water makes the reaction difficult to control and notably increases the quantity of phthalic acid produced. This important point has also escaped Cornillot (*Ann. Chim.*, 1927, 7, 281), and the presence of our relatively very large proportion of water renders Cornillot's delicate temperature control unnecessary, provided that the apparatus has a thoroughly efficient condenser such as of the Munich worm type. The phthalonic acid is worked up after von Braun, and our yields are intermediate between his and those of Cornillot. The conversion into homophthalic acid has been carried out almost quantitatively on a large scale; if the phthalonic acid is moist, or the hydriodic acid weaker than the constant-boiling mixture with water, a small quantity of phthalidecarboxylic acid (m. p. 152°, identified by the method of mixed melting points) is produced. This is separated from homophthalic acid by means of its greater solubility in water. The homophthalic acid so produced melts at 181°, and its anhydride at 141—142°.

Proof of the Existence of the Enolic Form of Homophthalic Anhydride (I).—Dieckmann (*loc. cit.*, p. 1429) states that homophthalic anhydride shows no distinct reaction with ferric chloride, but this can be obtained as follows: A dilute alcoholic solution of homophthalic anhydride is treated with *N*/10-potassium hydroxide, the cold yellow solution made faintly acid with dilute sulphuric acid, and a drop of ferric chloride solution immediately added. A bluish-violet coloration is produced which lasts a considerable time. If many minutes are allowed to elapse between the addition of the sulphuric acid and of the ferric chloride, the coloration is very faint or non-existent.

3-Chloroisocoumarin (II).—A tarry mass is produced when homophthalic anhydride is heated with phosphorus pentachloride and a small quantity of phosphorus oxychloride, but when homophthalic acid (20 g. : 1 mol.) is heated with phosphorus pentachloride (50 g. : 10% excess of 2 mols.) and phosphorus oxychloride as solvent (50 g.) for 3 hours at 140—150°, a smooth reaction ensues. The phosphorus oxychloride is removed by distillation in a vacuum, water added, and the 3-chloroisocoumarin distilled in steam. The product (about 5 g.) is readily obtained almost pure (m. p. 95°) by crystallisation

from light petroleum, but is obtained quite pure by crystallisation from ethyl ether. 3-*Chloroisocoumarin* forms lachrymatory white needles, m. p. 98.5—99°, b. p. about 150°/5 mm., and is very soluble in ether, benzene and alcohol, moderately easily soluble in light petroleum, sparingly soluble in hot and practically insoluble in cold water, from which it can be crystallised. The solutions of the pure substance in organic solvents have a strong blue fluorescence (Found: C, 59.5; H, 2.6; Cl, 19.5; *M* in benzene, 177; by Rast's method, 207. $C_9H_5O_2Cl$ requires C, 59.8; H, 2.8; Cl, 19.7%; *M*, 180.5). When it is boiled with a solution of excess of aniline in benzene, and the mixture kept for 48 hours, *homophthalanilide* (IV) is slowly precipitated; this crystallises from alcohol in very long, thin needles, m. p. 231.5°, which become electrified when shaken in a glass bottle or stirred with a glass rod (Found: N, 8.3, 8.5. $C_{21}H_{18}O_2N_2$ requires N, 8.5%).

3-*Chloroisocoumarin* is remarkably stable towards neutral or acid hydrolytic agents, no hydrogen chloride being obtained by boiling its aqueous or alcoholic solutions for a short time. It is also stable to prolonged treatment with boiling formic acid, sodium iodide in boiling acetone solution, hydriodic acid, and zinc with acetic acid. The chlorine atom is more labile in alkaline media. 3-*Chloroisocoumarin* in dry benzene reacts very slowly with dry ammonia, but when a trace of moisture is introduced by exposure to the atmosphere the reaction mixture rapidly becomes yellow, brownish-green, and finally bluish-green. From the green precipitate by solution in benzene a small quantity of colourless needles, m. p. 126°, is isolated. This substance is almost certainly *o*-carboxyphenylacetone nitrile (see Haworth and Pink, J., 1925, 127, 1370).

3-*Chloroisocoumarin* reacts readily with aqueous sodium hydroxide to form a yellow solution, and the ultimate product is homophthalic acid (this and the anhydride from it were identified by the method of mixed melting points). The yellow solution reduces permanganate to manganate instantly, but when it is boiled or acidified it loses its colour and reducing properties. 3-*Chloroisocoumarin* itself does not reduce potassium permanganate in neutral acetone solution. The qualitative behaviour of homophthalic anhydride in sodium hydroxide solution towards heat and towards potassium permanganate is the same as that of 3-chloroisocoumarin, the view that the chlorine atom is replaced by the —ONa group thus being confirmed.

3 : 3 : 4 : 4-*Tetrachloro-3 : 4-dihydroisocoumarin* (V).—Homophthalic acid (54 g.), mixed with phosphorus pentachloride (250 g. : 4 mols.) and phosphorus oxychloride (100 g.), was heated for 8 hours at 140—150°, and the phosphorus oxychloride and the residue were

then distilled in a vacuum. The main fraction (40 g.), b. p. 170—190°/21 mm., solidified on cooling. A further quantity of crystals was obtained by the addition of light petroleum (b. p. 80—100°), and crystallisation from this solvent gave pure 3:3:4:4-tetrachloro-3:4-dihydroisocoumarin (12 g.) in white, compact crystals, m. p. 122° (Found : C, 38.2; H, 1.8; Cl, 49.5; *M*, by Rast's method, 266. $C_9H_4O_2Cl_4$ requires C, 37.8; H, 1.4; Cl, 49.6%; *M*, 286). It slowly reacts with excess of aniline in hot benzene to produce a chlorine-free *anilide*, m. p. 225°, which is quite distinct from the *anilide* previously described, m. p. 231.5°.

The dihydroisocoumarin, which is further attacked by phosphorus pentachloride at high temperatures to give an oily mixture, resembles 3-chloroisocoumarin in the general inertness of the chlorine atoms, and in this case even the hydrolysis in boiling aqueous-alcoholic sodium hydroxide solution is extremely slow. The product of hydrolysis is phthalonic acid. This was identified by conversion into a *compound* (cream-coloured, felted needles, m. p. 239°) with *p*-nitrophenylhydrazine which was also obtained from an authentic specimen of phthalonic acid.

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