

Zinc salt: white plates.

Copper salt : beautiful, very light green needles.

Nickel salt : light green plates.

Cobalt salt : flesh colored plates.

β-PHENANTHROL.

The potassium or sodium salt of *β*-phenanthrene sulpho acid, on fusion with potash, yields readily a phenol-like body, $C_{14}H_9OH$. From petroleum benzine it can be obtained in crystals. It dissolves readily in alkalies, is reprecipitated by acids, is very little subject to change on exposure to air, and in alkaline solution unites with diazo bodies generally. The compounds formed with the diazo derivatives of sulphanic acid, of naphthionic acid, and of the sulpho acid of an amido phenanthrene, are dye-stuffs, differing much in shade from the corresponding compounds of *α*-phenanthrol. These bodies are still under investigation.

XXIV.—ON THE ACTION OF WATER AND OF ARGENTIC HYDRATE UPON BENZINE HEXACHLORIDE AND NAPHTHALENE TETRACHLORIDE.

BY A. R. LEEDS, PH.D., AND E. EVERHART, PH.D.

Before passing to a description of the results obtained, it is important to describe certain modifications in the methods of preparing the benzine hexachloride and naphthalene tetrachloride, which have yielded unexpectedly good results.

I. PREPARATION OF BENZINE HEXACHLORIDE.

The original mode of preparing benzine hexachloride, was by the exposure of benzine to an atmosphere of chlorine.* Subsequently it was stated by Heys,† that it was obtained most readily by acting on boiling benzine with excess of chlorine. This method was accordingly made use of in the first instance. The benzine was introduced into a flask heated over a water-bath. A stream of dry chlorine was sent into the flask, the excess passing off through a tube surrounded by a condenser. The exit tube was made to dip below the surface of water. After the chlorination had been continued for eighteen hours, a few drops of an oily liquid had collected beneath

* Mitscherlich, Pogg. Annal., 35, 374; Péligot, Ann. Chem. Phys. [2] 56, 66; Laurent, Ann. Chem. Phys. [2], 63, 27.

† Zeltschr. f. Chem. [2], 7, 293.

the surface of the water. The operation was then interrupted, the unaltered benzine distilled off, the residue washed with ligroine, and crystallized out of alcohol. The product obtained in this manner was so very small (only approximately 5 grms of the hexachloride from 100 grms benzine), that the process was abandoned.

The chlorination was then performed in the sun-light, the benzine being introduced into a tall two gallon bottle, of white glass, and the stream of chlorine flowing down through a wide glass tube ending just above the surface of benzine. The experiment was a very striking one. The interior of the bottle at once becomes filled with dense white clouds, the temperature of the benzine rises from the energy of the reaction, and presently the liquid becomes turbid, and precipitation of a white crystalline product ensues. After sixteen hours exposure, 600 grms benzine yielded 350 grms hexachloride, the bottom and sides of the bottle being covered with crystals of the almost pure product. On recrystallization from alcohol or benzine, they yielded after the third crystallization, rhombic crystals of great beauty, with a definite melting point (157°). The unaltered benzine was distilled off from the liquid portion, and, after allowing the residue to crystallize as far as it would, and washing with cold alcohol, it was thrice recrystallized out of alcohol or benzine, as above. This part of the process yielded the main portion of the benzine hexachloride obtained, the melting point of the product obtained after the third recrystallization always standing at 157° .

The residues extracted by alcohol were of a dark red color, and of an oily consistence. They were divided into two portions, *A* and *B*.

A was treated with an excess of water, and washed six times with the same. The undissolved oily matters were then treated repeatedly with cold ligroine. This dissolved out all the oil, and left behind on the filter, a white substance, soluble in alcohol and benzine. After recrystallization from alcohol, the melting point was found to be 157° , and the substance was benzine hexachloride.

The oily portions insoluble in ligroine, were purified by repeated washing with the same. From the final solutions, the ligroine was expelled by exposing them to a temperature of 65° for several days, and, finally, by heating on a water-bath, until the weight became constant. This yielded a heavy, dark red oil, which was set aside in a cold place for six months, in order to see whether any dissolved crystalline substance would crystallize out. Such proved to be the case, and at the expiration of this long interval, a small crop of crys-

tals of benzine hexachloride was obtained. The main portion was then treated with alcoholic potash. On distilling, α -trichlorbenzene, $C_6H_3Cl_3$, came over, and the residue boiled at 179° , and proved to be orthodichlorbenzene, $C_6H_4Cl_2$.

B was submitted to distillation. After the alcohol was driven off, the temperature rose quite rapidly, until the thermometer stood at 200 – 210° . Between 110° and 190° nothing came over except a small quantity of oil. At a higher temperature decomposition set in, as was shown by the hydrochloric acid fumes, and a pale yellow oil, accompanied by volatilized benzine hexachloride, distilled over. After removing the oil from the distillate by washing with ligroine, the solid residue was recrystallized from alcohol, and afforded crystals which, by their melting point of 157° , were proven to be benzine hexachloride. The ligroine was expelled from the oily portion by heating to about 65° for several days, at the end of which time, long, white needle-shaped crystals of α -trichlorbenzene separated out. Their melting point was 17° .

II. PREPARATION OF NAPHTHALENE TETRACHLORIDE.

Instead of passing a rapid stream of chlorine over naphthalene, as was done by Laurent, Faust and Saame made the dry chlorine to flow in a rapid stream into fused naphthalene until the mass assumed the consistency of butter, on cooling.* These methods were rejected by E. Fischer,† on the ground that the chlorination can never be carried to so high a stage by means of dry chlorine, as it can be by the action of potassium chlorate and hydrochloric acid, in the manner which he has described. He attributes this to the viscous condition into which the chlorinated mass eventually passes when dry chlorine is used, and which prevents further action. And the warming of this mass to render it fluid must be avoided, lest, as Laurent, Faust and Saame, and others have pointed out, an increased production of secondary products should occur. Fischer modified the process, which was originally proposed by A. and E. Depouilly,‡ in so far as he intimately mixed the naphthalene with the calculated amount of potassium chlorate, by pulverization in a mortar. Enough water was then added to allow the mass to be rolled into balls which, after drying, were porous and firm. After being subjected to the action of con-

* Naphthalene Derivatives, Ann. der Chem., 160, 65; Zeltschr. f. Chem. [2], 5, 705.

† Ber d. d. chem. Gesell., 11, 735.

‡ Bull. Soc. Chim., 4, 10.

concentrated hydrochloric acid, none of the naphthalene remained unaltered.

This method was found by the authors to give a somewhat larger product than that of Faust and Saame (the naphthalene tetrachloride obtained amounted to fifteen per cent. of the naphthalene employed), but to be excessively troublesome and unpleasant. A very large amount of a dark red oil was formed at the same time, the complete separation of which, by means of pressure, etc., was difficult, and the preparation of any considerable amount of pure naphthalene tetrachloride, by this method, most tedious.

The plan adopted by the authors, was to expose as large a surface as possible of the naphthalene, to the action of direct sun-light, in an atmosphere of chlorine. To this end a chlorinating chamber was arranged, which will be found convenient in similar cases where sun-light is to be used. A large bell-jar, placed in a porcelain tray, was closed by a cork through which three tubes were passed, the cork being protected from the action of chlorine, by plaster of Paris poured in so as to form a solid cap on the under side. One of the tubes, serving as an exit, was connected with a Peligot tube partially filled with water, so as to detain any volatile products of chlorination.

The other two were connected with large chlorine generators. Gallon bottles, partly filled with roughly powdered black oxide of manganese, and placed in tall tin boilers containing water kept at the boiling point, were found to be the most convenient arrangement. The hydrochloric acid was poured into the bottles through safety funnels, and the chlorine dried by passage through a sulphuric acid wash bottle. Such an arrangement would keep a continuous stream of chlorine flowing for an entire day, with no attention other than that of the occasional addition of acid. The naphthalene was contained in five shallow glass dishes, piled up one above another, with separating strips of kerite between. The absorption of a rapid stream of chlorine under these conditions was so energetic, that a constant pressure inward was produced. The interior became filled with dense white clouds, and the sides of the jar coated with a whitish-yellow, oily mass. In one chlorination, from 415 grms of naphthalene used, 185 grams, or 45 per cent., of tetrachloride, were obtained. When the absorption of chlorine ceased, the oily mass was scraped into a capacious flask, and treated four times with boiling ligroine. This removed most of the oily naphthalene dichloride, $C_{10}H_8Cl_2$. The ligroine extract, *A*, was set aside for further examination.

The portion insoluble in ligroine was treated two or three times with boiling alcohol, which removed the last traces of the oil, and left the residue almost perfectly white. This, after recrystallization from chloroform, yielded very large and beautiful monoclinic prisms of pure naphthalene tetrachloride, $C_{10}H_8Cl_4$, m. pt., 182° . The products obtained from the alcoholic extract, *B*, are given below.

The extract *A*, after standing for a number of hours, deposited a large, solid mass, which, after filtration and draining, was washed four or five times with small quantities of alcohol, until it became white. This dissolved in chloroform, in which it is readily soluble, and crystallized out in long prisms. The successive crystallizations from chloroform were dissolved in ether, and yielded, on repeated recrystallizations, the same long, prismatic needles of monochloronaphthalene tetrachloride, $C_{10}H_7ClCl_4$; m. pt., 128° .

The alcoholic extract, *B*, after being distilled to small bulk, deposited, on standing, a heavy crystalline mass which, after washing with alcohol and crystallization from ether, in which it dissolved with difficulty, proved to be naphthalene tetrachloride. The melting point of the crystals thus obtained was 182° . The mother liquor, on standing, gave a further deposit which, after repeated crystallizations, first from alcohol and then from acetic acid, proved to be prisms of dichloronaphthalene tetrachloride, $C_{10}H_6Cl_2Cl_4$; m. pt., 172° . It had been hoped that they would prove to be the β modification of naphthalene tetrachloride announced by Laurent. A further proof, if that had been needed, that they were not, was, that on treatment with alcoholic potash, they yielded silky needles of tetrachloronaphthalene, $C_{10}H_4Cl_4$, with a melting point of 130° .

III. ACTION OF WATER AND ARGENTIC HYDRATE UPON BENZINE HEXACHLORIDE.

After treatment of benzine hexachloride with water for a number of days, in sealed tubes, at a temperature of 200° , a dark mass was obtained which, on examination, proved to be chiefly unaltered hexachloride, with a little tarry matter. The latter yielded no crystallizable body on appropriate treatment.

Four sealed tubes, each containing fifteen grms benzine hexachloride and eighteen grms argentic hydrate, were heated in an oil-bath to 200° , for eighty hours. On opening the tubes, there was a strong outward pressure of a gas which proved to be carbonic acid. After removing the supernatant liquid, which contained much hydrochloric acid, it, and the aqueous extracts obtained on repeated washing, were evaporated to dryness. A tarry mass was obtained, from

which no crystalline substance could be derived, either by solvents, or by distillation or sublimation.

The residue, insoluble in water, proved to be merely unaltered benzine hexachloride and argentic hydrate. On distillation it yielded hydrochloric acid, benzine hexachloride, and a small amount of trichlorobenzene, arising from the decomposition of a portion of the hexachloride.

These negative results were highly disappointing, since the anticipation had been that a substitution of hydroxyl for chlorine would occur, giving rise to hydroxylated addition products, similar to, or identical with phenose, $C_6H_6(OH)_6$.

IV. ACTION OF ARGENTIC HYDRATE UPON NAPHTHALENE TETRACHLORIDE.

Four sealed tubes, each containing twenty grms of naphthalene tetrachloride and fifteen grms of argentic hydrate, the two substances being intimately mixed previous to their introduction into the tubes, were heated in the oil-bath to $200^\circ C.$, for eight hours a day, during an interval of three weeks. During the first few days, the small amount of water used in transferring the materials to the tubes, and floating above the solid matters at the bottom, assumed a light reddish tinge, but afterwards it became lighter and lighter, until finally, when the tubes were removed, it had become entirely colorless. On opening, there was a strong pressure outwards of carbonic acid. The contents consisted of two portions, a solid, tarry mass, and a colorless liquid, strongly acid from the presence of free hydrochloric acid. The solid portion was repeatedly washed with water, filtered, and the filtrates added to the original aqueous extract. The whole was then evaporated to dryness, and heated in a subliming chamber to 194° , at which temperature, very beautiful, long, silky white needles came off. The needles melt at 130° .

0.2249 grm of the substance yielded 0.5324 grm CO_2 , and 0.0639 grm H_2O .

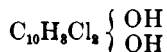
0.2229 grm yielded 0.1784 grm $AgCl$.

This would agree more nearly with the composition of monochloronaphthol, $C_{10}H_7ClOH$, than with any other derivative of this class.

	Found.	Theory
Carbon.....	64.56	67.22
Hydrogen.....	3.16	3.92
Chlorine.....	19.78	19.88
Oxygen.....	12.50	8.98

On recrystallization from alcohol, its melting point sank to 112°. This shows that the sublimed needles were probably accompanied by the dichloronaphthyhydreneglycol, which has a melting point of 155–156°. But the small amount of the substance obtained, and the unfortunate bursting of very many sealed tubes, prevented the repetition of the analysis.

The decomposition of naphthalene tetrachloride, by the action of water at high temperatures, has previously been studied by E. Grimaux. In his earlier work,* Grimaux found that by the combined action of water at 200–210°, a substance was obtained which was soluble in hot water, from which it separated in small crystals, melting at 142°. He assigned to this body the formula,



Later he recognized the substance as a glycol,† the twice chlorinated naphthyhydreneglycol, and stated that it crystallized in shining tables, melting at 155–156°. By the action of boiling hydrochloric or hydrobromic acid upon this compound, there distills off along with the steam, a body which, according to its composition and its reactions, is the once chlorinated naphthol, $\text{C}_{10}\text{H}_7\text{ClOH}$.

It crystallizes in long colorless needles, melting at 109°. By oxidation of the new glycols, phthalic acid only was obtained. But indirectly, by boiling naphthalene tetrachloride with a solution of argentic nitrate or with dilute nitric acid, Grimaux obtained an oxidation product crystallizing in hexagonal tables, and with a composition corresponding to the formula, $\text{C}_{10}\text{H}_8\text{Cl}_2\text{O}_2$. Its melting point was 195–196°.

The solid portion was repeatedly digested with alcohol. On distilling the alcoholic extracts, a blackish, oily residue remained, which was subjected to further distillation by heating the body of the retort in an air-bath. On raising the temperature, there was some disengagement of hydrochloric acid, due probably to the decomposition of a small amount of unchanged naphthalene tetrachloride, which had gone into the alcoholic solution. Up to 280° there was no constant temperature, although a thin, transparent oil was given off, from which crystals soon began to separate. After freeing these crystals as much as possible from the accompanying oil, by pressure between filter paper, they were crystallized again out of hot alcohol. The crystals proved to be the same as the main portions of the sublimate,

* Berl. Ber., 5, 391.

† Ber. Ber., 5, 827.

which came off at about 280° . After recrystallizing this a number of times from hot alcohol, crystals were obtained having a constant melting point of 120° .

They are insoluble in water, slightly soluble in cold alcohol, readily soluble in hot alcohol and in ether. They are in the form of extremely thin, transparent, colorless leaves. While separating rapidly from hot alcohol, these films exhibit magnificent prismatic tints, and present more or less of rhombic outlines, the edges of the rhomb being frequently as much as 0.5 cm in length. On sublimation, the crystals are deposited in beautiful white leaves of the same form and of a pearly lustre.

0.2974 grm yielded on analysis 0.6603 grm CO_2 , and 0.0978 grm H_2O .

0.3708 grm yielded 0.5104 grm AgCl .

These results would make the substance a modification of dichloronaphthalene, $\text{C}_{10}\text{H}_6\text{Cl}_2$.

	Found.	Theory.
Carbon	60.65 per cent.	60.91 per cent.
Hydrogen	3.29 “	3.04 “
Chlorine	36.20 “	36.05 “

But in its properties, this substance is entirely different from the two isomeric modifications of dichloronaphthalene, which, up to the present time, have been the only two that have been obtained directly from naphthalene tetrachloride. These two are the α , obtained by the action of alcoholic potash, and forming a crystalline mass, melting at $35\text{--}36^{\circ}$, and the β , obtained when small quantities of the tetrachloride are rapidly distilled, and forming colorless prisms, with a melting point of 68° .

Neither does it correspond with the other five modifications, which have been previously described, and which, it must also be remembered, are derived in an entirely new manner. They are:

γ . Obtained by acting upon α -dinitronaphthalene with phosphoric chloride, and by the passage of chlorine through melted naphthalene, and distilling the product. It forms colorless, brilliant crystalline scales, with a melting point of 107° .

δ . By heating α -naphthalenedisulphochloride with phosphoric chloride; it forms colorless leaves, with a melting point of 114° .

ϵ . From β -naphthalenedisulphochloride, in like manner; shining prisms, with melting point at 135° .

ζ . By acting upon β -dinitronaphthalene, with phosphoric chloride; large, rhombic crystals; m. pt., 83° .

7. By heating nitronaphthalenesulphochloride (obtained from β -naphthalenesulpho acid) with excess of phosphoric chloride; colorless needles; m. pt., 48°.

The only one of these which resembles in characters the one formed from the naphthalene tetrachloride, in sealed tubes, is the δ modification, but its melting point, as will be seen, is considerably lower. For these reasons, the modification described must be regarded as new, and to it, which is the eighth now known, we shall accordingly give the name ϑ -dichlornaphthalene.

XXV.—ON THE PROBABLE OCCURRENCE OF NORWEGIUM IN AMERICAN LEAD.

BY GEO. A. PROCHAZKA.

C. W. Blomstrand reports (Ber. d. d. chem. Gesell., 12, 1731) on the discovery of norwegium by Tellef Dahll, substantially as follows:

“On a small island, Oterö, in the neighborhood of Kragerö, where Mr. Dahll resides as mining director, towards the end of the year 1878, a calcite gangue, interspersed with small particles of copper, nickel and nickel glance, was discovered. The nickel glance, on analysis, gave nickel, cobalt, iron, arsenic and sulphur. The hydrogen sulphide precipitate was treated with ammonium sulphide to remove the arsenic; the black sulphide of a new metal remained undissolved. 10 kgrms of the ore were then roasted; the residue was dissolved in acid and precipitated by H₂S. The precipitate was dried and again roasted; the oxide thus produced was reduced to metal.

Further investigation proved that the metal contained copper. To remove the copper the metals were converted into chlorides, and the solution diluted with a large excess of water. The new metal was thereby precipitated as oxichloride, while copper remained in solution. The new metal in its properties bears very close resemblance to bismuth.

	Bismuth.	Norwegium.
Melting Point.....	264°	254°
Atomic Weight (R ₂ O ₃).....	210	218.9
Sp. Gravity.....	9.8	9.441

The oxides of both metals are fusible, and give in the flame, on porcelain, a metallic mirror. The main difference between the two metals consists in the solubility of the oxihydrate of the new metal in caustic alkali, as well as in ammonium and sodium carbonate solution, on boiling. The difference is well marked if carbonates are treated in the same manner.