

In the same way, I hope to arrive at the constitution of pyrene, which is $C_{16}H_{10}$, only, in this case, I am not certain what position the carbon atoms hold, and will, therefore, have to try all the three bromotolyl bromides. If we combine two molecules of, say, metabromtolyl bromide, and treat the mixture with sodium, we should get a bihydrated pyrene, and this, treated with H_2SO_4 , should yield pure pyrene.

XXIII.—ON A NEW SULPHO ACID OF PHENANTHRENE.

BY HENRY MORTON AND WILLIAM E. GEYER.

A monosulpho acid of phenanthrene was first prepared by Graebe,* and subsequently by Rehs.† Graebe heats phenanthrene with its own weight of oil of vitriol, for some time, on the water-bath. Rehs uses slightly fuming acid, apparently at ordinary temperatures.

Merz and Weith‡ have shown that when naphthalene is heated with sulphuric acid, at 100° , α -naphthalene sulpho acid is the main product, but if the temperature is raised to 160 – 170° , the β modification is almost exclusively formed. We have found that in the same way, phenanthrene, also, forms two distinct monosulpho acids. That formed according to Graebe's method, we propose to call the α -acid, ours the β -naphthalene sulpho acid.

To serve as a means of comparison, we first prepared the α -acid. The process is simple, but the yield is small, the greater part of the phenanthrene remaining unattacked. To prepare the β -acid, three parts of phenanthrene were heated with two parts of sulphuric acid, in a paraffine bath, to 170° , for three hours. Towards the end, the temperature was, for a short time, raised to 190° . Much vapor of water and sulphurous acid were given off, during the entire time of heating. On cooling, there was obtained a very black, tenacious pitch. This, with the exception of a little unaltered phenanthrene, dissolves in water to a very dark greenish-black liquid. When this liquid is much diluted, heated to boiling, and neutralized with lead carbonate, the black coloring matter is completely carried down with

* Ann Chem. u. Pharm.. 167, 152.

† Ber. d. d. chem. Gesell.. 10. 1252.

‡ Ber. d. d. chem. Gesell.. 3. 195.

the lead sulphate, and, on filtering hot, we obtain at once an almost colorless liquid, from which, on cooling, a nearly pure lead salt of the β -acid separates. By long continued digestion with boiling water, it can be redissolved and purified by recrystallization. The finely divided salt is suspended in water, and treated with sulphuretted hydrogen. On evaporating the filtrate from the lead sulphide, we obtain a thick syrup, which soon crystallizes. The yield is small: we have not yet had time to vary proportions, temperature, and time of heating, to ascertain the best conditions.

β -phenanthrene sulpho acid crystallizes in fine, white needles, with a strong, pearly lustre. It is greasy to the touch, very soluble in water and alcohol, but not deliquescent. Its salts are much less soluble than the corresponding α -salts. It is a powerful acid, displacing, for instance, chlorine, and precipitating its own salt when a solution of the acid is added to a solution of the chlorides of potassium, sodium, ammonium, barium, calcium, zinc, copper, etc.

Lead salt: $(C_{14}H_9SO_3)_2Pb + 3H_2O$, obtained in indistinctly crystalline crusts, on evaporating the solution. After drying between blotting-paper, its weight in the air is constant. 2.494 grms, dried at $155-160^\circ$, lose 0.173.

	Calculated for $3H_2O$.	Found.
H_2O ,	6.96 per cent.	6.93 per cent.

0.460 grm of the salt, dried at 160° , gave 0.193 $BaSO_4$.

	Calculated for $(C_{14}H_9SO_3)_2Pb$.	Found.
Pb,	28.71 per cent.	28.66 per cent.

Barium salt: $(C_{14}H_9SO_3)_2Ba + 3H_2O$, obtained by nearly neutralizing a boiling solution of the acid with barium hydrate. On cooling, the salt separates in brilliant scales, often grouped in rosettes. If the solution is not acid, the salt is apt to separate in light, fungoid growths, of indistinct crystals.

	Calculated for $3H_2O$.	Found.		
		l.	ii.	iii.
H_2O ,	7.65 per cent.	7.50	7.81	7.58 per cent.
Dried at 160° .				

	Calculated for $(C_{14}H_9SO_3)_2Ba$.	Found.
Ba,	21.04 per cent.	20.90 per cent.

Air dried.

	Calculated for $(C_{14}H_9SO_3)_2Ba + 3H_2O$.	Found.
Ba,	19.43 per cent.	19.30 per cent.

Potassium salt: brilliant plates; do not lose weight at $180-190^\circ$.

Ammonium salt: same appearance as potassium salt.

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 alkalis, 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 sulphanilic 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.

† Zeitschr. f. Chem. [2], 7, 293.