LXXIV.—*Sulphonic Acids derived from Isodinaphthyl ($\beta\beta$ -Dinaphthyl).*

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DINAPHTHYL($\beta\beta$)-MONOSULPHONIC ACID, $C_{10}H_7 \cdot C_{10}H_6 \cdot SO_2OH$.—15 grams of isodinaphthyl were heated with 3 grams of concentrated pure sulphuric acid in a small flask at 200° in the oil-bath for 5—6 hours. At that temperature the hydrocarbon melted easily with the acid, forming a dark-coloured oily liquid which, on cooling, solidified to a hard mass. After the 5—6 hours' heating, the mass was on cooling treated with boiling water several times, whereby it was in greatest part dissolved. Still a residue remained, and no inconsiderable one. The mixture, without filtering, was now neutralised with pure calcium carbonate, whereby the calcium salt of the sulphonic acid in question was obtained. The liquid was now filtered in the cold. The clear filtrate was evaporated down on a water-bath, whereby only a very small residue was obtained, too little for analysis. The insoluble residue (in the cold) remaining on the filter was now transferred to a flask and boiled up with water for 20 to 30 minutes. On filtering at the boiling heat, employing a hot-water funnel, a clear filtrate was obtained, which, on cooling, deposited a snow-white crystalline precipitate. This, on examination with a lens, was seen to consist of an aggregation of small white needles. The residue on the filter was now repeatedly boiled with water, until the cooled filtrate deposited no more crystalline precipitate.

The precipitate was now collected, and washed first with cold water and afterwards with dilute acetic acid, to remove any possible con-

tamination due to the presence of calcium carbonate. After a final washing with water, it was dried over sulphuric acid in a vacuum.

Analyses of the dried calcium salt thus obtained gave the following results:—

A weighed quantity was heated in the air-bath at 150–200°, till a constant weight was obtained. The residue was then ignited with a few drops of pure sulphuric acid, and the weight of the resulting CaSO_4 determined.

(I.) Weight of salt taken.....	0.1490 gram.		
Loss on heating at 150–200°..	0.0080	„	= 5.37 p. c. H_2O .
CaSO_4 obtained	0.0265	„	= 5.17 „ Ca .
(II.) Weight of salt taken.....	0.1620 gram.		
Loss on heating at 150–200°..	0.0085	„	= 5.24 p. c. H_2O .
CaSO_4 obtained	0.0305	„	= 5.53 „ Ca .

	I.	II.	Mean.	Calculated for $\text{C}_{10}\text{H}_7\cdot\text{C}_{10}\text{H}_6\cdot\text{SO}_3 > \text{Ca} + 2\text{H}_2\text{O}$.
Ca	5.17 p. c.	5.53 p. c.	5.35 p. c.	5.30 p. c.
H_2O	5.37 „	5.24 „	5.30 „	4.86 „

Calcium Dinaphthyl($\beta\beta$)-*monosulphonate*, $\text{C}_{10}\text{H}_7\cdot\text{C}_{10}\text{H}_6\cdot\text{SO}_3 > \text{Ca} + 2\text{H}_2\text{O}$, forms delicate white or colourless microscopic needles, only slightly soluble in cold water, and not easily in hot; insoluble in alcohol, ether, and benzene. The water of crystallisation is lost only after some hours' exposure to a temperature close upon 200° C.

Barium Dinaphthyl ($\beta\beta$)-*monosulphonate*,

—The barium salt of $\beta\beta$ -dinaphthylmonosulphonic acid was prepared exactly in the same way as in the case of the calcium salt.

The precipitate obtained on cooling the solution was very similar in appearance and solubility to the calcium salt.

A portion was dried at 150° in the air-bath, and the barium in it determined. The results were as follows:—

(I.) Weight of salt taken....	0.0975 gram	} = 16.31 p c. Ba.
BaSO_4 obtained	0.0270 „	
(II.) Weight of salt taken....	0.0660 gram	} = 16.31 p. c. Ba.
BaSO_4 obtained.....	0.0185 „	

	I.	II.	Calculated for $\text{C}_{10}\text{H}_7\cdot\text{C}_{10}\text{H}_6\cdot\text{SO}_3 > \text{Ba}$.
Ba	16.31 p. c.	16.31 p. c.	15.81 p. c.

Only small yields could be obtained of both calcium and barium salts, other products being formed at the same time as the monosulphonic acid, and apparently with greater facility.

In order to obtain a more highly substituted sulphonic acid than the monosulphonate, 10 grams of the $\beta\beta$ -dinaphthyl were heated with an excess of concentrated sulphuric acid (7 grams) in a flask in the oil-bath to a temperature of 180–200° for 5–6 hours. The mass in the flask, on cooling, solidified to a hard shining pitch-like substance. It was boiled with water, neutralised with barium carbonate, filtered in the cold, and the filtrate was evaporated to dryness on the water-bath. A much more soluble product was obtained than in the previous case, in which a smaller amount of sulphuric acid was employed; also by this manner of operating scarcely any monosulphonate could be detected.

By the above-mentioned process two isomeric sulphonic acids appear to be formed, one yielding a barium salt of difficult solubility, the other an easily soluble barium salt. Two similar lead salts are also obtained.

The soluble barium salt presented the appearance of a crystalline powder of a yellowish-white colour. This was heated for several hours in the air-bath to 200°, and in a portion the barium was determined:—

(I.) Substance taken	....	0.1410 gram	} = 25.02 p. c. Ba.
BaSO ₄ obtained	....	0.0600 „	
(II.) Substance taken	....	0.1680 gram	} = 25.55 p. c. Ba.
BaSO ₄ obtained	....	0.0730 „	

			Calculated for
			C ₁₀ H ₆ .SO ₃
			C ₁₀ H ₆ .SO ₃
			} Ba.
I.	II.		
Ba	Ba		
.....	.....		
25.02 p. c.	25.55 p. c.		24.97 p. c.

This is the soluble barium disulphonate, the preparation of which has already been described by one of us (*Chem. Soc. J.*, 1877, ii, 557). Its isomeride is a salt soluble with difficulty in water, and not to be confounded with the monosulphonate, which crystallises in microscopic needles, whereas the former falls as a fine white crystalline powder. This soluble disulphonate forms a glassy mass, which readily splits up into lanceolate leaflets. It is insoluble in alcohol, ether, and benzene.

Lead $(\beta\beta)$ *Dinaphthyl-disulphonate*, $\begin{array}{c} \text{C}_{10}\text{H}_5.\text{SO}_3 \\ | \\ \text{C}_{10}\text{H}_5.\text{SO}_3 \end{array} \text{Pb} + x\text{H}_2\text{O}.$ —The

soluble lead salt was a light yellowish-white crystalline powder, a portion of which on drying at $200^\circ \text{C}.$ and analysing with reference to the lead in the same way as with the barium salt, gave numbers indicating the formula given.

Lead $(\beta\beta)$ *Dinaphthyl-tetrasulphonate*, $\begin{array}{c} \text{C}_{10}\text{H}_5.(\text{SO}_3)_2.\text{Pb} \\ | \\ \text{C}_{10}\text{H}_5.(\text{SO}_3)_2.\text{Pb} \end{array} + 6\text{H}_2\text{O}.$ —

By employing a slightly larger quantity of sulphuric acid, this time Nordhausen acid, and afterwards neutralising with lead carbonate, the soluble lead salt was obtained of a dinaphthyl-tetrasulphonic acid.

(I.) 0.2260 gram substance gave 0.1290 PbSO_4 .

0.2400   ,,   ,,   0.0245 H_2O (at 208°).

(II.) 0.5005 gram substance dried in a vacuum over sulphuric acid till the weight became constant, gave 0.2745 gram of lead sulphate.

	I.	II.	Calculated for $\begin{array}{c} \text{C}_{10}\text{H}_5.(\text{SO}_3)_2.\text{Pb} \\ \\ \text{C}_{10}\text{H}_5.(\text{SO}_3)_2.\text{Pb} \end{array} + 6\text{H}_2\text{O}.$
Pb	38.39	37.46	37.91 p. c.
$\text{H}_2\text{O} . . . . .$	10.21	—	9.89 ,,

This salt was easily soluble in water, but insoluble in alcohol, ether, and benzene.