

III.—*On Propionic Coumarin and some of its Derivatives.*

By W. H. PERKIN, F.R.S.

OUR knowledge of the coumarins extends at present to the valeric derivative; but to render the series complete, as far as it goes, the propionic coumarin has been wanting; and it appeared to me that it would be desirable to prepare this substance, not only to complete the series, but also to compare its properties with ordinary or acetic coumarin, to which it is so closely related. I have, therefore, made some experiments upon the subject, the particulars of which I now beg leave to lay before the Society.

Propionic Anhydride.

The propionic anhydride employed in these experiments was obtained

by distilling propionic chloride with dry sodium propionate. The propionic acid used was prepared from ethylic cyanide. The anhydride is a colourless liquid, having an odour somewhat like that of butyric anhydride, but more irritating. It boils at 168° — 169° , and has a specific gravity of 1.0169 at 15° C. Specimens burnt with oxide of copper gave the following numbers:—

- I. .198 of substance gave
 .4035 of CO_2 and
 .140 of water.
- II. .293 of substance gave
 .5965 of CO_2 and
 .204 of water.

These give the following percentages:—

	I.	II.	$\text{C}_6\text{H}_{10}\text{O}_3$ requires.
Carbon	55.55	55.45	55.38
Hydrogen	7.89	7.73	7.69

Propionic Coumarin.

Propionic anhydride acts much more slowly on hydride of sodium-salicyl than acetic anhydride. If heat, however, be applied, chemical action sets in, and a fluid product is soon obtained.

In my experiments I have always used a considerable excess of propionic anhydride, and boiled it with the sodium compound for an hour or more, the excess of anhydride and the resulting propionic acid being afterwards distilled off. The crude coumarin remaining in the retort is freed from sodium propionate by pouring it into boiling water, in which it sinks as a heavy oil, but solidifies into a brownish crystalline mass on cooling. It is then collected and distilled to render it colourless, and, after being well pressed between bibulous paper, twice crystallised from alcohol. In this way it is obtained in beautiful transparent slightly oblique prisms. It gave on analysis the following numbers:—

- I. .273 of substance gave
 .760 of CO_2 and
 .126 of H_2O .
- II. .2675 of substance gave
 .738 of CO_2 and
 .1265 of water.

These numbers give percentages agreeing closely with those required by the formula—

	Theory.		Experiment.	
			I.	II.
C ₁₀	120	75·0	74·90	75·21
H ₈	8	5·0	5·12	5·25
O ₂	32	20·0	—	—
	160	100·0		

Propionic coumarin possesses an odour difficult to distinguish from that of ordinary coumarin. At 90° it melts, and on cooling solidifies to a beautifully crystalline mass. It can be distilled without decomposition. Boiling water dissolves it to a small extent, the solution becoming milky as it cools, and afterwards depositing fine hair-like crystals. It is moderately soluble in cold, and easily soluble in boiling alcohol.

Propionic coumarin is nearly insoluble in cold aqueous potassium hydrate, and when gently heated melts and floats as an oil on the surface of this alkaline solution. If boiled, however, it dissolves, forming a clear pale yellow liquid, which becomes opaque when concentrated. On standing, an oily liquid rises to the surface, and solidifies on cooling to a tenacious mass. It is easily soluble in water, and is decomposed, with separation of the propionic coumarin, upon the addition of an acid.

When fused with potassium hydrate, this coumarin yields a crystalline acid, probably a propionic coumaric acid, but when it is more strongly heated with potassium hydrate, salicylic acid is produced.

β-Bromopropionic Coumarin.

If the hydride of sodium-salicyl used in the preparation of propionic coumarin be replaced by the hydride of sodium-bromosalicyl, a brominated product is obtained homologous with *β*-bromocoumarin, or in other words a bromopropionic coumarin is produced, the bromine being in the C₆ group. This product when crystallised from alcohol is obtained in long thin needles.

When propionic coumarin is mixed with bromine in excess, it dissolves, and on driving off the excess of bromine and hydrobromic acid by heating the mixture over the water-bath and then over the lamp, a crystalline product is obtained which generally weighs nearly half as much again as the coumarin employed, showing that about one atom of hydrogen has been replaced. On recrystallising the product from alcohol, long thin needles are obtained, which are also *β*-bromopropionic coumarin. Analyses of specimens prepared by both the above processes gave the following numbers:—

- I. ·236 gram of substance prepared from hydride of sodium-bromosalicyl gave
 ·434 gram of CO₂ and
 ·063 gram of water.
- II. ·297 gram of substance prepared from propionic coumarin and bromine gave
 ·5455 gram of CO₂ and
 ·077 gram of H₂O.
- III. ·2385 gram of substance same as No. II gave
 ·4385 gram of CO₂ and
 ·065 gram of H₂O.

These give percentages agreeing closely with those required by the formula—

	Theory.		Experiment.		
			I.	II.	III.
C ₁₀	120	50·20	50·15	50·08	50·1
H ₇	7	2·92	2·96	2·88	3·03
Br	80	33·47	—	—	—
O ₂	32	13·41	—	—	—
	239	100·00			

β -bromopropionic coumarin when heated melts at 146°, and on cooling solidifies to a crystalline mass. It can be distilled with but little decomposition. It dissolves easily in boiling alcohol, but is less soluble than propionic coumarin. It gradually dissolves in a boiling solution of potassium hydrate, and may be precipitated unchanged by acids. When fused with potassium hydrate, it gives an orange-red coloured product, potassium bromide being formed.

β -Dibromopropionic Coumarin.

When propionic coumarin is heated for a few hours in a sealed tube to about 150° with twice its weight of bromine dissolved in carbon disulphide, large quantities of hydrobromic acid are formed, and on evaporating the carbon disulphide, and twice crystallising the residue from benzol, a crystalline product is obtained which gave on analysis the following numbers:—

- I. ·296 of substance gave
 ·417 of CO₂ and
 ·056 of H₂O.
- II. ·3085 of substance gave
 ·436 of CO₂ and
 ·053 of H₂O.

The formula, $C_{10}H_6Br_2O_2$, requires the following percentages:—

	Theory.		Experiment.	
			I.	II.
C_{10}	120	37·73	38·41	38·6
H_6	6	1·90	2·11	2·19
Br_2	160	50·31	—	—
O_2	32	10·06	—	—
	318	100·00		

These results are not so close to the theory as could be desired; the excess of carbon, however, is probably owing to the presence of the trace of monobromopropionic coumarin.

I believe that the bromine in this substance is all in the C_6 group, as it does not seem to be touched with caustic alkali until it is fused with it, when the mixture changes to an orange-red colour, in the same manner as the β -monobromo-derivative. I therefore have called it *β -dibromopropionic coumarin*.

Dibromide of Propionic Coumarin.

Propionic coumarin, when exposed to the action of bromine-vapour in the cold, changes to a viscid liquid, and greatly increases in weight. The product appears to be the dibromide corresponding with dibromide of coumarin, but I have not been able to get it sufficiently pure for analysis. With caustic alkali, propionic coumarin is separated from it. It will be remembered that the dibromide of coumarin, under these circumstances, yields α -bromocoumarin, which, if further treated with alkalis, gives coumarilic acid.

Sulphopropionic Coumarilic Acid.

Propionic coumarin dissolves in fuming sulphuric acid without any change of colour, and on gently heating the mixture in the water-bath, it is entirely converted into a sulpho-acid. This is easily converted into the barium salt by treatment with barium carbonate, and filtering from the barium sulphate. On concentrating the filtrate and allowing it to stand, small but brilliant crystals are obtained, which contain a considerable quantity of water of crystallisation; part of this is given off by drying *in vacuo*, and the rest at 150° C. It gave the following numbers on analysis:—

- I. ·0855 of substance dried at 150° C. gave
·0325 of barium sulphate = 22·26 p.c. barium.
- II. ·297 of substance air-dried lost
·068 of water at 150 = 22·9 p.c.

The formula, $C_{20}H_{14}O_4BaS_2O_6$, requires 22.77 p.c. barium, and $C_{20}H_{14}O_4BaS_2O_6.10$ aq. requires 22.9 of water.

From the foregoing results we see that, although this coumarin corresponds in most of its properties to those of ordinary coumarin, yet it differs in some particulars, especially in its tendency to produce β -derivatives with bromine, whereas with ordinary coumarin, the tendency is in the opposite direction.
