XXIV.—*On some New Derivatives of Anisoil (Anisol).*

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A SHORT time since I showed that methylparoxyphenyl-acrylic, -crotonic, and -angelic acids, when heated,—or, better, in the case of the two latter acids,—when converted into the hydrobromo-additive compounds, and then treated with sodium carbonate, yield para-derivatives of anisoil. I have now extended my experiments to the corresponding ortho-acids, and obtained the following results.

Orthovinylanisoil.

On boiling β -methylorthoxyphenylacrylic acid, it gradually decomposes, carbonic anhydride being given off, and an oil distilling over. This is purified by washing with dilute potassium hydrate and distillation with water; but with the view of obtaining it in a still purer state, it was thought desirable to see if an additive derivative of the acid could be formed, which would decompose when treated with an alkaline solution, and yield this body.

For this purpose dry precipitated methylorthoxyphenylacrylic acid was placed in contact with hydriodic acid, sp. gr. 1.94, for two or three days, the mixture being frequently agitated. The resulting product was drained from the excess of hydriodic acid by means of a filter-pump. It was found best not to wash it, as it is very unstable, and soon decomposes when in contact with water. It was then added in small quantities to a cold saturated solution of sodium carbonate, the mixture being well stirred and not allowed to get warm during the reaction, otherwise considerable quantities of a polymerised product are formed; this, however, sometimes happens even when great care is taken. The resulting milky fluid is then placed in a retort and boiled

until no more oily product distils over. The distillate is then warmed to promote the separation of the oil into a layer, which is then collected and dried with potassium carbonate. On analysis it gave the following numbers:—

·2158 of substance gave
·6364 of CO₂ and
·1438 of H₂O.

	Theory for C ₉ H ₁₀ O.	Experiment.
Carbon	80·59	80·42
Hydrogen	7·40	7·43

The formation of this substance, which I propose to call *orthovinylanisoi*l, may be written thus:—

Orthovinylanisoi

l polymerises so quickly when heated, that its boiling point could not be determined with certainty, but it seems to be between 195° and 200° C. When heated to 150° for about an hour, it solidifies to a transparent glassy substance, which is easily soluble in benzene, but insoluble in alcohol. This solid product when heated strongly distils, orthovinylanisoil being regenerated.

The odour of orthovinylanisoi

l is very different from that of its isomeride, paravinylanisoil, being somewhat similar to that of high-boiling coal-tar naphtha, but more fragrant and not so strong.

* Its specific gravity is—

at 15° 1·0095
at 30° 1·000

When agitated with bromine-water it decolorises the latter, forming a nearly solid product. Heated with dilute nitric acid, it changes to a yellowish-brown heavy oil, becoming quite thick on cooling; this product is partially soluble in aqueous potassium hydrate. With concentrated sulphuric acid it becomes solid and of a bright-red colour.

*Orthallylanisoi*l.

Methylorthoxyphenylcrotonic acid, when left in contact with hydrobromic acid, sp. gr. 1·74, for two or three days, combines with it; but the resulting acid, unlike the corresponding para-compound, when treated with an alkaline carbonate and then distilled, yields but a

* Compared with water at the same temperature.

small quantity of oily product; a large quantity of an uncrystallisable acid is, however, found in combination with the alkali; this is probably an oxy-acid. If, however, hydriodic acid, sp. gr. 1·94, be used in place of hydrobromic, the resulting acid yields a large quantity of an oil when treated with an alkaline carbonate or acetate. A specimen of this dried over potassium carbonate and then distilled gave, on analysis, the following numbers:—

- I. ·1894 of substance gave
 ·5647 of CO₂ and
 ·1384 of H₂O.
 II. ·2178 of substance gave
 ·6482 of CO₂ and
 ·1631 of H₂O.

	Theory for C ₁₀ H ₁₂ O.	Experiment.	
		I.	II.
Carbon	81·08	81·3	81·17
Hydrogen	8·10	8·11	8·3

This substance I propose to call *orthallylanisoïl*; the formula may be expressed thus:—

Orthallylanisoïl is a highly refracting liquid boiling without polymerising at 222—223° C. Its specific gravity is—

at 15° ·9972
 at 30° ·9884
 at 45° ·9793.

Its odour is similar to that of its vinylic homologue, but fainter. When cooled in a freezing mixture of snow and hydrochloric acid, it thickens but does not solidify.

It combines with bromine, forming a thick heavy oil. Cold nitric acid, sp. gr. 1·3, does not appear to act upon it in the cold, but on heating the mixture, red fumes are given off, and a brownish-yellow viscid oil, gradually solidifying to a resinous mass, results. With concentrated sulphuric acid it becomes solid and of a red colour; but on addition of water, it changes to a white opaque product soluble in benzene.

Orthobutenylanisoïl.

Methylorthoxyphenylangelic acid, when treated with hydrobromic acid, combines with it, but the resulting compound yields only a very

small quantity of oily product when treated with an alkaline carbonate; but if hydriodic acid be employed, the yield of product is good. The specimen of oil analysed was distilled with water and dried over potassium carbonate.

·2083 of substance gave

·6228 of CO₂ and

·1634 of H₂O.

	Theory for C ₁₁ H ₁₀ O.	Experiment.
Carbon	81·48	81·54
Hydrogen	8·64	8·71

The formation of this substance, which I propose to call *orthobutenylanisoil*, may be expressed thus :—

Orthobutenylanisoil boils at 232—234° without polymerising.

Its specific gravity is—

at 15° ·9817

at 30° ·9740.

When cooled in snow and hydrochloric acid, it does not solidify, but becomes thick. Like its homologues it combines with bromine, and also becomes solid and of a red colour when treated with concentrated sulphuric acid, the product losing its colour when washed with water.

Boiled with dilute nitric acid it becomes yellow, but is only slowly acted upon. Strong nitric acid acts upon it with violence and dissolves it; water precipitates from this solution a brown resin, which is mostly soluble in aqueous potassium hydrate.

Paravinylanisoil.

I mentioned in my paper, already referred to, that I endeavoured to produce paravinylanisoil from methylparoxyphenylacrylic acid by treating it with hydrobromic acid, hoping to obtain an addition-product which would decompose with alkaline carbonates in the usual manner; but no result was obtained, as the methylparoxyphenylacrylic acid decomposed when brought in contact with hydrobromic acid. As, however, I have succeeded in obtaining orthovinylanisoil by a modification of this process, viz., by substituting hydriodic for hydrobromic acid, I applied this form for the preparation of this body.

Dry precipitated methylparoxyphenylacrylic acid, when left in con-

tact with hydriodic acid, sp. gr. 1·94, for two or three days, combines with it, and the product, when drained from the excess of hydriodic acid and treated with an alkaline carbonate, yields the desired product. Unfortunately a good deal polymerises and becomes solid. The pure paravinylanisoil, however, was easily separated from this by distillation with water.

Thus obtained, it differed but little from that prepared by the distillation of methylparoxyphenylacrylic acid; it was, however, somewhat purer, as its fusing point was higher, viz., $+3^{\circ}$ instead of -1° . Its specific gravity is—

at 15° 1·002
at 30° ·9956.

It will be, perhaps, worth while to notice in what respects the para- and ortho-derivatives of anisoil I have obtained differ from each other.

The difference in the boiling points appears to be about 10° .

Paravinylanisoil	204—205°
Orthovinylanisoil	uncertain
Parallylanisoil	232°
Orthallylanisoil	222—223°
Parabutenylanisoil	242—245°
Orthobutenylanisoil	232—234°

The density is also slightly higher in the ortho-derivatives.

	15°	30°	45°
Paravinylanisoil	1·0029	·9956	—
Ortho „	1·0095	1·000	—
Parallylanisoil	—	·9852	·9761
Ortho „	·9972	·9884	·9793
Parabutenylanisoil	—	·9733	—
Ortho „	·9817	·9740	—

The ortho-compounds also refuse to crystallise, even when placed in a freezing mixture; the para-derivatives crystallise freely.

α -Methylorthoxyphenylacrylic acid obtained from coumarin, when treated with hydriodic acid and then with an alkaline carbonate, yields an oil which is apparently identical with the orthovinylanisoil prepared from the β -acid. I am at present investigating this remarkable α -acid, and endeavouring to obtain some of its homologues.