XLI.—*Condensation of Phenols with Esters of Unsaturated Acids. Part VII.*

By SIEGFRIED RUHEMANN.

BENZO-1:4-PYRONE (chromone) and its homologues, as shown in this paper, have basic properties; they dissolve in hydrochloric acid, and these solutions give precipitates with cobalticyanic acid (Baeyer and Villiger, *Ber.*, 1901, **34**, 2679), as well as with platinic chloride. The hydrochlorides and the platinichlorides are, however, much less stable than the corresponding salts of dimethyl- γ -pyrone, which can be recrystallised from water (Collie and Tickle, *Trans.*, 1899, **75**, 710).

Previously, only the monohydric phenols have been used for the formation of chromone and its homologues; since then, however, experiments have been made with the view of obtaining hydroxybenzopyrones from polyhydric phenols, but as these have been unsuccessful, I have attempted to prepare those compounds from the mono-ethers of the polyhydric phenols. One of these ethers, namely, guaiacol, had some time ago (Ruhemann and Stapleton, *Trans.*, 1900, **77**, 1180) been subjected to the action of ethyl phenylpropiolate, and the product which was thus formed had been found to suffer a decomposition analogous to that of the other aryl ethers of β -hydroxycinnamic acid. Guaiacol, as stated in this paper, reacts with ethyl chlorofumarate and forms ethyl guaiacoloxymumarate, which, on treatment with potash, yields the corresponding acid. Its transformation into methoxybenzo-1:4-pyrone and the subsequent hydrolysis of the methyl ether have not yet been carried out, as the study of the action of ethyl chlorofumarate on the naphthols has lately occupied my whole attention.

Whilst the ethyl ester behaves towards β -naphthol in the same manner as towards other phenols, and yields β -naphthoxymumaric ester, it reacts with α -naphthol partly to form ethyl α -naphthoxymumarate in the normal way, but chiefly to form two substances, one of which is an ester of the formula $C_{16}H_{12}O_4$, the other a compound of the composition $C_{24}H_{12}O_4$.

The facts, on the one hand, that this reaction is accompanied by the loss of alcohol, and, on the other, that the compounds have properties unlike those of the chromones, lead to the following view as to the formation and the constitution of the ester $C_{16}H_{12}O_4$:

F F 2

This compound may be derived from the tricyclic type,

which I call naphtharone, and, accordingly, may be termed *ethyl naphtharonylacetate*.

The second substance, $\text{C}_{24}\text{H}_{12}\text{O}_4$, is perhaps formed from the first, according to the equation

The isolation of ethyl fumarate, figuring above, has not been effected as yet, but experiments to accomplish this task are in progress. The compound $\text{C}_{24}\text{H}_{12}\text{O}_4$, is, most probably, to be represented by the symbol

and may be called *bisnaphtharonyl*.

EXPERIMENTAL.

Formation of Salts from Benzo-1 : 4-pyrone and its Homologues.

The members of the chromone group dissolve in concentrated hydrochloric acid either in the cold or on slightly warming, and form salts which, however, are unstable, since the benzo-1 : 4-pyrones are precipitated on adding water, and are extracted by ether from their solutions in the acid. Cobalticyanic acid gives white, crystalline precipitates with solutions of the chromones in hydrochloric acid, and platonic chloride, dissolved in concentrated hydrochloric acid, yields platini-chlorides which separate in yellowish needles. These, however, are readily decomposed by water with the re-formation of benzopyrones.

The platinichlorides of chromone and some of its homologues have been analysed ; for this purpose, they were washed with concentrated hydrochloric acid and dried in a vacuum over sulphuric acid and soda-lime. Owing to the unstable nature of those salts, the analytical numbers differ somewhat from those required by theory, as is shown in the following table :

Platinichlorides of—

Benzo-1 : 4-pyrone :

0.2605 left on ignition 0.0710 Pt. Pt = 27.21.

$(C_9H_6O_2)_2, H_2PtCl_6$ requires Pt = 27.71 per cent.

o-Toluo-1 : 4-pyrone :

0.2690 gave 0.0715 Pt. Pt = 26.58.

$(C_{10}H_8O_2)_2, H_2PtCl_6$ requires Pt = 26.65 per cent.

p-Toluo-1 : 4-pyrone :

0.2835 gave 0.0725 Pt. Pt = 26.58.

$(C_{10}H_8O_2)_2, H_2PtCl_6$ requires Pt = 26.65 per cent.

6 : 8-Dimethylbenzo-1 : 4-pyrone :

0.2937 gave 0.0732 Pt. Pt = 24.92.

$(C_{11}H_{10}O_2)_2, H_2PtCl_6$ requires Pt = 25.67 per cent.

Action of the Sodium Derivative of Guaiacol on Ethyl Chlorofumarate.

This compound is formed by adding ethyl chlorofumarate (1 mol.) to the hot solution of sodium (1 at.) in an excess of guaiacol. The dark, viscous product, when cold, is agitated with dilute sulphuric acid and ether ; the ethereal layer is then freed from the excess of guaiacol by potash, the ether evaporated, and the remaining oil distilled in a vacuum. It has a yellow colour and boils at 212—213° under 15 mm. pressure. On analysis :

0.1925 gave 0.4333 CO_2 and 0.1075 H_2O . C = 61.38 ; H = 6.20.

$C_{15}H_{18}O_6$ requires C = 61.22 ; H = 6.12 per cent.

Guaiacoloxymumaric Acid, $(CH_3O) \cdot C_6H_4 \cdot O \cdot C^{[1]}(CO_2H) : CH \cdot CO_2H$.—The potassium salt of the acid separates on boiling the ethyl ester with alcoholic potash for 2 hours. After evaporation of the alcohol, the residue is dissolved in water and the solution treated with an excess of dilute sulphuric acid, when an oil is precipitated consisting of the organic acid and guaiacol. The latter compound, which is

formed along with guaiacoloxyfumaric acid on hydrolysis of the ester, is removed by shaking the ethereal solution of the oil with sodium carbonate, adding dilute sulphuric acid to the aqueous layer, and extracting the organic acid about sixteen times with fresh quantities of ether. On distilling off the ether, a solid is left behind; this readily dissolves in boiling water and on cooling crystallises in yellowish needles, which melt at 138° with evolution of gas. On analysis:

0.2028 gave 0.4115 CO_2 and 0.0803 H_2O . $\text{C} = 55.34$; $\text{H} = 4.39$.

$\text{C}_{11}\text{H}_{10}\text{O}_6$ requires $\text{C} = 55.46$; $\text{H} = 4.20$ per cent.

Guaiacoloxyfumaric acid readily dissolves in concentrated sulphuric acid, forming a yellowish solution which, after standing for 24 hours, is poured into cold water. As no solid separates, the solution is extracted with ether, and on evaporation of the latter, a yellowish solid remains behind; this crystallises from hot water in slightly coloured needles which melt and decompose at 251° . This substance, which has not yet been further examined, is probably *o*-methoxybenzo-1:4-pyrone-carboxylic acid.

For the preparation of this compound, a method has been used similar to that which served for the formation of ethyl α -naphthoxycinnamate (Ruhemann and Beddow, *Trans.*, 1900, **77**, 989). β -Naphthol (1 mol.) is added to a solution of sodium (1 at.) in absolute alcohol, the alcohol is removed by heating the solution in a vacuum, first at 100° and finally at 180 — 190° ; ethyl chlorofumarate (1 mol.), dissolved in toluene, is then added to the dry naphtholate, when a dark brown solution is produced with development of heat. This is boiled in a flask, attached to a reflux condenser for 1 hour in order to complete the reaction, and, when cold, is agitated with dilute sulphuric acid and ether. The ethereal layer is freed from unchanged β -naphthol by shaking with potash, and, on evaporation of the ether and toluene, yields a dark oil which is fractionated under diminished pressure. Almost the whole quantity distils at 240 — 242° under 12 mm. pressure as a very viscous, fluorescent yellow oil. On analysis:

0.2145 gave 0.5398 CO_2 and 0.1130 H_2O . $\text{C} = 68.63$; $\text{H} = 5.85$.

$\text{C}_{18}\text{H}_{18}\text{O}_5$ requires $\text{C} = 68.79$; $\text{H} = 5.73$ per cent.

β -Naphthoxyfumaric acid, $\text{C}_{10}\text{H}_7\cdot\text{O}\cdot\text{C}(\text{CO}_2\text{H})\cdot\text{CH}\cdot\text{CO}_2\text{H}$, is obtained on hydrolysis of the ethyl ester by means of alcoholic potash. On mixing the reagents, a red coloration is produced, and, after a short time, the potassium salt of the acid is precipitated as a yellowish solid.

After boiling on the water-bath for 1 hour, the alcohol is distilled off, the residue dissolved in water, and the organic acid liberated by hydrochloric acid. For the removal of β -naphthol, which is formed along with β -naphthoxyfumaric acid, the precipitate is dissolved in sodium carbonate, the solution filtered and mixed with an excess of hydrochloric acid. β -Naphthoxyfumaric acid is insoluble in water, it dissolves with difficulty in ether, readily, however, in hot alcohol; but on boiling the solution for some time, decomposition takes place with liberation of β -naphthol. The acid crystallises in small, yellowish plates, which darken at about 230° and melt at 236° with evolution of gas. On analysis:

0.1773 gave 0.4223 CO_2 and 0.0613 H_2O . $\text{C} = 64.96$; $\text{H} = 3.84$.

$\text{C}_{14}\text{H}_{10}\text{O}_5$ requires $\text{C} = 65.11$; $\text{H} = 3.87$ per cent.

I am at present engaged in the study of the action of concentrated sulphuric acid on β -naphthoxyfumaric acid with the view of condensing it to β -naphtha-1:4-pyronecarboxylic acid, and hope to publish the result shortly.

Action of Ethyl Chlorofumarate on α -Naphthol.

This reaction is of especial interest since, as mentioned in the introduction, α -naphthol differs from the other phenols in its behaviour towards the ethyl ester, inasmuch as it yields two substances which belong to a new class of cyclic compounds. The reaction is carried out in a manner similar to that employed in the preparation of ethyl β -naphthoxyfumarate; namely, by adding α -naphthol (1 mol.) to an alcoholic solution of sodium (1 at.), removing the alcohol by distillation in a vacuum, finally at 190° , and mixing the dry naphtholate with ethyl chlorofumarate (1 mol.) dissolved in toluene. The action takes place with development of heat and is completed by boiling in a flask attached to a reflux condenser for 1—2 hours. The contents of the vessel consist of a yellowish, crystalline substance and a brown liquid; these are agitated with dilute sulphuric acid, and the crystals are collected and washed with ether. The solid represents the bisnaphtharonyl, $\text{C}_{24}\text{H}_{12}\text{O}_4$, referred to in the introduction, whilst the dark filtrate contains ethyl naphtharonylacetate, $\text{C}_{16}\text{H}_{12}\text{O}_4$, and ethyl α -naphthoxyfumarate.

Bisnaphtharonyl is almost insoluble in all the ordinary solvents, hot alcohol only dissolving traces and yielding a yellowish, fluorescent solution. It dissolves readily, however, in boiling nitrobenzene, forming a dark red solution with a deep green fluorescence, from which, on cooling, it separates in orange needles. These are freed from the adhering solvent by washing with hot alcohol; they do not melt at 335° . On analysis:

0.1787 gave 0.5171 CO_2 and 0.0548 H_2O . $\text{C} = 78.92$; $\text{H} = 3.40$.

0.1760 „ 0.5100 CO_2 „ 0.0525 H_2O . $\text{C} = 79.02$; $\text{H} = 3.31$.

$\text{C}_{24}\text{H}_{12}\text{O}_4$ requires $\text{C} = 79.11$; $\text{H} = 3.30$ per cent.

Bisnaphtharonyl is insoluble in cold alkali, but dissolves when boiled with concentrated aqueous potash for 2 hours in a flask provided with a reflux condenser, forming a red solution. On adding hydrochloric acid, a yellowish solid is precipitated, which is insoluble in alcohol or acetic acid, but dissolves in nitrobenzene. From this solution, orange needles separate, which are no longer dissolved by cold potash. The properties of this compound point to its identity with bisnaphtharonyl, and this conclusion is supported by the following analysis:

0.1863 gave 0.5391 CO_2 and 0.0590 H_2O . $\text{C} = 78.91$; $\text{H} = 3.51$.

$\text{C}_{24}\text{H}_{12}\text{O}_4$ requires $\text{C} = 79.11$; $\text{H} = 3.30$ per cent.

This experiment proves that one or both rings, containing oxygen, in bisnaphtharonyl, open up by the action of potassium hydroxide, but under the influence of an acid close again to form the original compound. This may be symbolised as follows:

In the hope of effecting a deep-seated decomposition of bisnaphtharonyl which would supply further evidence for its constitution, I have subjected the compound to the action of fused potash, but found that complete carbonisation takes place.

On adding concentrated sulphuric acid to the substance, it becomes purple and then dissolves very slowly at the ordinary temperature, but rapidly on slightly warming, to yield a red solution. This, when poured into water, gives a yellowish solid which is soluble in water with great ease. Most probably there is thus formed a sulphonic acid of bisnaphtharonyl; this view seems to be supported by the behaviour of nitric acid towards bisnaphtharonyl.

Tetranitrobisnaphtharonyl, $\text{C}_{24}\text{H}_8(\text{NO}_2)_4\text{O}_4$.—Bisnaphtharonyl dissolves in fuming nitric acid on warming slightly, and the red solution gives, with water, a yellowish solid. This is insoluble in the ordinary solvents, but dissolves in hot nitrobenzene, and on cooling crystallises in minute, yellowish-brown prisms, which are freed from the adhering

solvent by washing with hot alcohol. The compound does not melt at 325°. On analysis :

0.2590 gave 22.8 c.c. moist nitrogen at 19° and 778 mm. $N = 10.36$.

$C_{24}H_{18}O_{12}N_4$ requires $N = 10.29$ per cent.

The dark mother liquor from bisnaphtharonyl, after being diluted with ether, is agitated with an excess of potash in order to free it from unchanged α -naphthol. The ethereal layer, which has a deep green fluorescence, is then dried with calcium chloride, the ether evaporated, and the last traces of toluene removed by heating in a vacuum on the water-bath. The dark oil which remains behind partly solidifies on standing. This product is dissolved in hot alcohol, and the solution, on cooling, deposits long, yellowish needles which, after recrystallisation from the same solvent, melt at 146—147°. The substance is ethyl naphtharonylacetate. On analysis :

0.1992 gave 0.5225 CO_2 and 0.0805 H_2O . $C = 71.54$; $H = 4.49$.

$C_{16}H_{12}O_4$ requires $C = 71.64$; $H = 4.48$ per cent.

Ethyl naphtharonylacetate may be distilled in a vacuum, when it passes over as a yellowish oil which quickly solidifies ; it is sparingly soluble in cold alcohol or acetic acid, but readily so on boiling. The hydrolysis of the ethyl ester is still under examination, but the results of a few experiments undertaken in that direction may be recorded here. On using alcoholic potash, a deep purple coloration of the solution takes place, and the alkaline liquor, after removal of the alcohol by distillation and solution of the residue in water, yields a brown, gelatinous precipitate on treatment with hydrochloric acid. This is insoluble in water, but dissolves in alcohol with the greatest ease and separates from the solution in an amorphous state. If aqueous, instead of alcoholic, potash is used for the hydrolysis, the ethyl ester dissolves on boiling for 2 hours. On adding hydrochloric acid to the reddish solution, a yellow precipitate is formed ; this is a mixture of two or more acids which have not yet been separated.

ester reacts with alcoholic ammonia on remaining in contact with it at the ordinary temperature for some time. The needles of

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the ester gradually disappear, being transformed into a yellowish, crystalline product, whilst the solution turns pink. After 2 days, the precipitate is collected, washed with water, and then with alcohol. It is insoluble in either of these solvents, but dissolves in glacial acetic acid and crystallises from this solution in groups of yellowish needles which blacken at 258° and melt to a dark liquid at 265° . On analysis:

0.2395 gave 12 c.c. moist nitrogen at 14° and 749 mm. $N = 5.88$.

$C_{14}H_9O_3N$ requires $N = 5.85$ per cent.

The dark alcoholic mother liquor from ethyl naphtharonylacetate, on concentration, yields a further crop of crystals of the same ester; finally, an oil remains which is fractionated under diminished pressure. The greater part distils at $246-248^{\circ}$ under 16 mm. pressure as a viscous, yellow oil. This is ethyl naphthoxyfumarate. On analysis:

0.1995 gave 0.5025 CO_2 and 0.1090 H_2O . $C = 68.68$; $H = 6.07$.

$C_{18}H_{18}O_5$ requires $C = 68.79$; $H = 5.73$ per cent.

In conclusion, it may be mentioned that the action of ethyl chlorofumarate on α -naphthol takes place, also, at the ordinary temperature on adding to the dry sodium derivative of α -naphthol a solution of the ethyl ester in absolute ether; heat is developed, the mixture turns red, and deposits a solid. After standing for several days in a flask provided with a drying tube, the product is treated as in the former case in order to separate the above-mentioned compounds.

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