6: 7-BENZOCOUMARANONE

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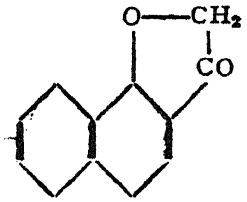
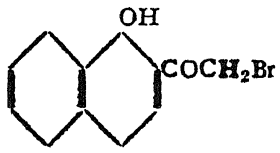
In the course of a study of the action of alkaline condensing agents on ethyl 2-acetyl-1-naphthyl carbonate,[1] it appeared that a possible product was 6: 7-benzocoumaranone (I), and the substance had to be prepared for a direct comparison. It was first described by Ullmann,[2] who prepared it by the cyclization of 2-bromacetyl-1-naphthol (II) and recorded the m.p. 91–92°.

Fries,[4] quoting van Paul Lanz,[3] has stated that a benzocoumaranone constituted as (I) and melting at 116°, is obtained by the intramolecular acylation of α-naphthoxyacetyl chloride (III); the m.p. was slightly higher (119°), when the corresponding bromide was used. Ingham, Stephen and

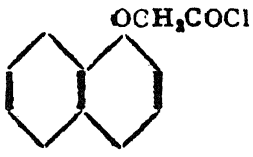


(I)

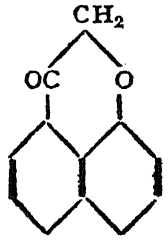


(II)

Timpe,[5] who have not referred to the work of Fries and Lanz, carried out the intramolecular acylation of α-naphthoxyacetyl chloride (III) with aluminium chloride in benzene, and obtained a product, m.p. 119°, which they



(III)



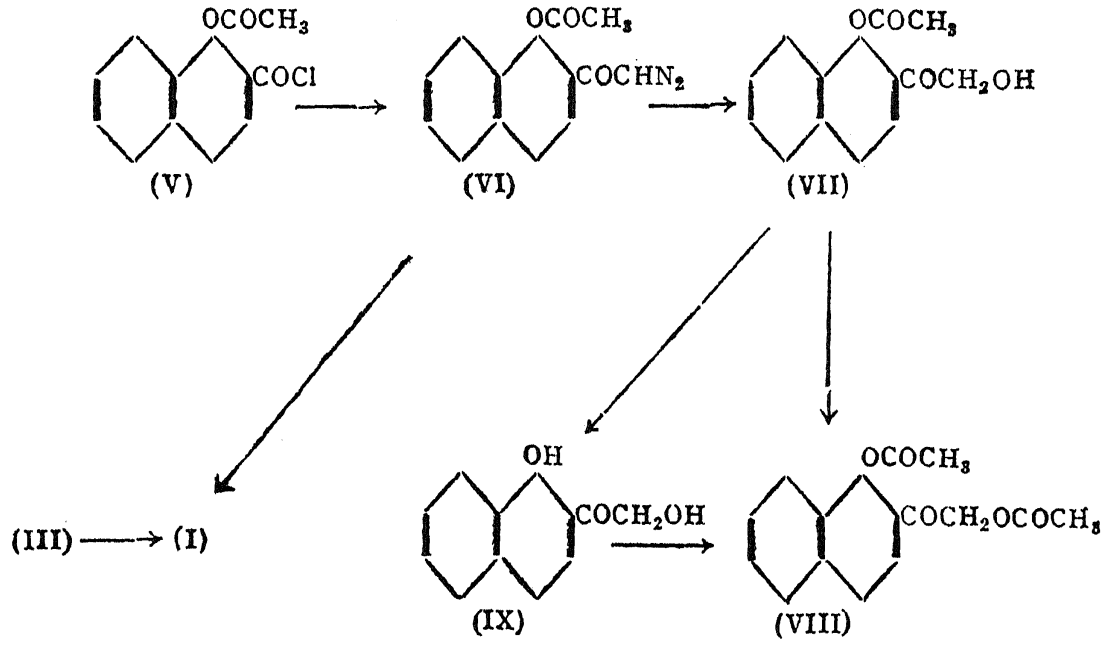
(IV)

considered to be the *peri*naphthopyrone (IV), rather than the coumaranone (I), since it condensed with benzaldehyde to form the benzylidene derivative, which could not be converted through its dibromide into the corresponding flavonol. Another argument advanced in favour of (IV) was the non-identity of its melting point with that of 6: 7-benzocoumaranone (I), reported

to have been synthesised by Ullmann[2] by an unambiguous method from 2-bromacetyl-1-naphthol (II) in which the 1:2-position is already fixed. Several similar instances of *peri*-ring closure are known such as the condensation of α-naphthylacetyl chloride to give acenaphthenone, and the formation of benzanthrone from α-benzoylnaphthalene in presence of aluminium chloride.

Reviewing Ullmann's work[2] on the ω-bromination of 2-acetyl-1-naphthol, it was found that conflicting results have been recorded for this bromination. Ullmann obtained 2-bromacetyl-1-naphthol (II) (m.p. 124·5°) by brominating acetonaphthol or its acetyl derivative in carbon tetrachloride solution, while Torrey and Brewster[6] obtained 4-bromo-2-acetyl-1-naphthol, m.p. 127°, under the same conditions. Fries[7] also failed to get (II), and it has now been found that even bromination with N-bromosuccinimide, which normally leads to ω-bromination, yields 4-bromo-2-acetyl-1-naphthol. Bromination in acetic acid with two molecules of bromine gave a quantitative yield of the ω-4-dibromo derivative.

6:7-Benzocoumaranone (I) has now been synthesised by an unambiguous route starting from 1-hydroxy-2-naphthoic acid, through the intermediate diazoketone, by the following scheme.



The acid chloride (V) of the acetate of 1-hydroxy-2-naphthoic acid, on treatment with an etheral solution of diazomethane gave the diazoketone (VI). This on treatment with dilute sulphuric acid in dioxane gave the carbinol (VII), which on acetylation gave the corresponding acetate (VIII). Eistert[8] has shown that the corresponding diazoketone from 2-hydroxy-3-naphthoic acid gives the benzocoumaranone on treatment with alcohol and

dilute sulphuric acid, but the diazoketone (VI) when treated under similar conditions gave the carbinol (VII). Eistert[8] further found that the corresponding carbinol from 2-hydroxy-3-naphthoic acid, on longer treatment with alcohol and sulphuric acid, also gave the benzocoumaranone. It was found, however, that the carbinol (VII) under similar conditions gave merely the deacetylated compound (IX), which was also obtained by treatment of the carbinol (VII) with sodium hydroxide. This gave the same diacetate (VIII) as that obtained from the carbinol (VII). However, the diazoketone (VI) on treatment with concentrated sulphuric acid in the cold gave a compound, m.p. 119°, which from its properties and those of its derivatives proved to be 6:7-benzocoumaranone (I). The carbinol (VII) or (IX) did not give the 6:7-benzocoumaranone under the same conditions. As the 6:7-benzocoumaranone had the same melting point and properties as those described by Ingham[5] *et al.* for their product, obtained by the intramolecular acylation of α-naphthoxyacetyl chloride, it was considered desirable to repeat their work.

The acid chloride, prepared by the action of phosphorus pentachloride on α-naphthoxyacetic acid, gave on treatment with aluminium chloride in benzene a substance, m.p. 119°, identical in all respects with 6:7-benzocoumaranone. Thus cyclization of α-naphthoxyacetyl chloride takes place in the 2-position and not in the *peri* position.

Experimental

1-Acetoxy-2-naphthyl diazomethyl ketone (VI).—1-Acetoxy-2-naphthoic acid, obtained by refluxing 1-hydroxy-2-naphthoic acid with four parts of 1:1-mixture of acetic acid and acetic anhydride for three hours, crystallised from benzene in colourless needles, m.p. 156°. The acetate was unstable to long keeping, and to the action of hot water or even hot alcohol. The acid chloride, m.p. 114°, was obtained by treatment with thionyl chloride in petroleum ether (60–80).

The finely powdered acid chloride (5 g.), dissolved in ether (100 c.c.), was added dropwise in the course of one hour to an agitated, ice-cold solution of diazomethane in ether, prepared from nitrosomethylurea (12 g.), 40% potassium hydroxide (30 c.c.) and ether (100 c.c.), and kept in the refrigerator for 24 hours. The diazoketone which separated as a light yellow crystalline precipitate was filtered (3 g.) and the filtrate on concentration gave more of the diazoketone. The substance crystallised from benzene in small shining plates (3·2 g.), m.p. 131° (decomp.) (Found: N, 11·2. $C_{14}H_{10}O_3N_2$ requires N, 11·0%.) It decomposes on long standing. It

dissolves in concentrated sulphuric acid with decomposition giving a deep orange solution, with a bright green fluorescence.

1-*Acetoxy*-2-*naphthoylcarbinol* (*VII*).—To a solution of the diazoketone (VI) (0·5g.) in dioxane (10 c.c.), 2N sulphuric acid (2 c.c.) was added with shaking, and the solution allowed to stand at room temperature for two hours. The diazoketone slowly gave off nitrogen, and the solution became slightly deeper in colour. On dilution with water, the crystalline precipitate was collected and crystallised from alcohol. The shining yellow flat plates (0·35 g.) had m.p. 121°. (Found: C, 69·1; H, 4·9. $C_{14}H_{12}O_4$ requires C, 68·8; H, 4·9%.) The substance gives a deep green colour with ferric chloride, and an orange solution in concentrated sulphuric acid, and dissolves in cold 1% caustic soda solution from which it can be reprecipitated unchanged. Because of its ferric chloride colouration and its solubility in ice-cold aqueous caustic soda, the possibility of the carbinol (VII) being 1-hydroxy-2-naphthoylacetyl carbinol cannot be ruled out. The product is being studied further to finally decide the position of the acetyl group.

The *diacetate*, prepared by refluxing (VII) with acetic anhydride and pyridine crystallised from alcohol in long colourless needles, m.p. 119°. (Found: C, 67·4; H, 5·1. $C_{16}H_{14}O_5$ requires C, 67·12; H, 4·9%).

The method used by Eistert[8] for converting a diazoketone of the type of (VI) to the coumaranone was then studied, and instead of the coumaranone (I), the carbinol (VII) was obtained. The diazoketone (0·2 g.) was suspended in alcohol (2 c.c.), 2N sulphuric acid (0·2 c.c.) added, and the mixture warmed on the water-bath, when a brisk evolution of nitrogen took place. When nitrogen was no longer evolved, the solution was heated on the water-bath for about 5 minutes (Norit), filtered and cooled, when light brown crystals separated (0·1 g.). The product crystallised from alcohol in light yellow plates, m.p. 121°, identical with (VII).

1-*Hydroxy*-2-*naphthoylcarbinol* (*IX*).—To a solution of (VII) (0·1 g.) in alcohol (2 c.c.), four drops of concentrated sulphuric acid were added and the solution refluxed on the water-bath for 30 minutes (Norit), filtered and cooled. The yellow crystalline mass, which separated, crystallised from alcohol or benzene in small yellow plates, m.p. 151°, with darkening in colour. (Found: C, 71·3; H, 5·2. $C_{12}H_{10}O_3$ requires C, 71·3; H, 4·9%.) The substance was also obtained by warming a dilute alkaline solution of the acetylated carbinol on the water-bath for 2 minutes, and acidifying. It gives a green colour with ferric chloride and an orange solution in concentrated sulphuric acid.

Acetylation gave the same *diacetate* (VIII) described earlier.

6 : 7-*Benzocoumaranone* (*I*)

(A) The diazoketone (VI) (0·2 g.) was added slowly with stirring to ice-cold concentrated sulphuric acid (2 c.c.); nitrogen was evolved and the substance slowly went into solution. The brownish orange solution, which had a strong green fluorescence, was kept in the refrigerator for one hour, poured over crushed ice, and ether extracted. The ether extract was washed with ice-cold sodium hydroxide solution, which removed a trace of a colouring matter. The ether layer was washed and dried, and on removal of the ether the residue crystallised from dilute alcohol in shining colourless plates, m.p. 119° (Ullmann, 91–2°; Lanz, 116°; Fries and Ingham, *et al.*, 119°). (Found: C, 78·1; H, 4·5. $C_{12}H_8O_2$ requires C, 78·3; H, 4·3%.) The substance does not give a colour with ferric chloride, and is not soluble in cold aqueous sodium hydroxide; but when slightly warmed it goes into solution with a deep red colour; deep reddish violet flakes then separate (*cf.* Ullmann[2]). It reduces Fehling's solution, and the brownish orange solution in concentrated sulphuric acid shows a bright green fluorescence. The *acetate* prepared by refluxing with acetic anhydride and pyridine, crystallised from alcohol in light brown needles, m.p. 88 (Ingham and co-workers, 85). (Found: C, 74·7; H, 4·7. $C_{14}H_{10}O_3$ requires C, 74·3; H, 4·4%.)

(B) α-Naphthoxyacetic acid was prepared by condensing chloracetic acid and α-naphthol in alkaline solution. The acid chloride, obtained by treatment of the acid (5 g.) with phosphorus pentachloride (5 g.) in benzene, followed by removal of the benzene and phosphorus oxychloride under vacuum on the water-bath, was taken up in benzene (25 c.c.). Aluminium chloride (4 g.) was then slowly added, when the colour of the solution changed from brownish red to green. After heating on the water-bath for 6 hours, the solution which had now become coppery red was poured into ice and hydrochloric acid, and steam-distilled. The white crystalline mass that separated in the distillate was taken up in ether, and the ether removed. The residue (1·2 g.) crystallised from dilute alcohol in colourless shining plates, m.p. 119°, not depressed by admixture with 6 : 7-benzocoumaranone prepared earlier. The residue in the distillation flask was a deep red resinous mass and could not be crystallised.

Summary

6- 7-Benzocoumaranone was first described by Ullmann who prepared it by the cyclization of 2-bromacetyl-1-naphthol and recorded the m.p. 91–2°. Fries prepared it later by the intramolecular acylation of α-naphthoxyacetyl bromide and recorded the m.p. 119°. A compound of the same m.p. prepared similarly from α-naphthoxyacetyl chloride has been considered by

Ingham *et al.*, to be *peri*naphthapyrone. 6:7-Benzocoumaranone, m.p. 119,° has now been synthesised by an unambiguous route, starting from 1-hydroxy-2-naphthoic acid through the intermediate diazoketone, and it has been shown that the product obtained by Ingham *et al.* was 6:7-benzocoumaranone.

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References

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