13. 3 : 4-*Benzoxanthens. Part I. The Synthesis and Oxidation of 3 : 4-Benzoxanthen.*

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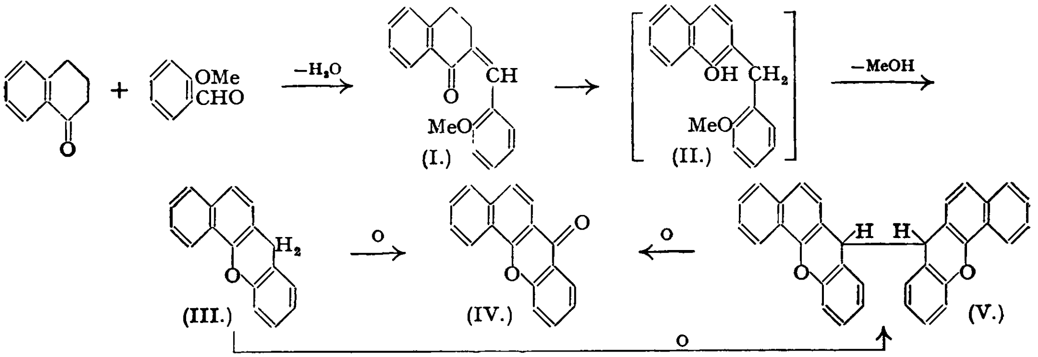
Condensation of *o*-methoxybenzaldehyde with 1-tetralone gives 2-*o*-methoxybenzylidene-1-tetralone. When this is heated with fused potassium hydrogen sulphate–sodium sulphate, there is obtained a mixture of 3 : 4-benzoxanthen and a by-product, most probably 9 : 9′-di-3 : 4-benzoxanthyl. Both compounds are easily oxidised to 3 : 4-benzoxanthone. Careful oxidation of 3 : 4-benzoxanthen gives 9 : 9′-di-3 : 4-benzoxanthyl.

In an attempt to prepare 8-methoxy-3 : 4-benzofluorene by the cyclisation of 2-*o*-methoxybenzylidene-1-tetralone (I) with phosphoric oxide in xylene (cf. Rapson and Shuttleworth, *J.*, 1940, 638), a very poor yield of a colourless substance, m. p. 90—91°, was obtained. The yield was greatly increased when the cyclisation was effected by fused potassium hydrogen sulphate–sodium sulphate at 260—270° (cf. Baddar and Gindy, *Nature*, 1946, **157**, 409), or better at 230—240° (cf. Gindy, *ibid.*, 1949, **164**, 577). The product was shown to be 3 : 4-benzoxanthen (III), as it gave 3 : 4-benzoxanthone (IV) on oxidation. The cyclisation of (I) to (III) is believed to proceed through the intermediate formation of (II).

Together with 3 : 4-benzoxanthen a by-product, m. p. 230—231°, was obtained which is believed to be 9 : 9′-di-3 : 4-benzoxanthyl (V), resulting from the oxidation of 3 : 4-benzoxanthen by potassium pyrosulphate (formed by the strong heating of potassium hydrogen sulphate). This view is supported by the following facts: (*a*) when a benzene solution of 3 : 4-benzoxanthen and *p*-benzoquinone is exposed to sunlight in a carbon dioxide atmosphere, the same product, m. p. 230—231°, was obtained, (*b*) when 3 : 4-benzoxanthen was heated with potassium hydrogen sulphate–sodium sulphate at 260—270° for ½ hour, it was partly converted into 3 : 4-benzoxanthone, 9 : 9′-di-3 : 4-benzoxanthyl, and a thermochromic substance melting above 317°, and (*c*) when the product, m. p. 230—231°, was oxidised with atmospheric oxygen in sunlight it gave 3 : 4-benzoxanthone.

The attempted synthesis of 9 : 9′-di-3 : 4-benzoxanthyl (V) through an Ullmann condensation of 9-bromo-3 : 4-benzoxanthen failed, as attempts to prepare this bromo-compound by the action of dry hydrogen bromide on 3 : 4-benzoxanthhydrol (cf. Gomberg and Cone, *Annalen*, 1910, **376**, 192) resulted in the isolation of 3 : 4-benzoxanthone.



Experimental.

(M.p.s are not corrected. Microanalyses are by Drs. Weiler and Strauss, Oxford.)

2-o-*Methoxybenzylidene*-1-*tetralone* (I).—A mixture of freshly distilled *o*-methoxybenzaldehyde (13·6 g., 1 mol.) and 1-tetralone (14·6 g., 1 mol.) was treated with 4% alcoholic potassium hydroxide (100 c.c.), and the mixture was left overnight, neutralised with acetic acid, and diluted with water until the solution became turbid. The precipitated product was filtered off, washed thoroughly with cold alcohol, and dried. It had m. p. 107—108° (yield, 25 g., 95%). On crystallisation from alcohol 2-o-*methoxybenzylidene*-1-*tetralone* was obtained in light-yellow crystals, m. p. 110—111° (Found: C, 81·6; H, 6·1. $C_{18}H_{16}O_2$ requires C, 81·1; H, 6·1%). It was soluble in concentrated sulphuric acid giving an orange-red solution.

3 : 4-*Benzoxanthen* (III).—A well powdered mixture of potassium hydrogen sulphate (60 g.) and sodium sulphate (15 g.) was melted and thoroughly stirred. 2-*o*-Methoxybenzylidene-1-tetralone (20 g.) was then added in one lot, and the mixture heated at 230—240° for ¾ hour, and, after cooling, extracted with hot water, and the product was filtered off, dried, and then extracted with benzene. The benzene extract on being kept deposited a by-product, m. p. 210—225°, which was removed. Evaporation of the solvent left a tarry, dark residue, which was purified by repeated vacuum-distillation (b. p. 210°/3 mm.). It was crystallised from alcohol giving 3 : 4-*benzoxanthen* (7·1 g., 40%), m. p. 90—91° [Found: C, 88·4; H, 5·3%; *M* (Rast), 236. $C_{17}H_{12}O$ requires C, 87·9; H, 5·2%; *M*, 232]. It was soluble in hot alcohol and most organic solvents. The *picrate*, prepared in alcohol, formed red needles, m. p. 125—126°, from alcohol (Found: C, 59·8; H, 3·4; N, 9·1. $C_{17}H_{12}O,C_6H_3O_7N_3$ requires C, 59·9; H, 3·3; N, 9·1%). It was soluble in alcohol and acetone, difficulty soluble in benzene; it decomposed when heated with light petroleum.

A poorer yield of benzoxanthen was obtained when the reaction was carried out at 260—270°; efficient stirring was essential. Attempted cyclisation of 2-*o*-methoxybenzylidene-1-tetralone by means of phosphoric oxide in xylene (cf. Rapson and Shuttleworth, *loc. cit.*) gave a very poor yield of 3 : 4-benzoxanthen.

The by-product, m. p. 210—225°, was purified by repeated crystallisation from chloroform–ethyl alcohol giving 9 : 9′-*di*-3 : 4-*benzoxanthyl* (V) in needles, m. p. 230—231° [Found: C, 88·7; H, 5·1%; *M* (Rast), 404. $C_{34}H_{22}O_2$ requires C, 88·3; H, 4·8%; *M*, 462.]

Oxidation of 3 : 4-*Benzoxanthen to* 3 : 4-*Benzoxanthone.*—In all cases the product was crystallised from methyl alcohol or dilute acetone, and identified by m. p. and mixed m. p. with an authentic specimen prepared as described by Knapp (*J. pr. Chem.*, 1936, **146**, 116).

(*a*) *With potassium permanganate.* To a warm (40—50°) solution of 3 : 4-benzoxanthen (2 g.) in acetone (50 c.c.) and water (20 c.c.), powdered potassium permanganate (2·8 g.) was added portionwise at such a rate that the temperature did not exceed 50°. The manganese dioxide was removed by sulphur dioxide, and the acetone evaporated. The precipitate was filtered off and crystallised, giving 3 : 4-benzoxanthone (*ca.* 1·6 g.) in needles, m. p. 160—161° [Found: C, 82·9; H, 4·2%; *M* (Rast), 250. Calc. for $C_{17}H_{10}O_2$: C, 82·9; H, 4·1%; *M*, 246].

(*b*) *With selenium dioxide.* A mixture of 3 : 4-benzoxanthen (2 g.), selenium dioxide (4 g.), and water (4 c.c.) was heated in a sealed tube at 230—240° for 4 hours. The contents of the tube were filtered and the product was purified as stated above, and proved to be 3 : 4-benzoxanthone (1·9 g.).

(*c*) *With atmospheric oxygen.* A solution of 3 : 4-benzoxanthen (0·2 g.) in dry thiophen-free benzene (15 c.c.) or chloroform (15 c.c.) was exposed in a Pyrex tube to sunlight for 3—5 days (September). Evaporation of the solvent left a product which was identified as 3 : 4-benzoxanthone.

(*d*) *With* p-*benzoquinone.* A solution of 3 : 4-benzoxanthen (0·2 g.) and *p*-benzoquinone (0·2 g.) in benzene was exposed to sunlight for a few hours. The precipitated quinhydrone was filtered off, and the filtrate evaporated to dryness. The residue was repeatedly crystallised from dilute acetone to give 3 : 4-benzoxanthone.

Oxidation of 3 : 4-benzoxanthen to 3 : 4-benzoxanthone could also be effected by means of alkaline ferricyanide at 80—90° or potassium dichromate in cold or boiling acetic acid. Hydrogen peroxide, however, failed to effect this oxidation.

Oxidation of 3 : 4-*Benzoxanthen to* 9 : 9′-*Di*-3 : 4-*benzoxanthyl.*—3 : 4-Benzoxanthen (0·4 g.), *p*-benzoquinone (0·08 g.), and dry thiophen-free benzene (5 c.c.) were sealed in a Pyrex tube filled with carbon dioxide, and exposed to sunlight for 3 hours. The precipitated quinhydrone was filtered off and washed with warm chloroform. The combined solutions were washed with dilute alkali, and the solvent removed under reduced pressure. The residue was crystallised from chloroform–methyl alcohol to give a product, m. p. 175—200° (*ca.* 0·05 g.). On repeated crystallisation from chloroform–methyl alcohol, 9 : 9′-di-3 : 4-benzoxanthyl was obtained and identified by m. p. and mixed m. p.

The mother-liquor was found to contain unchanged 3 : 4-benzoxanthen.

Fusion of 3 : 4-*Benzoxanthen with Potassium Hydrogen Sulphate and Sodium Sulphate.*—3 : 4-Benzoxanthen (2 g.) was heated with potassium hydrogen sulphate (20 g.)-sodium sulphate (5 g.) at 260—270° for ½ hour with efficient stirring. The product was extracted as stated in the second experiment, and the benzene solution was concentrated and set aside overnight. A small amount of an amorphous substance, m. p. 210—220°, was deposited; this was crystallised from chloroform–methyl alcohol and proved to be 9 : 9′-di-3 : 4-benzoxanthyl by m. p. and mixed m. p.

A second thermochromic fraction (0·2 g.) was precipitated when the benzene mother-liquor was concentrated and set aside; it had m. p. 254—260°, raised to above 317° on recrystallisation from chloroform–alcohol. Its toluene solution acquired a green coloration on being heated, This material is under investigation.

Unchanged 3 : 4-benzoxanthen and 3 : 4-benzoxanthone were identified in the residual solid obtained by evaporation of the benzene.

Action of Hydrogen Bromide on 3 : 4-*Benzoxanthhydrol.*—Dry hydrogen bromide was bubbled into a suspension of 3 : 4-benzoxanthhydrol (Werner, *Ber.*, 1901, **34**, 3303) in glacial acetic acid. The saturated solution was set aside for 3 hours and then filtered from a small amount of a red compound. The product was precipitated with water and extracted with benzene. The benzene was evaporated and the residue crystallised from light petroleum (b. p. 60—80°) to give a crystalline product which was proved to be 3 : 4-benzoxanthone by m. p. and mixed m. p.

Oxidation of 9 : 9′-*Di*-3 : 4-*benzoxanthyl with Atmospheric Oxygen.*—A solution of 9 : 9′-di-3 : 4-benzoxanthyl (0·05 g.) in chloroform (5 c.c.) was exposed to sunlight for 3 days (September). The solvent was evaporated and the product was crystallised from methyl alcohol to give 3 : 4-benzoxanthone, identified by m. p. and mixed m. p.

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