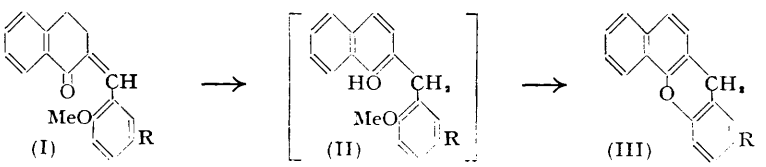
183. 3 : 4-*Benzoxanthens. Part III.* The Synthesis and Oxidation of* 5-, 6-, 7-, *and* 8-*Methyl*-3 : 4-*benzoxanthen.*

By MUNIR GINDY and IBRAHIM M. DWIDAR.

Methyl-3 : 4-benzoxanthens are prepared by heating 2-(2-methoxy-*x*-methylbenzylidene)-1-tetralone with fused potassium hydrogen sulphate and sodium sulphate. Their structures are elucidated by oxidation to the known methyl-3 : 4-benzoxanthones (Part II).

BADDAR and GINDY (*J.*, 1951, 64; *Nature*, 1946, **157**, 409) and Gindy (*Nature*, 1949, **164**, 577), who prepared 3 : 4-benzoxanthen by the cyclisation of 2-*o*-methoxybenzylidene-1-tetralone (I; R = H) with potassium hydrogen sulphate and sodium sulphate at an elevated temperature, considered that the phenol (II; R = H) was an intermediate. Attempts to cyclise 2-*o*-methoxybenzylidene- or 2 : 6-di-*o*-methoxybenzylidene-*cyclo*-hexanone similarly gave resins that proved to be free from the benzoxanthen; this pointed



to the necessity for a double bond between $C_{(5)}$ and $C_{(6)}$ in the alicyclic ketonic ring in (I), as is essential if the intermediate (as II) is to be aromatic.

1-Tetralone and 2-methoxy-5-methylbenzaldehyde in 4% alcoholic potassium hydroxide gave 2-(2-methoxy-5-methylbenzylidene)-1-tetralone (I; R = Me), which with

* Part II, *J.*, 1951, 1933.

potassium hydrogen sulphate and sodium sulphate at 260—265° gave 7-methyl-3 : 4-benzoxanthen (III; R = Me). The benzoxanthen was readily oxidised by various oxidising agents (cf. Baddar and Gindy, *J.*, 1951, 64) to the known 7-methyl-3 : 4-benzoxanthone (Gindy and Dwidar, *J.*, 1951, 1933). However, attempted oxidation of the methyl group to a carboxyl group by the usual reagents failed. Similarly, when bromine was added in carbon tetrachloride, a red crystalline (oxonium) compound was precipitated (cf. Collie and Tickle, *J.*, 1899, **75**, 710; Kendall, *J. Amer. Chem. Soc.*, 1914, **36**, 1222) which dissolved slowly when the mixture was boiled in sunlight to give a monobromo-7-methyl-3 : 4-benzoxanthone.

5- and 6-Methyl-3 : 4-benzoxanthen were prepared similarly and their structures were proved by oxidation to the known ketones. The 8-methyl compound was also prepared.

Experimental

Microanalyses are by Drs. Weiler and Strauss, Oxford.

2-o-*Methoxybenzylidene- and* 2 : 6-*Di*-o-*methoxybenzylidene*-cyclo*hexanone*.—A suspension of *o*-methoxybenzaldehyde (5·0 g.) and *cyclo*hexanone (3·6 g.) in 4% aqueous potassium hydroxide (40 c.c.) was refluxed for 3 hours, left overnight, and then neutralised with acetic acid. The solid product, isolated by means of ether and distilled, gave: (1) a fraction, b. p. 165—168°/1 mm., which crystallised from methyl alcohol to light yellow tetrahedral crystals of 2-o-*methoxybenzylidene*cyclo*hexanone*, m. p. 80—81° (4·2 g., 51%) (Found: C, 77·6; H, 7·3; OMe, 14·1. $C_{14}H_{16}O_2$ requires C, 77·8; H, 7·4; OMe, 14·4%), giving a blood-red colour with concentrated sulphuric acid; (2) a fraction, b. p. 240—250°/1 mm., which crystallised from methyl alcohol to yellow needles of 2 : 6-*di*-o-*methoxybenzylidene*cyclo*hexanone*, m. p. 143° (1·1 g., 9%) (Found: C, 78·7; H, 6·7; OMe, 18·5. $C_{22}H_{22}O_3$ requires C, 79·0; H, 6·6; OMe, 18·6%).

2 - (2′ - *Methoxy* - 3′ - *methylbenzylidene*) - 1 - *tetralone*. — 2 - Methoxy - 3 - methylbenzaldehyde (Simonsen, *J.*, 1918, **113**, 777) (6·5 g., 1 mol.) and 1-tetralone (6·5 g., 1 mol.) were dissolved together in 4% alcoholic potassium hydroxide (20 c.c.). The solution acquired a dark blue colour and became hot. On being left overnight it deposited crystals. Acetic acid was added dropwise to neutralise the alkali, followed by a few drops of water to turbidity. The solution was cooled and the product was collected. Recrystallisation from methyl alcohol gave 2-(2′-*methoxy*-3′-*methylbenzylidene*)-1-*tetralone*, m. p. 85—86° (90%) (Found: C, 81·7; H, 6·6; OMe, 9·8. $C_{19}H_{18}O_2$ requires C, 82·0; H, 6·5; OMe, 11·2%).

2-(2-*Methoxy*-4-*methylbenzylidene*)-1-*tetralone*, prepared from 2-methoxy-4-methylbenzaldehyde (Perkin and Weizmann, *J.*, 1906, **89**, 1652) and 1-tetralone, had m. p. 105—106° (yield, 90%) (from methyl alcohol) (Found: C, 81·7; H, 6·4; OMe, 10·5%).

2-(2-*Methoxy*-5-*methylbenzylidene*)-1-*tetralone* (I; R = Me), obtained from 2-methoxy-5-methylbenzaldehyde (Auwers, *Annalen*, 1915, **408**, 241; Schotten, *Ber.*, 1878, **11**, 784) and 1-tetralone, had m. p. 95—96° (from methyl alcohol) (yield, 91%) (Found: C, 81·4; H, 6·6; OMe, 11·1%).

2-(2-*Methoxy*-6-*methylbenzylidene*)-1-*tetralone*, prepared from 2-methoxy-6-tolualdehyde (Chuit and Bolsing, *Bull. Soc. chim.*, 1906, **35**, 142) and 1-tetralone, had m. p. 75° (from methyl alcohol) (yield, 58%) (Found: C, 81·9; H, 6·4; OMe, 11·1%).

7-*Methyl*-3 : 4-*benzoxanthen* (III; R = Me).—2-(2-Methoxy-5-methylbenzylidene)-1-tetralone (6 g., 1 mol.) was added to a molten mixture of potassium hydrogen sulphate (13·5 g.) and anhydrous sodium sulphate (3·4 g.) heated in a boiling ethyl cinnamate bath. The mixture was thoroughly stirred at this temperature for 1 hr., after which it was poured into water (50 c.c.). The organic material was extracted with ether and worked up as usual. The ethereal extract slowly deposited a light brown amorphous product (0·3 g.) which crystallised from benzene as colourless needles, m. p. 230°. It was oxidised with potassium permanganate in boiling acetic acid to 7-methyl-3 : 4-benzoxanthone, and was, most probably, the dimer thereof (cf., Baddar and Gindy, *J.*, 1951, 64). The ether was evaporated off and the residual oil distilled (b. p. 230—235°/5 mm.). The distillate crystallised from methyl alcohol as colourless crystals of 7-*methyl*-3 : 4-*benzoxanthen*, m. p. 97—98° (50%) [Found: C, 87·6; H, 5·5%; *M* (Rast), 247. $C_{18}H_{14}O$ requires, C, 87·8; H, 5·7%; *M*, 246]. It gave with pure dry picric acid in chloroform red needles of the picrate, m. p. 130—131° (yield, 95%).

Other Methyl-3 : 4-*benzoxanthens*.—The 5-*methyl* derivative was prepared from the appropriate methoxymethylbenzylidenetetralone in a boiling α-methylnaphthalene bath (50 min.). The product was extracted with ether and distilled at 180—200°/4 mm. The oily distillate obtained was dissolved in absolute alcohol and a small excess of picric acid was added, whereupon

fine red needles of the picrate separated. These were twice recrystallised from the same solvent, then decomposed with water, and the picric acid washed away and the product extracted with ether. The solvent was evaporated and the residue crystallised from light petroleum (b. p. 60—70°) as colourless needles, m. p. 95—96° (1·3 g., 29·5%) [Found : C, 88·0; H, 5·5%; *M* (Rast), 230]. It gave with pure dry picric acid in absolute alcohol red needles of the picrate, m. p. 131—132°.

The 6-*methyl* compound, prepared as was the 5-methyl derivative, extracted with chloroform, and distilled at 120—130°/1 mm., crystallised directly from alcohol as colourless plates, m. p. 99—100° (45%) [Found : C, 87·7; H, 5·6%; *M* (Rast), 214]. With picric acid in chloroform it gave red needles of the picrate, m. p. 129—130°.

The 8-*methyl* compound, prepared by cyclisation for 40 min. in an α-methylnaphthalene bath, was isolated by means of ether, distilled (195—200°/1 mm.), and crystallised from methyl alcohol in light olive-green plates, m. p. 95—96° (43%) [Found: C, 87·3; H, 5·9%; *M* (Rast), 216]. It gave in chloroform red needles of the picrate, m. p. 128—129°.

Methyl-3 : 4-*benzoxanthones*.—Potassium permanganate (1·7 g.) in acetone (150 c.c.) and water (40 c.c.) was added portionwise, with shaking, during 30 min. to a warm (35—40°) solution of 7-methyl-3 : 4-benzoxanthen (2 g.) in acetone (150 c.c.) and water (40 c.c.), and the mixture left for ½ hr. The reaction was strongly exothermic and the mixture was kept at the given temperature by cooling. The mixture was then acidified with one drop only of sulphuric acid, and sulphur dioxide bubbled in to dissolve the inorganic precipitate. The acetone was evaporated off and water added. The crystalline precipitate was washed and crystallised from acetone to give colourless needles of 7-methyl-3 : 4-benzoxanthone, m. p. 165—166° alone or mixed with an authentic specimen (Gindy and Dwidar, *loc. cit.*) (yield, 75%) [Found : C, 82·6; H, 4·6%; *M* (Rast), 251. Calc. for $C_{18}H_{12}O_2$: C, 83·1; H, 4·6%; *M*, 260].

The 5- and the 6-methyl derivative, prepared and crystallised in the same way, formed needles (95—96% yields), m. p. 225—226° (Found : C, 83·5; H, 4·5%; *M*, 297), and 172° (Found : C, 82·8; H, 5·1%; *M*, 252) respectively, both undepressed on admixture with authentic specimens.

The 8-*methyl* derivative, similarly prepared, crystallised from acetone as needles, m. p. 185—186° (96%) (Found : C, 82·9; H, 5·0%; *M*, 287).

Bromo-7-*methyl*-3 : 4-*benzoxanthone*.—Bromine (0·9 g., 1 mol. in 30 c.c. of carbon tetrachloride) was added dropwise to 7-methyl-3 : 4-benzoxanthone (1·5 g., 1 mol.) in carbon tetrachloride (75 c.c.) boiling in sunlight. Crimson-red crystals separated at once but dissolved after 15 minutes' refluxing which was then continued until the brisk evolution of hydrogen bromide ceased (about 1 hr.). On cooling, light yellow crystals separated which were collected, dried, and washed with sodium sulphite solution followed by water. Crystallisation from acetic acid gave x-*bromo*-7-*methyl*-3 : 4-*benzoxanthone*, colourless needles, m. p. 233° (73%) (Found : C, 63·6; H, 3·2; Br, 23·6. $C_{18}H_{11}O_2Br$ requires C, 63·7; H, 3·2; Br, 23·6%).

FOUAD I UNIVERSITY, FACULTY OF SCIENCE,
GIZA, EGYPT.

[*Received, November 3rd*, 1952.]