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FURANO COMPOUNDS—IX

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Abstract—Starting with the appropriate 3-hydroxybenzoxanthones and the following the sequence of reactions allylation, Claisen migration, acetylation, bromine addition and dehydrobromination, 7:8-benzo- and 5:6-benzo-3:4, 2′:3′-furanoxanthones have been synthesized.

NATURALLY occurring furanochromones like khellin and visnagin have pronounced physiological properties. In view of this, some furanoxanthones which contain an additional fused benzene ring as compared to the furanochromones were synthesized recently.[1] The present communication deals with the synthesis of two compounds (III and IV) having one more fused benzene ring, which may be called benzofuranoxanthones. Compounds of this type may be expected to possess photodynamic activity and may be discovered in nature in the future.

For the synthesis of III, β-naphthol has been condensed with 2-chloro-4-methoxybenzoic acid[2] and the resulting phenylnaphthylether carboxylic acid cyclized to give 3-methoxy-7:8-benzoxanthone (Ia). The mode of ring closure involving position 1 of the naphthalene molecule is arrived at by analogy and depends on the fact that in β-naphthol and derivatives there is an apparent fixation of the double bond in the 1,2-position. This is also supported by the IR absorption of Ia at 828 cm^{-1} indicative of an angular four-ring compound.[3] By the alternative method of ring closure, a linear four-ring compound would have resulted which would be characterized by absorption around 900 cm^{-1}.

The next step is demethylation of Ia with aluminium chloride to give the corresponding 3-hydroxyxanthone (Ib). This was allylated with allylbromide in the presence of potassium carbonate and the allyl ether (Ic) allowed to undergo Claisen migration to yield 3-hydroxy-4-allyl-7:8-benzoxanthone (Id). It was acetylated (Ie) to prevent any possible nuclear bromination in the subsequent step, viz. addition of bromine. The resulting dibromo compound (If) was heated with alcoholic potassium hydroxide resulting in simultaneous dehydrobromination and cyclization to give the desired 5′-methyl furano [2′:3′,3:4]-7:8-benzoxanthone (III).

For the alternate mode of fusion of benzene ring involving positions 5:6 to give a 5:6-benzoxanthone, α-naphthol was condensed with 2-chloro-4-methoxybenzoic acid to give the corresponding phenyl nephthyl ether carboxylic acid, which in the normal manner cyclized to give 3-methoxy-5:6-benzoxanthone (IIa). This was

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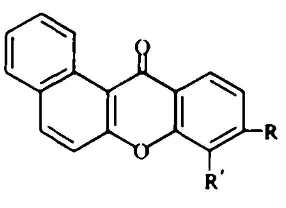
[1] Y. S. Agasimundin and S. Rajagopal, *Monatsh.* **97**, 423 (1966) and earlier papers.

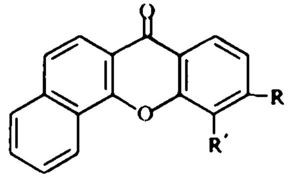
[2] F. Ullmann and C. Wagner, *Liebigs Ann.* **355**, 364 (1907).

[3] R. H. Martin, N. Defay, F. Geerts-Evrard, P. H. Given, R. H. Jones and R. H. Wedel, *Tetrahedron* **21**, 1833 (1965).

submitted to the above sequence of reactions passing through IIb . . . . IIf, to give the required 5-methyl-furano-5:6-benzoxanthone (IV).

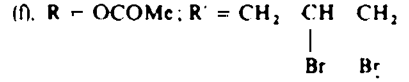


I



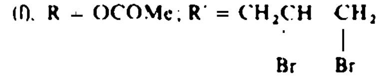
II

I (a). R = OMe; R' = H
(b). R = OH; R' = H
(c). R = $OCH_2CH{=}CH_2$; R' = H
(d). R = OH; R' = $CH_2\ CH{=}CH_2$
(e). R = OCOMe; R' = $CH_2CH{=}CH_2$

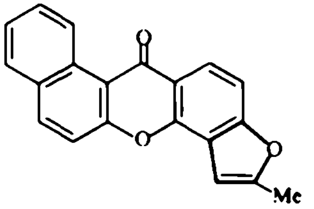


(f). R = OCOMe; R' = $CH_2\ \underset{\mathrm{Br}}{\underset{|}{CH}}\ \underset{\mathrm{Br}}{CH_2}$

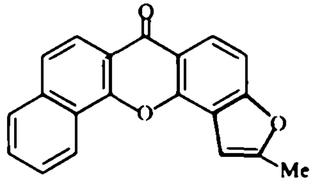
II (a). R = OMe; R' = H
(b). R = OH; R' = H
(c). R = $OCH_2\ CH{=}CH_2$; R' = H
(d). R = OH; R' = $CH_2\ CH{=}CH_2$
(e). R = OCOMe; R' = $CH_2\cdot CH{=}CH_2$



(f). R = OCOMe; R' = $CH_2\underset{\mathrm{Br}}{CH}\ \underset{\mathrm{Br}}{\underset{|}{CH_2}}$



III



IV

These compounds show strong IR bands similar to those of furanoxanthones mentioned in an earlier paper.[4]

EXPERIMENTAL

3-*Methoxy-7:8-benzoxanthone* (Ia)

(a) 2-Chloro-4-methoxybenzoic acid (18·7 g), K_2CO_3 (20·7 g), β-naphthol (15·8 g), copper bronze (0·5 g), CuI (0·5 g) and nitrobenzene (74·8 g) were stirred at 160° for 6 hr. After cooling, the mixture was diluted with water and the solvent removed in steam. The residual aqueous solution was filtered from tar and acidified to pH 2, when the naphthyl phenylether carboxylic acid was collected.

(b) To the cold soln of the above ether carboxylic acid (5·8 g) in acetyl chloride (58·8 g) conc H_2SO_4 (1 ml) was added and the mixture left at room temp for 1 hr. After removing acetyl chloride, the residue was poured on to crushed ice and the solid was collected. 3-Methoxy-7:8-benzoxanthone crystallized from alcohol as rectangular plates, m.p. 161–162°. (Found: C, 78·3; H, 4·4. Calc. for $C_{18}H_{12}O_3$: C, 78·3; H, 4·3%.)

3-*Hydroxy-7:8-benzoxanthone* (Ib)

A soln of 3-methoxy 7:8-benzoxanthone (1·3 g) in dry benzene (80 ml) was treated with anhyd $AlCl_3$ (3 g). The mixture was heated in a water-bath for 2 hr and benzene distilled off. The residue was decomposed

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[4] Y. S. Agasimundin and S. Rajagopal, *Chem. Ber.* **98**, 1910 (1965).

with ice and HCl and the resulting green solid collected. 3-Hydroxy-7:8-benzoxanthone (1 g) crystallized from alcohol as colourless needles, m.p. 279–280° (Found: C, 77·4; H, 3·9 Calc for $C_{17}H_{10}O_3$: C, 77·8; H, 3·8%.)

3-*Allyloxy-7:8-benzoxanthone* (Ic)

A soln of 3-hydroxy-7:8-benzoxanthone (1·31 g) in dry acetone (120 ml) was treated with allyl bromide (1 g) and K_2CO_3 (5 g) and the mixture refluxed for 8 hr. Evaporation of the filtered soln gave 3-allyloxy-7:8-benzoxanthone (1·1 g). It crystallized from alcohol as colourless plates, m.p. 157–158°. (Found: C, 78·8; H, 4·5 Calc. for $C_{20}H_{14}O_3$: C, 79·4; H, 4·6%.)

3-*Hydroxy-4-allyl-7,8-benzoxanthone* (Id)

The allyl ether (1·52 g) when refluxed for 2 hr with freshly distilled diethylaniline (12 ml) underwent smooth Claisen migration. The migration product (1 g) crystallized from alcohol as rectangular plates, m.p. 264–265°. (Found: C, 78·9; H, 4·6. Calc. for $C_{20}H_{14}O_3$: C, 79·5; H, 4·6%.) Its acetyl (Ie) derivative, prepared by heating with Ac_2O and pyridine crystallized from alcohol as rhombs, m.p. 183–184°. (Found: C, 76·1; H, 4·9. Calc. for $C_{22}H_{16}O_4$: C, 76·7; H, 4·6%.)

3-*Acetoxy-4-(2',3'-dibromo)-propyl-7:8-benzoxanthone* (If)

A soln of Br_2 (0·32 g) in $CHCl_3$ (15 ml) was added to a well stirred soln of 3-acetoxy-4-allyl-7:8-benzoxanthone (0·65 g) in $CHCl_3$ (40 ml) at room temp. Evaporation of the solvent yielded the dibromo compound (0·6 g) which was washed with alcohol. It crystallized from AcOH as colourless needles, m.p. 215°. (Found: C, 52·5; H, 3·4. Calc for $C_{22}H_{16}O_4Br_2$: C, 52·1; H, 3·2%.)

5'-*Methylfurano*[2':3',3:4]-7:8-*benzoxanthone* (III)

The above bromo compound (0·524 g, 0·001 mole) in a soln of KOH (0·56 g, 0·01 mole) in alcohol (12 ml) was refluxed for 2 hr. After cooling, the soln was diluted with water and acidified with dil HCl and left overnight. The furano compound that separated (0·25 g) was collected and crystallized from alcohol when it was obtained as rectangular plates, m.p. 206–208°. (Found: C, 79·7; H, 4·2 Calc. for $C_{20}H_{12}O_3$: C, 80·0; H, 4·0%.) Typical IR bands (Nujol) at 1650, 1600, 1480, 1450, 1260, 1240, 1090, 1070, 1030, 899 and 828 cm^{-1}.

3-*Methoxy-5:6-benzoxanthone* (IIa)

2-Chloro-4-methoxybenzoic acid (28 g), K_2CO_3 (31 g), α-naphthol (43·2 g), copper bronze (1·0 g), CuI (1·0 g) and nitrobenzene (110 g) were stirred at 160° for 6 hr. The mixture was cooled and worked up as in the case of Ia when the naphthyl phenyl carboxylic acid was obtained as a colourless solid.

(b) To a cooled soln of the above acid (8 g) in acetyl chloride (80 ml) was added conc H_2SO_4 (2 ml) and the mixture allowed to stand for 1 hr at room temp. Subsequent working up of the product yielded 3-methoxy-5:6-benzoxanthone as a colourless solid (4 g). It crystallized from alcohol as rectangular plates, m.p. 161–162° (Found: C, 78·0; H, 4·6 Calc. for $C_{18}H_{12}O_3$: C, 78·3; H, 4·3%.)

3-*Hydroxy-5:6-benzoxanthone* (IIb)

A soln of e-methoxy-5:6-benzoxanthone (1·9 g) in dry benzene (120 ml) was treated with anhyd $AlCl_3$ (5 g) and the mixture refluxed for 2 hr. Subsequent working up gave 3-hydroxy-5:6-benzoxanthone as a dark brown solid (1·5 g). This crystallized from alcohol as fine needles, m.p. above 300°. (Found: C, 78·2; H, 4·2 Calc. for $C_{17}H_{10}O_3$: C, 77·8; H, 3·8%.)

3-*Allyloxy-5:6-benzoxanthone* (IIc)

A soln of 3-hydroxy-5:6-benzoxanthone (2 g) in dry acetone (150 ml) containing allylbromide (2 g) was refluxed with K_2CO_3 (10 g) for 8 hr. Evaporation of the filtered soln gave 3-allyloxy-5:6-benzoxanthone (2 g). It crystallized from alcohol as rectangular plates, m.p. 148–150°. (Found: C, 78·8; H, 5·1. Calc. for $C_{20}H_{14}O_3$: C, 79·4; H, 4·6%.)

3-*Hydroxy-4-allyl-5:6-benzoxanthone* (IId)

The allyl ether (2·3 g) when refluxed for 2 hr with freshly distilled dimethylaniline (18 ml) underwent smooth Claisen migration. The migration product (1·8 g) crystallized from alcohol as pale yellow rectangular plates, m.p. 295–296°. (Found: C, 78·9; H, 5·0. Calc. for $C_{20}H_{14}O_3$: C, 79·5; H, 4·6%.) Its acetyl derivative

(IIe) crystallized from alcohol as rhombs, m.p. 177–178°. (Found: C, 76·0; H, 4·8. Calc. for $C_{22}H_{16}O_4$: C, 76·7; H, 4·6%.)

3-*Acetoxy-4-(2',3'-dibromo)-propyl-5:6-benzoxanthone* (IIf)

A soln of Br_2 (0·64 g) in $CHCl_3$ (25 ml) was added to a well stirred soln of 3-acetoxy-4-allyl-5:6-benzoxanthone (1·3 g) in $CHCl_3$ (75 ml) at room temp. The product was worked up as usual to yield the dibromo compound. It crystallized from AcOH as colourless long needles, m.p. 204°. (Found: C, 52·3; H, 3·4. Calc. for $C_{22}H_{16}O_4Br_2$: C, 52·2; H, 3·2%.)

5'-*Methylfurano*[2':3',3:4]-5:6-*benzoxanthone* (IV)

3-Acetoxy-4-(2',3'-dibromo)-propyl-5:6-benzoxanthone (1 g, 0·002 mole) in a soln of KOH (1·12 g, 0·02 mole) in alcohol (18 ml) was refluxed for 2 hr. After cooling the reaction product was worked up as usual to get the furano compound (0·4 g). It crystallized from alcohol as colourless tiny needles, m.p. 264–266°. (Found: C, 79·4; H, 4·1. Calc. for $C_{20}H_{12}O_3$: C, 80·0; H, 4·0%.) Typical IR bands (Nujol) at 1650, 1478, 1260, 1218, 1100, 940 and 830 cm^{-1}.

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