SYNTHESIS OF $2''\cdot3''\cdot7\cdot8$-FURANOFLAVONE

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LIMAYE\(^1\) has stated that he has synthesised a furano flavone, m.p., 225°, starting from "Karanj methyl ketone". Since we were also engaged on the same problem we give below details of the synthesis, and the compound, $2''\cdot3''\cdot7\cdot8$-furano flavone\(^*\) was found to melt at 229°.

Furanosalicylic acid\(^2\) when treated with diazomethane gave the corresponding ester, which was further methylated by treatment with methyl iodide and sodium, and was subsequently saponifed to yield furano-methoxy benzoic acid, I. This was converted to the acid chloride and the latter, on treatment with zinc methyl iodide gave furano-$\alpha$-methoxy acetophenone which was demethylated by hydriodic acid to furano-$\alpha$-hydroxy acetophenone, II, ("Karanj methyl ketone"). This was converted into $2''\cdot3''\cdot7\cdot8$-furano flavone, III, when heated with sodium benzoate and benzoic anhydride.

\[ I \quad III \]

Experimental

Methyl ester of furanosalicylic acid.—Furanosalicylic acid, m.p., 218° (decomp.), (12 g.), was suspended in 200 c.c. of absolute ether, cooled in ice and treated with excess of diazomethane. There was a vigorous reaction and the reaction mixture was left over-night. The solution retained a pale yellow colour indicating that diazomethane was still present. When ether was distilled over, a colourless material was left behind. It crystallised in glistening white thin silky needles from ethyl alcohol, yield, 10 g., m.p., 109°.

11\,529 mg. Subst.: 26\,390 mg., CO\(_2\), 4\,611 mg., H\(_2\)O.

C\(_{10}\)H\(_8\)O\(_4\). Calc.: C 62\,5, H 4\,2.

Found: C 62\,4, H, 4\,4.

\* For the system of numbering adopted vide Ber., 1939, 72B, 97.

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The compound was soluble in sodium hydroxide solution from which it was precipitated on saturation with carbon dioxide. It imparted a blue colour to ferric chloride in alcohol.

*Methyl ester of furano-o-methoxy benzoic acid.*—1·2 g. of sodium were dissolved in 25 c.c. of absolute methyl alcohol. 10 g. of the above phenolic ester dissolved in 25 c.c. of warm absolute methyl alcohol were added. Immediately the white sodium salt separated. After thorough stirring 10 g. of methyl iodide were added and the mixture refluxed on a water-bath for 18 hrs. At the end of 12 hrs. a further small quantity (2·5 g.) of methyl iodide was added. The refluxing was continued till the mixture in the flask did not give an alkaline reaction with moist red litmus paper. Most of the alcohol was distilled off and the cooled solution added to 130 c.c. of water. The methoxy methyl ester separated as a light yellow oil which was extracted with ether. The ether solution was washed with dil. KOH, dried over anhydrous sodium sulphate and ether distilled over. The pale yellow oil left behind was distilled in vacuum, b.p., 114-116°/0·3 mm., when the ester was obtained as a colourless oily liquid (yield, 8·6 g.), with a mild pleasant odour.

11·171 mg., Subst.: 26·146 mg. CO₂, 4·942 mg., H₂O.

C₁₁H₁₀O₄. Calc.: C 64·1, H 4·9.

Found: C 63·8, H 4·9.

*Furano-o-methoxy benzoic acid, I.*—5 g. of the above ester were added to 50 c.c. of 10% alcoholic potash and the mixture refluxed on a water-bath for an hour. Alcohol was then distilled over and the residue dissolved in 40 c.c. of water and acidified with 10% sulphuric acid. The white precipitate of the acid that separated was collected at the pump, washed with water, dried and crystallised from methyl alcohol, colourless needles, m.p., 149°, yield, 3·0 g.

10·774 mg. Subst.: 24·734 mg. CO₂, 4·310 mg. H₂O.

0·2090 g. Subst.: 23·30 c.c. 0·04673 N. NaOH.

C₁₀H₈O₄. Calc.: C 62·5, H 4·2, Mol. wt. 192.

Found: C 62·6, H 4·4, Mol. wt. 191·8.

*Acid chloride of furano-o-methoxy benzoic acid.*—3 g. of the acid, I, were dissolved in 10 c.c. of warm toluene and 4 g. of freshly distilled thionyl chloride were added. The mixture was refluxed for 3 hrs.; 1 g. more of thionyl chloride was added and the refluxing continued for another 2 hrs. The excess of thionyl chloride and toluene were removed by distillation under
reduced pressure and the oily material left behind was distilled in vacuum. The acid chloride readily solidified to a white crystalline solid, m.p., 71–72°, yield, 2·5 g.

0·2658 g. Subst.: 13·15 c.c. 0·0944 N. Ag NO₃ (Parr).
C₁₀H₉O₃Cl. Calc.: Cl 16·9.
Found: Cl 16·6.

**Furano-o-methoxy acetonaphone.**—The acid chloride (3 g.) dissolved in 20 c.c. of toluene was added in small quantities with vigorous shaking during the course of 5 mins., to zinc methyl iodide³ (from 4·1 g. of zinc copper couple, 4·2 g. of methyl iodide and 0·8 g. of absolute ethyl acetate). The mixture was allowed to stand overnight. It was then cooled in a mixture of ice and salt and a little cold water was added to it carefully. The flask was allowed to warm up to room temperature and 25 c.c. of dil. H₂SO₄ were added and then a little benzene. The aqueous layer was removed in a separating funnel. The combined benzene–toluene layer was washed with 5% KOH and then with water. The solvents were removed by distillation under reduced pressure. The residue was a black viscous liquid. It was distilled in vacuum, when it was obtained as a mobile light yellow oil (2 g.).

The pure compound, furano-o-methoxy acetonaphone, was prepared by refluxing its semicarbazone (1·5 g.) with 10% oxalic acid solution (50 c.c.) for 2 hrs. On cooling an oily material separated out which on standing solidified. It was crystallised twice from petroleum ether (50–60°), white needles, m.p., 56–57°, yield, 0·7 g.

11·821 mg. Subst.: 30·126 mg. CO₂, 5·885 mg. H₂O.
C₁₁H₁₀O₂. Calc.: C 69·4, H 5·3.
Found: C 69·5, H 5·5.

**Semicarbazone of furano-o-methoxy acetonaphone.**—The crude ketone (2 g.) was dissolved in 90% ethyl alcohol together with semicarbazide hydrochloride (1·3 g.) and sodium acetate (1·4 g.). The solution was refluxed for 2 to 3 hrs. On cooling a light yellow crystalline material separated out in needles. The crystals were collected at the pump. The mother liquors on concentration gave a further quantity of the semicarbazone. It was crystallised twice from methyl alcohol, white silky needles, m.p., 165°; yield, 1·6 g.

12·134 mg. Subst.: 26·028 mg. CO₂, 6·050 mg. H₂O.
2·366 mg. Subst.: 0·397 c.c. N (30°, 686 mm.).
C₁₂H₁₃O₃N₃. Calc.: C 58·3, H 5·3, N 17·0.
Found: C 58·5, H 5·5, N 17·3.
Furano-o-hydroxy acetophenone, II.—0.3 g. of the above ketone was dissolved in 10 c.c. of glacial acetic acid and 1 c.c. of freshly distilled HI (d, 1.7) was added. The solution was heated on a water-bath for 1 hr. and a further 0.5 c.c. of HI was added. The heating was continued for an hour more. The solution was cooled and diluted with water (75 c.c.) when a light yellow coloured crystalline material separated which was collected at the pump, and twice crystallised from 75% methyl alcohol, colourless long needles, m.p., 92°; yield, 0.20 g.

12.360 mg. Subst.: 30.912 mg. CO₂, 5.426 mg. H₂O.

C₁₆H₈O₃. Calc.: C 68·2, H 4·6.

Found: C 68·2, H 4·8.

The compound imparted a blue colouration to an alcoholic solution of ferric chloride.

2°.3° : 7·8 Furanoflavone, III.—0.12 g. of the phenolic ketone, II, was mixed with 1.8 g. of benzoic anhydride and 0.16 g. of anhydrous sodium benzoate and heated in an oil-bath at 180–185° for 7½ hrs. The mixture was cooled, refluxed with 90% ethyl alcohol and added to 100 c.c. of warm 3% solution of NaOH, well stirred and allowed to stand over-night. The yellow solid that had settled at the bottom was collected at the pump and crystallised thrice from small quantities of ethyl acetate (charcoal) when the furanoflavone was obtained in the form of glistening pale yellow plates, m.p., 229°; yield, 0.03 g.

9·806 mg. Subst.: 27·958 mg. CO₂, 3·624 mg. H₂O.

C₁₇H₁₀O₃. Calc.: C 77·9, H 3·9.

Found.: C 77·8, H 4·1.

The furanoflavone was very sparingly soluble in methyl and ethyl alcohols.

REFERENCES