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SYNTHESIS OF 2,3-DIPHENYL-4H-BENZOFURO[3,2-g]FURO[3,2-c][1]-BENZOPYRAN-4-ONES AND 2,3-DIPHENYL-4H-BENZOFURO[3,2-g]-PYRROLO[3,2-c][1]BENZOPYRAN-4-ONES

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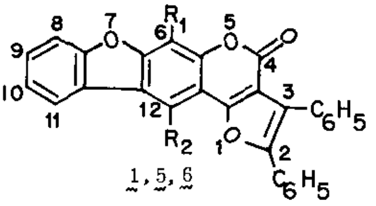
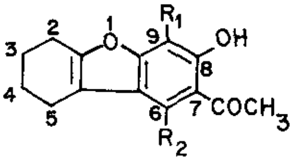
Abstract - The synthesis of 2,3-diphenyl-4H-benzofuro[3,2-g]furo[3,2-c][1]-benzopyran-4-ones (1, 5, 6) and 2,3-diphenyl-4H-benzofuro[3,2-g]pyrrolo[3,2-c][1]-benzopyran-4-ones (15, 18) is described.

In continuation of our synthetic work[1-3] on hydroxycoumarin derivatives, we now report a facile synthesis of 2,3-diphenyl-4H-benzofuro[3,2-g]furo[3,2-c][1]benzopyran-4-ones and 2,3-diphenyl-4H-benzofuro[3,2-g]pyrrolo[3,2-c][1]benzopyran-4-ones. Although these heterocyclic systems have not been reported in the literature so far but their potentiality as physiologically active compounds cannot be ruled out in view of the various similar activities associated with benzofurocoumarins[4] and 2,3-diphenylfurocoumarins[5].

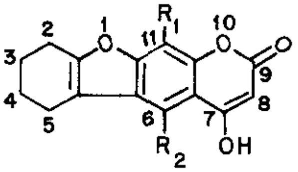
Firstly, synthesis of 2,3-diphenyl-4H-benzofuro[3,2-g]furo[3,2-c][1]benzopyran-4-one (1) was carried out in the following way. Condensation of 7-acetyl-2,3,4,5-tetrahydro-8-hydroxydibenzofuran[6] (2) with diethyl carbonate in the presence of sodium gave 2,3,4,5-tetrahydro-7-hydroxy-9H-benzofuro[3,2-g][1]benzopyran-9-one (3). The structure of 3 was established on the basis of its elemental analysis, IR and ^{1}H NMR spectral data. In the IR spectrum, two bands at 1660 and 1610 cm^{-1} confirmed the presence of coumarin moiety. Compound 3 when condensed with benzoin in dry xylene in the presence of p-toluene sulphonic acid monohydrate (PTS) furnished only one product, $C_{29}H_{20}O_4$. Its IR spectrum showed absorption at 1740 and 1615 cm^{-1} and ^{1}H NMR spectrum, besides other signals, showed the disappearance of the signal due to C-8 proton. Therefore, it was assigned the structure of 8,9,10,11-tetrahydro-2,3-diphenyl-4H-benzofuro[3,2-g]furo[3,2-c][1]benzopyran-4-one (4). Dehydrogenation of 4 with 2,3-dichloro-5,6-dicyano-p-benzoquinone (DDQ) in anhydrous benzene afforded the desired 1. The structure of 1 was established on the basis of its elemental analysis, IR and ^{1}H NMR spectral data (Table-I). Using the above method syntheses of 12-methyl-2, 3-diphenyl-4H-benzofuro [3, 2-g]furo [3, 2-c][1] benzopyran-4-one (5) and 6-methyl-2, 3-diphenyl-4H-benzofuro [3, 2-g] furo [3, 2-c] [1] benzopyran-4-one (6) were also effected. Thus, 7-acetyl-2, 3, 4, 5-tetrahydro-8-hydroxy-6-methyldibenzofuran[6] (7) when reacted with diethyl carbonate/sodium yielded 8 which was condensed with benzoin/PTS to form 9 and 7-acetyl-2, 3, 4, 5-tetrahydro-8-hydroxy-9-methyldibenzofuran[6] (10) yielded 11 which in turn was condensed with benzoin to give 12. Dehydrogenation of 9 and 12 with DDQ afforded 5 and 6 respectively. All these products were characterised on the basis of elemental analysis, IR and ^{1}H NMR spectral data (Table-I).



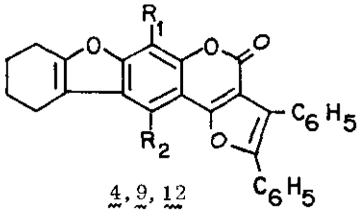
1, 5, 6



2, 7, 10



3, 8, 11



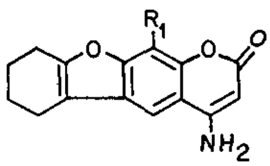
4, 9, 12

1, 2, 3, 4 $R_1 = R_2 = H$

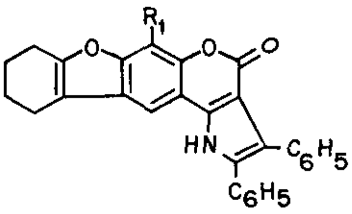
5, 7, 8, 9 $R_1 = H;\ R_2 = CH_3$

6, 10, 11, 12 $R_1 = CH_3;\ R_2 = H$

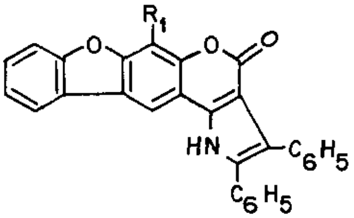
2, 3-Diphenyl-4H-benzofuro [3, 2-g] pyrrolo [3, 2-c] [1] benzopyran-4-one (13) has been synthesised as follows : The hydroxy compound (3) when condensed with anhydrous ammonium acetate in dry xylene, gave 7-amino-2, 3, 4, 5-tetrahydro-9H-benzofuro [3, 2-g][1] benzopyran-9-one (13). Its structure was established on the basis of its elemental analysis, IR [3350, 3230 (NH$_2$), 1630 (C=O) and 1555 cm^{-1} (C=C)] and ^{1}H NMR spectral data. Condensation of 13 with benzoin in dry xylene in presence of PTS furnished a single product viz., 8, 9, 10, 11-tetrahydro-2, 3-diphenyl-4H-benzofuro [3, 2-g] pyrrolo [3, 2-c] [1] benzopyran-4-one (14) which on dehydrogenation with DDQ in anhydrous benzene resulted in the formation of 15. Similarly, 11 reacted with anhydrous ammonium acetate to give 16 which on condensation with benzoin/PTS and subsequent dehydrogenation of the intermediate 17 with DDQ afforded 18. The proposed structures of the above compounds were in agreement with their elemental analysis, IR and ^{1}H NMR spectral data (Table-I).



13, 16



14, 17



15, 18

13, 14, 15 R_1 = H

16, 17, 18 R_1 = CH_3

EXPERIMENTAL

All melting points are uncorrected and in degree centigrade. Light petroleum had boiling range 60-80°C and silica gel were used for column chromatography and TLC. IR spectra were recorded on a Shimadzu IR-435 using Nujol. ^{1}H NMR spectra were recorded on a Perkin Elmer R-32 (90 MHz) spectrometer and Jeol JNM FX-200 MHz FT NMR spectrometer. Table-I summarizes the yield, mp and spectral data for all the new compounds.

2,3,4,5-Tetrahydro-7-hydroxy-9H-benzofuro[3,2-g][1]benzopyran-9-one (3) :

General Procedure

A solution of 2 (2.0 g, 8.6 mM) in diethyl carbonate was added to a suspension of pulverised sodium (1.0 g) and the reaction mixture was heated on a boiling water bath for 4 h and water (25 ml) was added to the cooled reaction mixture. The aqueous layer was extracted with ether to remove an excess of diethyl carbonate and the clear alkaline solution on acidification gave a solid product (3) which crystallised from ethanol as colourless flakes (0.84 g), mp 274-275°C.

8,9,10,11-Tetrahydro-2,3-diphenyl-4H-benzofuro[3,2-g]furo[3,2-c][1]benzopyran-4-one (4) :

General Procedure

A mixture of 3 (1.0 g, 3.9 mM), benzoin (0.83 g, 3.9 mM) and PTS (0.78 g, 4.5 mM) in xylene (50 ml) was refluxed for 24 h while collecting the water formed as an azeotrope by Dean-Stark apparatus. It was allowed to cool overnight and the separated crystalline matter filtered off. Removal of xylene from the filtrate gave a sticky mass which was purified by column chromatography to give 4. It crystallised from benzene-petroleum ether as colourless prismatic crystals (0.9 g), mp 194-195°C.

2,3-Diphenyl-4H-benzofuro[3,2-g]furo[3,2-c][1]benzopyran-4-one (1):

General Procedure

A mixture of 4 (0.2 g, 0.46 mM) and DDQ (0.27 g, 0.92 mM) in anhydrous benzene (25 ml) was refluxed for 36 h. The reaction mixture was filtered and the filtrate was washed successively with aqueous Na_2CO_3 (10%), water, dried and distilled of the solvent. The residue was subjected to column chromatography while elution of column with benzene-petroleum ether (1:1) gave 1. It crystallised from benzene-petroleum ether as colourless shining needles (0.15 g), mp 204-205°C.

7-Amino-2,3,4,5-tetrahydro-9H-benzofuro[3,2-g][1]benzopyran-9-one (13):

General Procedure

A mixture of 3 (1.0 g, 3.9 mM), anhydrous ammonium acetate (0.65 g, 8.4 mM) and dry xylene (80 ml) was refluxed for 48 h. After removal of xylene the sticky mass was treated with crushed ice to give a solid which was filtered, washed with aqueous Na_2CO_3 (5%) and then water. It crystallized from ethanol as yellow flakes of 13 (0.65 g), mp 234-235°C.

Table - I : Compounds prepared

Product[a]	Yield (%)	mp (°C)	IR Nujol $\nu_{max}(cm^{-1})$	^1H NMR (TMS) (ppm)
1	75	204-205	1735,1635	7.34-7.79 (m,15H), 8.02(s,1H)
3	38	274-275	3400,1660, 1610	1.85-2.05(m,4H), 2.60-2.88(m,4H), 6.32(s,1H), 7.38(s,1H), 7.93(s,1H)
4	53	194-195	1740,1615	1.78-2.00(m,4H), 2.56-2.80(m,4H), 7.13 7.56(m,11H), 7.80(s,1H).
5	70	261-262	1745,1625	3.20(s 3H), 7.30-7.60(m,15H)
6	71	245-246	1735,1630	2.48(s,3H), 7.20-7.54(m,14H), 8.12(s,1H)
8	38	>300	3390,1730, 1615	1.69-1.96(m,4H), 3.59-2.88(m ,7H), 5.85(s,1H), 7.04(s,1H)
9	55	135-136	1730,1615	1.78-1.97(m,4H), 2.58-2.85(m,4H), 3.00(s,3H), 7.27-6.77(m,11H)
11	37	284-285	3350,1650, 1620	1.80-2.02(m,4H), 2.50(s,3H), 2.50-2.85 (m,4H), 6.25(s,1H), 7.74(s,1H)
12	54	227-228	1745,1640	1.67-1.88(m,4H), 2.36-2.68(m,7H), 7.05-7.44(m,10H), 7.65(s,1H)

contd..

Table-I contd..

13	62	234-235	3350-3230, 1630, 1555	1.95-2.18(m, 4H), 2.66-2.98(m, 4H), 5.97(s, 1H), 7.52(s, 1H), 7.95(m, 1H)
14	50	180-182	3480-3400, 1675-1630	1.78-2.00(m, 4H), 2.61-2.70(m, 4H), 7.08-7.33(m, 12H)
15	71	263-264	3480-3410, 1690, 1610	3.28(s, 1H), 7.28-7.64(m, 15H), 7.70(s, 1H)
16	60	205-206	3350-3100, 1620, 1560	1.88-2.06(m, 4H), 2.44-2.84(m, 7H), 5.40(s, 1H), 7.86(s, 1H)
17	48	275-276	3490-3400, 1690, 1630	1.88-2.08(m, 4H), 2.52-2.82(m, 7H), 3.22(s, 1H), 7.22-7.56(m, 10H), 8.08(s, 1H)
18	70	>300	3470-3400, 1695, 1620	2.44(s, 1H), 2.68(s, 3H), 7.20-7.66(m, 14H), 8.20(s, 1H)

[a] Satisfactory microanalysis obtained for all the products

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