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A Facile Synthesis of 4-Aryl-2*H*-1-benzopyran-2-ones

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Reaction of 2-hydroxybenzophenones (**1**, **3**, **7**, **8**) with ethoxycarbonylmethylenetriphenylphosphorane affords 4-aryl-2*H*-1-benzopyran-2-ones (**2**, **4**–**6**) in excellent yields.

(Keywords: 4-Aryl-2H-1-benzopyran-2-ones; Ethoxycarbonylmethylenetriphenylphosphorane; Friedel-Crafts reaction; 2-Hydroxybenzophenones; Wittig reaction)

Eine einfache Synthese für 4-Aryl-2H-1-benzopyran-2-one

Die Reaktion der 2-Hydroxybenzophenone **1**, **3**, **7** und **8** mit Ethoxycarbonylmethylentriphenylphosphoran ergab die 4-Aryl-2*H*-1-benzopyran-2-one **2** und **4**–**6** in ausgezeichneten Ausbeuten.

Introduction

Several 4-aryl-2*H*-1-benzopyran-2-ones have been reported[1] in the literature from various natural sources. Recently, some 4-aryl-2*H*-1-benzopyran-2-ones have been isolated from *Courtarea hexandra*[2] and their structure established by spectroscopic methods only. Earlier, *Perkin*[3,4] and *Pechmann*[5,6] condensations have been used in the synthesis of 4-aryl-2*H*-1-benzopyran-2-ones. In general, the yields reported by these methods are not satisfactory. In this communication, we report a facile and general method for the synthesis of 4-aryl-2*H*-1-benzopyran-2-ones. The method involves *Wittig* reaction[7,8] of 2-hydroxybenzophenones with ethoxycarbonylmethylenetriphenylphosphorane $[(C_6H_5)_3P = CHCOOC_2H_5]$.

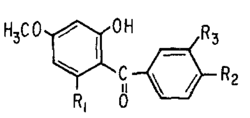
Results and Discussion

Initially, the reaction of 2-hydroxy-4-methoxybenzophenone[9] (**1**) with ethoxycarbonylmethylenetriphenylphosphorane in anhydrous benzene gave only one product in excellent yield (70%). The product was assigned the structure of 7-methoxy-4-phenyl-2*H*-1-benzopyran-2-one (**2**) on the basis of its IR and ^{1}H-NMR spectral data. The structure **2** was further confirmed by comparison with literature[10] (m.p.). Similar condensation of 2-hydroxy-4,6-dimethoxybenzophenone[11] (**3**) with ethoxycarbonylmethylenetriphenylphosphorane in dry benzene afforded 5,7-dimethoxy-4-phenyl-2*H*-1-benzopyran-2-one (**4**). Using the same procedure, synthesis of 5,7,4′-trimethoxy-4-phenyl-2*H*-1-benzopyran-2-one (**5**) and 5,7,3′,4′-tetramethoxy-4-phenyl-2*H*-1-benzopyran-2-one (**6**) has been carried out starting from 2-hydroxy-4,6,4′-trimethoxybenzophenone (**7**) and 2-hydroxy-4,6,3′,4′-tetramethoxybenzophenone (**8**), respectively. The latter ketones **7** and **8** were obtained by *Friedel-Craft*'s reaction of 1,3,5-trimethoxybenzene with 4-methoxybenzoyl chloride and 3,4-dimethoxybenzoyl chloride, respectively, in dry ether. 5,7,4′-Trimethoxy-4-phenyl-2*H*-1-benzopyran-2-one has recently been isolated[2] from *Courtarea hexandra*. The compounds **4** and **6** are methyl ethers of naturally occurring 5,7-dihydroxy-4-phenyl-2*H*-1-benzopyran-2-one[12] and 3′,4′-dohydroxy-5,7-dimethoxy-4-phenyl-2*H*-1-benzopyran-2-one[2], respectively.

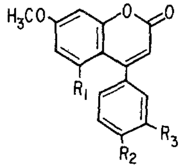
Table 1. *Data for the*

No.	Reaction time (h)	Yield (%)	M.p. (°C)	IR (KBr) γ (cm^{-1})
2	34	70	146–147 (116–118[10])[a]	1710 1620
4	36	65	167–168 (167[12])[a]	1710 1605
5	30	75	151–152 (151–152[2])[a]	1710 1610
6	34	70	169–170 (169–170[2])[a]	1705 1610
7	–	70	150–151	–
8	–	50	135–136	–

[a] Lit. m.p.



1,3,7,8



2,4-6

	R_1	R_2	R_3
1,2	H	H	H
3,4	OCH_3	H	H
5,7	OCH_3	OCH_3	H
6,8	OCH_3	OCH_3	OCH_3

All these coumarins exhibited a C = O band in their IR spectra between 1 710 and 1 705 cm^{-1}. The ^{1}H-NMR spectral data were in agreement with the proposed structures. The yields and spectroscopic data are summarised in Table 1.

Neutral conditions, high yield and ready availability of the phosphorane enhances the utility of the method.

compounds **2** *and* **4–8**

^{1}H-NMR ($CDCl_3$) *TMS*, δ (ppm)
3.77 (s, 3 H, O*Me*), 5.90 (s, 1 H, H-3), 6.62–6.81 (m, 2 H, H-6 and H-8), 7.07–7.31 (m, 5 H, C_6H_5), 7.43 (d, *J* = 9 Hz, 1 H, H-5)
3.70 (s, 3 H, O*Me*), 3.83 (s, 3 H, O*Me*), 5.84 (s, 1 H, H-3), 6.27 (d, *J* = 2.5 Hz, 1 H, H-6), 6.47 (d, *J* = 2.5 Hz, 1 H, H-8), 7.13–7.40 (m, 5 H, C_6H_5)
3.50 (s, 3 H, O*Me*-5), 3.89 (s, 6 H, O*Me*-7, O*Me*-4′), 5.85 (s, 1 H, H-3), 6.14 (d, *J* = 2.5 Hz, 1 H, H-6), 6.45 (d, *J* = 2.5 Hz, 1 H, H-8), 6.84 (d, *J* = 9 Hz, 2 H, H-3′, H-5′), 7.17 (d, *J* = 9 Hz, 2 H, H-2′, H-6′)
3.47 (s, 3 H, O*Me*-5), 3.86 and 3.92 (each s, 6 H and 3 H, O*Me*-7, O*Me*-3′, O*Me*-4′), 6.01 (s, 1 H, H-3), 6.25 (d, *J* = 2.5 Hz, 1 Hz, H-6), 6.52 (d, *J* = 2.5 Hz, 1 H, H-8), 6.79–6.94 (m, 3 H, H-2′, H-5′, H-6′)
3.32 and 3.64 (each s, 3 H and 6 H, O*Me*-4, O*Me*-6, O*Me*-4′), 5.70 (d, *J* = 2.5 Hz, 1 H, H-5), 5.88 (d, *J* = 2.5 Hz, 1 H, H-3), 6.61 (d, *J* = 9 Hz, 2 H, H-3′, H-5′), 7.33 (d, *J* = 9 Hz, 2 H, H-2′, H-6′), 11.72 (s, 1 H, OH, D_2O exchangeable)
3.50, 3.80, 3.86 and 3.90 (each s, each 3 H, O*Me*-4, O*Me*-6, O*Me*-3′, O*Me*-4′), 5.93 (d, *J* = 2.5 Hz, 1 H, H-5), 6.14 (d, *J* = 2.5 Hz, 1 H, H-3), 6.82 (d, *J* = 9 Hz, 1 H, H-5′), 7.21 (dd, *J* = 9 Hz and 2.5 Hz, 1 H, H-6′), 7.57 (d, *J* = 2.5 Hz, 1 H, H-2′), 11.96 (s, 1 H, OH, D_2O exchangeable)

Experimental

Preparation of 2-Hydroxy-4,6,4'-trimethoxybenzophenone (**7**), *General Procedure*

To a cooled and stirred solution of 1,3,5-trimethoxybenzene (5 g, 0.029 mol) in absolute diethyl ether (15 ml) and anhydrous aluminium chloride (9.94 g, 0.074 mol) was added 4-methoxybenzoyl chloride (5.05 g, 0.029 mol) over 1 h. The stirring continued for further 4 h and the reaction mixture was left overnight. Working up of the reaction gave **7** (6.01 g) which crystallised from benzene – petroleum ether as colourless needles, m.p. 150–151°.

Preparation of 7-Methoxy-4-phenyl-2H-1-benzopyran-2-one (**2**), *General Procedure*

A mixture of 2-hydroxy-4-methoxybenzophenone (2 g, 0.0088 mol) and ethoxycarbonylmethylenetriphenylphosphorane (4.57 g, 0.0132 mol) was refluxed in anhydrous benzene (25 ml) according to the time mentioned in Table 1. After evaporation of the solvent, the residue was chromatographed over silica gel. Elution of the column with benzene : petroleum ether (3 : 1) gave **2** (1.54 g). It was crystallised from benzene – petroleum ether as colourless prisms, m.p. 146–147°.

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