

Some phenoxy-2*H*-benzo[*b*]pyrans

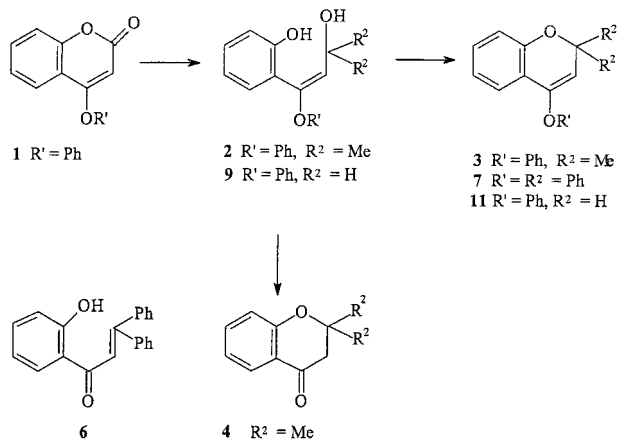
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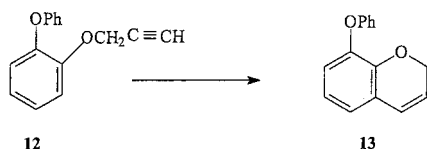
J. Chem. Research (S),
2000, 308–309J. Chem. Research (M),
2000, 0801–0820Successful methods have been found for the preparation of a wide range of phenoxy-2*H*-benzo[*b*]pyrans.

2,2-Dimethyl-4-phenoxy-2*H*-benzo[*b*]pyran **3** was obtained by the cyclization in boiling toluene of 3-hydroxy-1-(2-hydroxyphenyl)-3-methyl-1-phenoxybut-1-ene **2**, prepared by the Grignard reaction between 4-phenoxybenzo[*b*]pyran-2-one **1** and methylmagnesium iodide. Cyclization of the vinyl ether **2** under acid conditions resulted in the expected hydrolysis and formation of 2,3-dihydro-2,2-dimethylbenzo[*b*]pyran-4-one **4**.¹

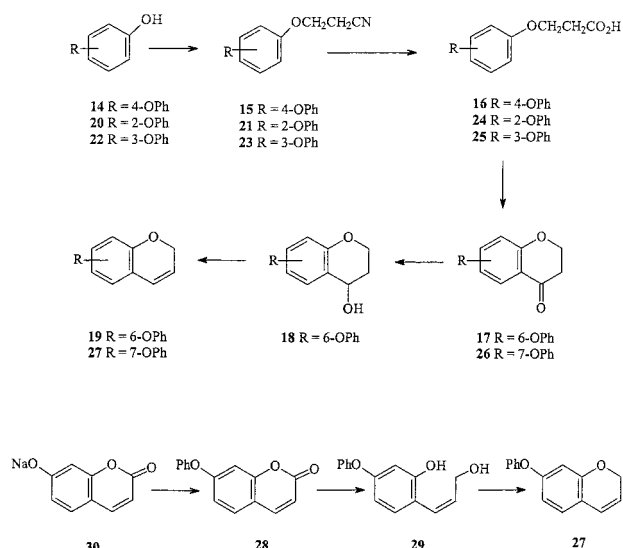
3,3-Diphenyl-1-(2-hydroxyphenyl)prop-2-en-1-one **6** was the main product, along with a small amount of 4-phenoxy-2,2-diphenyl-2*H*-benzo[*b*]pyran **7** resulting from the Grignard reaction between 4-phenoxybenzo[*b*]pyran-2-one **1** and phenylmagnesium bromide. It was not found possible to obtain 4-phenoxy-2*H*-benzo[*b*]pyran **11** by cyclization of 3-hydroxy-1-(2-hydroxyphenyl)-1-phenoxyprop-1-ene **9** obtained by the lithium aluminium hydride reduction of 4-phenoxybenzo[*b*]pyran-2-one **1**, under non-acidic conditions.



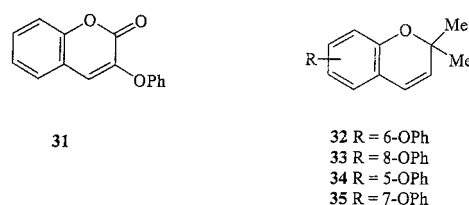
8-Phenoxy-2*H*-benzo[*b*]pyran **13** was prepared by the thermal cyclization of 3-(2-phenoxyphenoxy)prop-1-yne **12** in boiling *N,N*-diethylaniline.³ It was not found possible to obtain 6- and 7-phenoxy-2*H*-benzo[*b*]pyrans by this method.



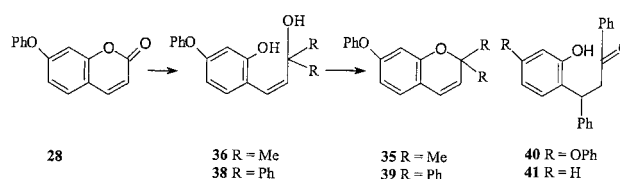
6-Phenoxy-2*H*-benzo[*b*]pyran **19** was synthesized from 4-phenoxyphenol **14** via cyanoethylation, followed by hydrolysis of the resulting nitrile **15** to give 3-(4-phenoxyphenoxy)propanoic acid **16**. Cyclization of acid **16** yielded ketone **17**, which on sodium borohydride reduction to the alcohol **18**, followed by dehydration furnished 6-phenoxy-2*H*-benzo[*b*]pyran **19**. Although some of the intermediates (indicated in diagram) were obtained by the above route it was not found possible to obtain 7- and 8-phenoxy-2*H*-benzo[*b*]pyrans **13** and **27**.



7-Phenoxy-2*H*-benzo[*b*]pyran **27** was obtained in low yield by the cyclization in boiling acetic acid of the diol **29**, prepared by the reduction of 7-phenoxybenzo[*b*]pyran-2-one **28** with lithium aluminium hydride. Coumarin **28** was prepared by the phenylation^{6,7} of sodium benzo[*b*]pyran-2-one-7-oxide **30**, using diphenyliodonium chloride in boiling methanol. Similarly 3-phenoxybenzo[*b*]pyran-2-one **31** was prepared in boiling dioxane from sodium benzo[*b*]pyran-2-one-3-oxide.



2,2-Dimethyl-6- and 8-phenoxy-2*H*-benzo[*b*]pyrans **32** and **33** were prepared by the cyclization of 3-methyl-3-(4-phenoxyphenoxy)- and 3-methyl-3-(2-phenoxyphenoxy)but-1-yne, respectively. Similar treatment of 3-methyl-3-(3-phenoxyphenoxy)but-1-yne afforded a mixture of 2,2-dimethyl-5- and -7-phenoxy-2*H*-benzo[*b*]pyrans **34** and **35** in equal amounts. Partial separated by thin layer or column chromatography. The 7-phenoxy derivative **35** was also obtained by the cyclization in boiling acetic acid of the diol **36**, prepared by the Grignard reaction between 7-phenoxybenzo[*b*]pyran-2-one **28** and methylmagnesium iodide.

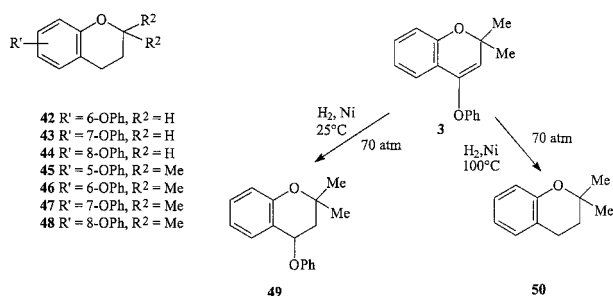


7-Phenoxybenzo[*b*]pyran-2-one **28** reacted with phenylmagnesium bromide in ether to give a gum containing

* To receive any correspondence.

3-hydroxy-1-(2-hydroxy-4-phenoxyphenyl)-2,2-diphenylprop-1-ene **38**, which cyclized readily at room temperature to give 7-phenoxy-2,2-diphenyl-2H-benzo[b]pyran **39**, in small yield. No evidence was obtained for the presence of 3-(2-hydroxy-4-phenoxyphenyl)-1,3-diphenylpropan-1-one **40** in the gum. In contrast 3-(2-hydroxyphenyl)-1,3-diphenylpropan-1-one **41** was formed, along with the related diol, in the reaction between the Grignard reagent and benzo[b]pyran-2-one.¹⁰

The hydrogenation of 6-, 7- and 8-phenoxy-2H-benzo[b]pyrans **19**, **27** and **13** and 5-, 6-, 7- and 8-phenoxy-2,2-dimethyl-2H-benzo[b]pyrans **34**, **32**, **35** and **33** in ethanol at 1 atmosphere in the presence of platinum oxide furnished the corresponding 3,4-dihydrophenoxy-2H-benzo[b]pyrans **42**, **43** and **44** and 3,4-dihydro-2,2-dimethylphenoxy-2H-benzo[b]pyrans **45**, **46**, **47** and **48**. Dihydro derivatives **43** and **45** were also obtained by direct phenylation of sodium 3,4-dihydro-2H-benzo[b]pyran-7-oxide and sodium 3,4-dihydro-2,2-dimethyl-2H-benzo[b]pyran-5-oxide, respectively, in ethanol with diphenyliodonium chloride.



Hydrogenation of 2,2-dimethyl-4-phenoxy-2H-benzo[b]pyran **3** at room temperature and 70 atmospheres, using Raney nickel as catalyst, afforded, 3,4-dihydro-2,2-dimethyl-4-phenoxy-2H-benzo[b]pyran **49**. At higher temperatures a mixture

of dihydrophenoxybenzopyran **49** and 3,4-dihydro-2,2-dimethyl-2H-benzo[b]pyran **50** was obtained, only the hydrogenolysis product **50** was formed at 100 °C. Dihydrophenoxybenzopyran **49** was also prepared by direct phenylation of sodium 3,4-dihydro-2,2-dimethyl-2H-benzo[b]pyran-4-oxide.

Techniques used: ¹H NMR and ¹³C NMR and mass spectrometry

References: 14

Table 1: ¹H NMR data of 6-, 7- and 8-phenoxy-2H-benzo[b]pyrans

Table 2: ¹H NMR data of 5-, 6-, 7- and 8-phenoxy-2,2-dimethyl-2H-benzo[b]pyrans

Table 3: ¹H NMR data of dihydrophenoxy-2H-benzo[b]pyrans

Table 4: ¹³C NMR data for 5-, 6-, 7- and 8-phenoxy-3,4-dihydro-2,2-dimethyl-2H-benzo[b]pyrans

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