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A Study of the Claisen Rearrangement of 7-(3-Phenyl-2-propenyloxy)-3-phenyl-(4 *H*)-1-benzopyran-4-one Derivatives**

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Summary. The Claisen rearrangement of 7-(3-phenyl-2-propenyloxy)-3-phenyl-(4 *H*)-1-benzopyran-4-one (**2a**) gave 7-hydroxy-8-(1-phenyl-2-propenyl)-3-phenyl-(4 *H*)-1-benzopyran-4-one (**3a**) and 2,3-dihydro-2,6-diphenyl-3-methyl-(7 *H*)furo[2,3-h]-1-benzopyran-7-one (**7a**). 2-Methyl-7-(3-phenyl-2-propenyloxy)-3-phenyl-(4 *H*)-1-benzopyran-4-one (**2b**) afforded **4b** and **7b**. 8-Methyl-7-(3-phenyl-2-propenyloxy)-3-phenyl-(4 *H*)-1-benzopyran-4-one (**12**) gave only the alkali soluble product 7-hydroxy-8-methyl-6-(1-phenyl-2-propenyl)-3-phenyl-(4 *H*)-1-benzopyran-4-one (**13**). **3a**, **4b**, and **13** were further cyclized in acidic medium to **9a**, **10b**, and **14** followed by dehydrogenation.

Keywords. Claisen rearrangement; 7-(3-Phenyl-2-propenyloxy)-3-phenyl-(4 *H*)-1-benzopyran-4-one; 8-Methyl-7-(3-phenyl-2-propenyloxy)-3-phenyl-(4 *H*)-1-benzopyran-4-one.

Die Claisen-Umlagerung von 7-(3-Phenyl-2-propenyloxy)-3-phenyl-(4 *H*)-1-benzopyran-4-on

Zusammenfassung. Die Claisen-Umlagerung von 7-(3-Phenyl-2-propenyloxy)-3-phenyl-(4 *H*)-1-benzopyran-4-on (**2a**) ergab 7-Hydroxy-8-(1-phenyl-2-propenyl)-3-phenyl-(4 *H*)-1-benzopyran-4-on (**3a**) und 2,3-Dihydro-2,6-diphenyl-3-methyl-(7 *H*)furo[2,3-h]-1-benzopyran-7-on (**7a**). 2-Methyl-7-(3-phenyl-2-propenyloxy)-3-phenyl-(4 *H*)-1-benzopyran-4-on (**2b**) ergab **4b** und **7b**. 8-Methyl-7-(3-phenyl-2-propenyloxy)-3-phenyl-(4 *H*)-1-benzopyran-4-on (**12**) führte lediglich zum alkalilöslichen Produkt 7-Hydroxy-8-methyl-6-(1-phenyl-2-propenyl)-3-phenyl-(4 *H*)-1-benzopyran-4-on (**13**). **3a**, **4b** und **13** wurden außerdem in saurem Medium zu **9a**, **10b** und **14** cyclisiert und weiter dehydrogeniert.

Introduction

Some polyphenolics such as neoflavonoids [1] and cinnamylphenols [2] have a cinnamyl unit present in various forms. Occurrence of these in nature led chemists to study Claisen rearrangements of different cinnamyl ethers of (4 *H*)-1-benzopyran-4-ones [3 – 5]. Direct cinnamylation [6, 7] is an alternate method to Claisen rearrangement. Jain et. al. [8] carried out the Claisen rearrangement of 7-(3-phenyl-2-propenyloxy)-3-phenyl-(4 *H*)-1-benzopyran-4-one, to obtain 7-hydroxy-8-(1-phenyl-1-propenyl)-3-phenyl-(4 *H*)-1-benzopyran-4-one. It appeared to us that this work needs further systematic investigation of the Claisen rearrangement of cinnamyl ethers of (4 *H*)-1-benzopyran-4-ones and their subsequent ring closure followed by dehydrogenation.

** This paper is dedicated to Dr. F. M. Dean, Department of Organic Chemistry, Robert Robinson Laboratories, University of Liverpool, Liverpool, U. K., on his retirement

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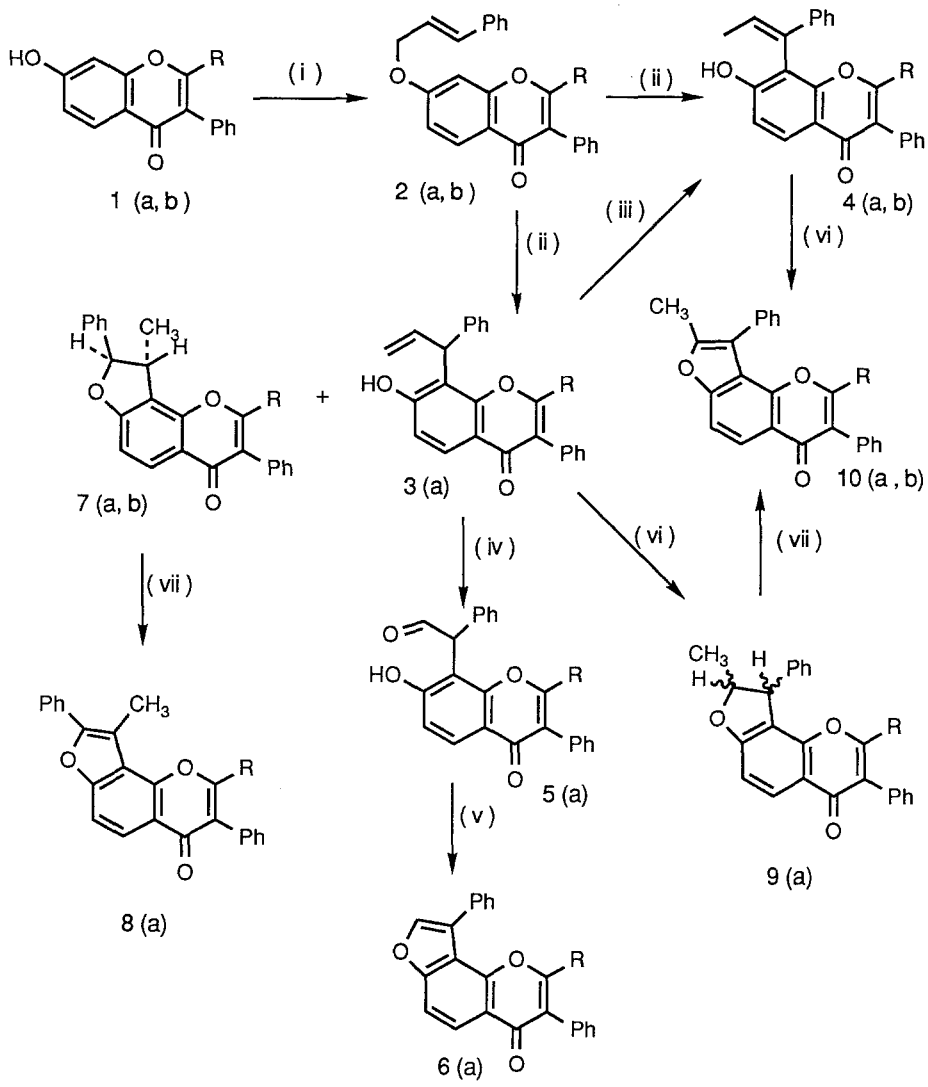
Results and Discussion

The Claisen rearrangement of cinnamyl ethers of 7-hydroxy-3-phenyl-(4*H*)-1-benzopyran-4-one [9], 7-hydroxy-8-methyl-3-phenyl-(4*H*)-1-benzopyran-4-one and 7-hydroxy-2-methyl-3-phenyl-(4*H*)-1-benzopyran-4-one [10−11] has been carried out in the present work. These cinnamyl ethers were prepared by the reaction of the corresponding hydroxy compound with one mole of cinnamyl chloride in the presence of potassium carbonate and acetone.

7-(3-Phenyl-2-propenyloxy)-3-phenyl-(4*H*)-1-benzopyran-4-one (**2a**) when refluxed in dimethylaniline for 8 h, gave 7-hydroxy-8-(1-phenyl-2-propenyl)-3-phenyl-(4*H*)-1-benzopyran-4-one (**3a**), m.p. 190−192°C. The pmr spectra of **3a** exhibited double doublet for two vinylic protons of the side chain at δ 5.25, $J=18$ and 8 Hz. Another doublet was also observed at δ 5.5, $J=8$ Hz for the single benzylic proton of the side chain. Hence the structure of **3a** was established as 7-hydroxy-8-(1-phenyl-2-propenyl)-3-phenyl-(4*H*)-1-benzopyran-4-one (**3a**). It is observed that **3a** which is first formed in the Claisen rearrangement, isomerized to **4a**, m.p. 180−182°C, by refluxing in acetone for 70−72 h in the presence of potassium carbonate. Pmr ($CDCl_3$) of **4a** exhibited a doublet, $J=7$ Hz, for a methyl group at δ 1.68. No signal appeared at δ 5.5 for a benzylic proton. The position of the double bond in the side chain in **3a** was confirmed by treating it with osmium tetroxide in ethylacetate in the presence of potassium periodate to obtain the corresponding aldehyde **5a**, which after cyclodehydration in polyphosphoric acid afforded 3,6-diphenyl(7*H*)furo[2,3-h]-1-benzopyran-7-one (**6a**). The pmr ($CDCl_3$) spectrum of **6a** exhibited signals at δ 7.0, doublet, 1 H, $J=9$ Hz, C-9; 7.4, multiplet, 5 H, *Ar*-H; 7.65, multiplet, 6 H, *Ar*-H; 7.75, singlet, 1 H, C-5; 7.85, doublet, 1 H, $J=9$ Hz, C-8; this sequence established the structure of **3a**. Jain and coworkers [8] reported the formation of **4a** (m.p. 192°C) when **2a** was refluxed in dimethylaniline for 8 h.

It was observed that in Claisen rearrangements different products were obtained on changing the heating period of the reaction. When the heating period was extended, a cyclized product together with the open chain compound was obtained. In the present case of Claisen rearrangement of **2a** the reaction mixture was refluxed for 12 h. The alkali insoluble product 2,6-diphenyl-2,3-dihydro-3-methyl-(7*H*)furo[2,3-h]-1-benzopyran-7-one (**7a**) was obtained along with **3a**. The pmr ($CDCl_3$) spectrum of **7a** exhibited a downfield doublet of the proton at C-2 at δ 5.3 in comparison to the proton at C-3 which appeared as multiplet at δ 3.7. If the isomeric structure **9a** was present, then the doublet of proton at C-3 would have appeared upfield in comparison with the multiplet of the proton at C-2. The isomeric product **9a** was prepared from **3a** and will be discussed later. Dehydrogenation of **7a** furnished 2,6-diphenyl-3-methyl (7*H*)furo[2,3-h]-1-benzopyran-7-one (**8a**). The pmr ($CDCl_3$) spectrum of **8a** exhibited signals at δ 2.7, singlet, 3 H, C_3-CH_3; 7.4, multiplet, *Ar*-H; 7.7, multiplet, 5 H, *Ar*-H; 8.0, singlet, 1 H, C-5; 8.15, doublet, 1 H, $J=9$ Hz, C-8. The cyclization of **3a** was carried out with a mixture of glacial acetic acid and hydrobromic acid to obtain 2,3-dihydro-3,6-diphenyl-2-methyl-(7*H*)furo[2,3-h]-1-benzopyran-7-one (**9a**). The pmr ($CDCl_3$) spectrum of the compound **9a** showed a mixture of *cis* and *trans* isomers. The methyl group at C-2 appeared at δ 1.15 (d, $J=10$ Hz, 3 H), which was from the *cis* isomer of the furan moiety; another doublet at δ 1.6 ($J=8$ Hz, 3 H) was from



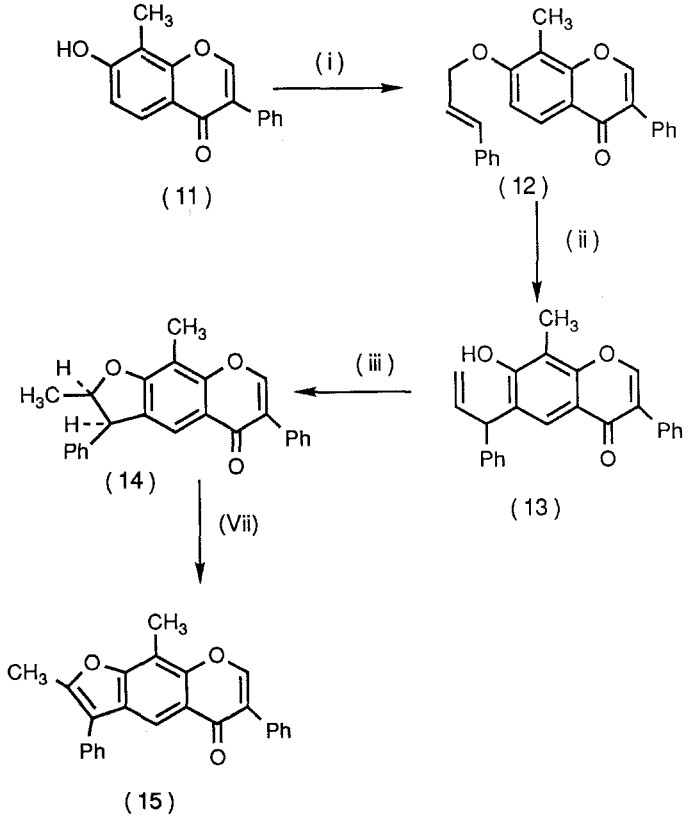
(i) C_6H_5-CH =CH-CH_2Cl, K_2CO_3, $(CH_3)_2C{=}O$
(ii) N, N- Dimethyl aniline
(iii) K_2CO_3, $(CH_3)_2C{=}O$
(iv) OsO_4, KIO_4
(v) Polyphosphoric acid
(vi) HOAc, HBr
(vii) Pd / C, 10%, Ph_2O

a : R =H
b : R = CH_3

the methyl group at C-2 of the *trans* isomer. The Proton at C-3 showed doublets in two different regions at δ 4.45 (J=7 Hz, 1 H) due to the *trans* isomer and at δ 4.75 (J=9.5 Hz, 1 H) due to the *cis* isomer. Similarly there were two multiplets existing at different positions for protons at C-2 from two isomers. The multiplet at δ 4.95 was due to the *trans* isomer, the other one at δ 5.3 was due to the *cis* isomer. At δ 8.25 and 8.28 there were two singlets for protons at C-5 from both *cis* and *trans* isomers. In order to group together the signals from each isomer more

precisely, a decoupling study was carried out for this molecule. On irradiating the C_2-H signal at δ 5.3, the doublet at 1.1 appeared as singlet and the doublet at 4.8 also changed to a singlet. Hence the doublet at 1.1 for $-CH_3$ at C-2, the doublet at 4.8 for C_3-H and the multiplet at 5.3 for C_2-H was from the same isomer. When the C_2-H multiplet at δ 4.9 was irradiated, the doublet at 1.6 was changed to a singlet and also the doublet at 4.45 became a singlet. Hence the doublet at δ 1.6 for $-CH_3$ at C-2, the doublet at 4.45 for C_3-H, and the multiplet at 4.9 for C_2-H were from the same isomer. Separation of the two isomers was not possible as it was showing only one spot on the chromatographic plate. Dehydrogenation of **9a** with Pd/C furnished 3,6-diphenyl-2-methyl-(7*H*)furo[2,3-h]-1-benzopyran-7-one (**10a**); pmr ($CDCl_3$) δ 2.45, singlet, 3 H, C_2-CH_3; 7.4, multiplet, *Ar*-H; 7.7, singlet, 1 H, C-5; 8.1, doublet, $J=9$ Hz, 1 H, C-8.

2-Methyl-7-(3-phenyl-2-propenyloxy)-3-phenyl-(4*H*)-1-benzopyran-4-one (**2b**) when refluxed with N,N-dimethylaniline for 8 h gave two products. The alkali soluble product was assigned to 7-hydroxy-2-methyl-8-(1-phenyl-1-propenyl)-3-phenyl-(4*H*)-1-benzopyran-4-one (**4b**), while the alkali insoluble product was assigned to 2,3-dihydro-3,5-dimethyl-2,6-diphenyl-(7*H*)furo[2,3-h]-1-benzopyran-7-one (**7b**); pmr (**4b**) (*DMSO-d_6*) δ 1.7, doublet, $J=8$ Hz, 3 H, $=CH-CH_3$; 2.0, singlet, 3H, C_2-CH_3; 6.3, quartet, 1 H, $=CH-CH_3$; 7.0, doublet, $J=9$ Hz, C_6-H; 7.2, multiplet, 10 H, *Ar*-H; 7.9, doublet, $J=9$ Hz, C_5-H; 9.55, singlet, 1 H, −OH; pmr (**7b**) ($CDCl_3$) δ 1.6, doublet, $J=8$ Hz, 3 H, C_3-CH_3; 2.2, singlet, 3 H, C_5-CH_3; 3.7, multiplet, 1 H, C_3-H; 5.3, doublet, $J=8$ Hz, C_2-H; 6.85, doublet, J = 9 Hz, C_8-H; 7.3, multiplet, 10 H, *Ar*-H; 8.05, doublet, $J=9$ Hz, C_9-H. The attempt to



dehydrogenate **7b** either with palladium on charcoal or with *DDQ* met with failure and the unreacted product was obtained back. Cyclization of **4b** with a mixture of hydrobromic acid and glacial acetic acid gave the product 2,5-dimethyl-3,6-diphenyl-(7*H*)furo[2,3-h]-1-benzopyran-7-one (**10b**). The pmr exhibited a signal at δ 2.0, singlet, 3 H, methyl protons at C-5; 2.5, singlet, 3 H, methyl protons; 7.2-7.4, multiplet, 10 H, *Ar*-H; 8.05, doublet, $J=9$ Hz for C_8-H. This proves that cyclodehydrogenation has occurred during this reaction.

7-Hydroxy-8-methyl-3-phenyl-(4*H*)-1-benzopyran-4-one (**11**) when condensed with cinnamyl chloride gave 8-methyl-7-(3-phenyl-2-propenyloxy)-3-phenyl-(4*H*)-1-benzopyran-4-one (**12**) which after refluxed with N,N-dimethylaniline gave an alkali soluble product 7-hydroxy-8-methyl-6-(1-phenyl-2-propenyl)-3-phenyl-(4*H*)-1-benzopyran-4-one (**13**); pmr ($CDCl_3$) δ 2.3, singlet, 3 H; 5.0, multiplet, 2 H, vinylic protons; 5.3, doublet, 1 H, $J=10$ Hz, allylic; 6.3, multiplet, 1 H, vinylic; 7.2, singlet, 1 H, C-5; 7.3, multiplet, 5 H, *Ar*-H; 7.9, singlet, 1 H, C-2. Cyclization was carried out by refluxing in a mixture of acetic acid and hydrobromic acid solution to furnish 7,9-dimethyl-3,6-diphenyl-6,7-dihydro-(4*H*)furo[3,2-g]-1-benzopyran-4-one (**14**); pmr ($CDCl_3$) δ 1.1, doublet, 3 H, $J=7$ Hz, C-2; 2.4, singlet, 3 H, C-9; 4.7, doublet, 1 H, $J=10$ Hz, C-3; 5.3, multiplet, 1 H, C-2; 7.0−7.5, multiplet, 10 H, *Ar*-H; 7.95, singlet, 1 H, C-4; 8.1, singlet, 1 H, C-7. Dehydrogenation was carried out by refluxing it with diphenyl ether and palladium on charcoal furnishing 7,9-dimethyl-3,6-diphenyl-(4*H*)furo[3,2-g]-1-benzopyran-4-one (**15**); pmr (*DMSO-d_6*) δ 2.55, singlet, 3 H, C_3-CH_3; 2.6, singlet, 3 H, C_9-CH_3; 7.4, multiplet, 10 H, *Ar*-H; 7.9, singlet, 1 H, C_7-H; 8.2, singlet, 1 H, C_4-H. In order to assign the stereochemistry of **14**, the technique of NOE difference spectra was applied. The NOE difference spectrum of **14** shows the enhancement of signals for the protons at C-2, the proton on the phenyl ring at C-3 and the proton at C-4, while the proton at C-3 shows a negative NOE (relaying NOE to the proton at C-4). Thus there is a NOE between C_2-H and C_3-H, between C_3-H and C_4-H and also between the $-CH_3$ group at C-2 with the aromatic proton of the phenyl ring at C-3. These compound have therefore the methyl group and the phenyl ring *cis* to each other. This is also evident from the chemical shift of the C_2-CH_3 group. In the case of 2,3-dihydrofuro compounds, when there is no phenyl ring in the 3 position, the normal chemical shift of the C_2-CH_3 group is in the region of 1.5. In the present case C_2-CH_3 and C_3-phenyl are *cis* to each other and hence the C_2-CH_3 group is shielded by the phenyl ring and therefore the chemical shift of C_2-CH_3 moves upfield to δ 1.1. When the methyl group and the phenyl ring are *trans* to each other, the chemical shift of the methyl group is observed at ca. δ 1.6−1.7. Thus the structure of **14** is *cis*. Based on this argument the stereochemistry of other dihydrofuro compounds could be assigned. Thus **7a** and **7b** are *trans*, because the chemical shift of the methyl group is at δ 1.6.

Experimental Part

Unless otherwise stated, melting points are uncorrected. pmr spectra were recorded on a 90 MHz spectrophotometer in $CDCl_3$ using Me_4Si as internal standard and chemical shifts are expressed in δ values; light petroleum had a boiling range 40−60°C; silica gel was used for column chromatography and TLC; solvent systems for TLC were: (A) petroleum ether (B) petroleum ether : benzene (1 : 1) (C) benzene.

7-(3-Phenyl-2-propenyloxy)-3-phenyl-(4H)-1-benzopyran-4-one (**2a**)

A mixture of **1a** (4.8 g, 0.02 mol), cinnamyl chloride (4.1 g, 0.027 mol), anhydrous potassium carbonate (15 g) and few crystals of potassium iodide was refluxed in dry acetone (300 ml) for 15 h. The reaction mixture was poured over crushed ice, the separated solid filtered and washed with dilute alkali solution to remove any unreacted material. The compound was dried and titurated with light petroleum ether to remove any unreacted reagent, if present. It crystallized from benzene (3.5 g, 49.0%); m.p. 154°C; found C 81.2, H 4.8; $C_{24}H_{18}O_3$ requires C 81.3, H 5.1%.

7-Hydroxy-8-(1-phenyl-2-propenyl)-3-phenyl-(4H)-1-benzopyran-4-one (**3a**)

2a (1 g, 0.0028 mol) was refluxed with N,N-dimethylaniline (10 ml) for 8 h. The reaction mixture was poured into cold conc. hydrochloric acid and a solid separated. It was dissolved in ether which was further washed with dilute alkali solution. On acidification with conc. hydrochloric acid it gave **3**. It crystallized from benzene + petroleum ether (0.7 g, 70%); m.p. 190 − 192°C; found C 81.7, H 4.9; $C_{24}H_{17}O_3$ requires C 81.3, H 5.1%.

2,3-Dihydro-2,6-diphenyl-3-methyl-(7H)furo[2,3-h]-1-benzopyran-7-one (**7a**)

2a (1 g, 0.0028 mol) was refluxed with N,N-dimethylaniline (10 ml) for 12 h. The reaction mixture was cooled and poured into cold conc. hydrochloric acid. The separated solid was filtered and dissolved in ether. The etheral solution was washed with dilute alkali solution. On acidification with conc. hydrochloric acid, **3a** separated which was filtered, dried and purified. It crystallized from a benzene-light petroleum ether mixture (0.25 g, 25%) and was identical with the above sample in every respect. The etheral layer gave **7a** on evaporation. It crystallized from benzene (0.4 g, 40%); m.p. 155°C; found C 81.6, H 5.3; $C_{24}H_{18}O_3$ requires C 81.3, H 5.1%.

7-Hydroxy-8-(phenyl ethanal)-3-phenyl-(4H)-1-benzopyran-4-one (**5a**)

3a (0.7 g, 0.002 mol) in ethyl acetate (30 ml) and OsO_4 (500 mg) in water (10 ml) were vigorously stirred for 15 min. Potassium iodide (1.5 g) was added in small quantities to the dark solution over a period of 2 h. The reaction mixture was stirred 1 h more. The ethyl acetate layer was separated, washed with water, dried with sodium sulfate and distilled. The residue crystallized from glacial acetic acid (0.2 g, 28.6%); m.p. 240°C; found C 77.6, H 4.4; $C_{23}H_{16}O_4$ requires C 77.5, H 4.5%; MS: *m/z* (M^+ 356; M-1$^+$ 355; M-CO$^+$ 327).

3,6-Diphenyl-(7H)furo[2,3-h]-1-benzopyran-7-one (**6a**)

5a (0.2 g, 0.0005 mol) was mixed with polyphosphoric acid (5 ml) and heated at 200°C for 2 h. The reaction mixture was cooled and poured over crushed ice. The separated solid was filtered, dried and crystallized from benzene (0.06 g, 31.6%); m.p. 210°C; found C 81.4, H 4.6; $C_{23}H_{14}O_3$ requires C 81.6, H 4.1%.

2,6-Diphenyl-3-methyl-(7H)furo[2,3-h]-1-benzopyran-7-one (**8a**)

A mixture of **7a** (0.7 g, 0.002 mol) and palladium on carbon (0.5 g, 10%) was refluxed in diphenyl ether (5 ml) for 18 h. The reaction mixture was filtered hot, excess of solvent removed and the product crystallized from benzene (0.25 g, 35.9%); m.p. 195°C; found C 82.1, H 4.4; $C_{24}H_{16}O_3$ requires C 81.8, H 4.5%.

2,3-Dihydro-3,6-diphenyl-2-methyl-(7H)furo[2,3-h]-1-benzopyran-7-one (**9a**)

3a (1 g, 0.003 mol) was refluxed in a mixture of glacial acetic acid (12 ml) and hydrobromic acid (8 ml, 48%) for 8 h. The reaction mixture was poured over crushed ice, the separated solid filtered,

dried and purified by column chromatography using benzene as eluent. It crystallized from benzene (0.55 g, 55.0%); m.p. 170°C; found C 81.0, H 4.7; $C_{24}H_{18}O_3$ requires C 81.3, H 5.1%.

3,6-Diphenyl-2-methyl-(7 H)furo[2,3-h]-1-benzopyran-7-one (**10 a**)

0.7 g, 0.002 mol of **9 a** was mixed with palladium on carbon (0.6 g, 10%) and refluxed with diphenyl ether (5 ml) for 18 h. The reaction mixture was filtered hot, excess of solvent removed and the product separated. It was dissolved in benzene and passed through a column of silica gel for purification. It crystallized from benzene (0.3 g, 43.1%); m.p. 180°C; found C 82.3, H 4.9; $C_{24}H_{16}O_3$ requires C 81.8, H 4.5%.

7-Hydroxy-8-(1-phenyl-1-propenyl)-3-phenyl-(4 H)-1-benzopyran-4-one (**4 a**)

3 a (1.0 g, 0.003 mol) was dissolved in dry acetone (400 ml) and anhydrous potassium carbonate (4 g) was added. The reaction mixture was refluxed for 70 – 72 h, then filtered, excess of solvent was removed and the product crystallized from benzene (0.8 g, 80%); m.p. 181 – 182°C; found C 81.7, H 5.4; $C_{24}H_{18}O_3$ requires C 81.3, H 5.0%. pmr ($CDCl_3$): δ 1.68 (d, J=7 Hz, $-CH_3$), 6.6 (q, J=7 Hz, =CH– of side chain), 7.15 (m, 6 H, *Ar*-H + C_6 – H), 7.3 (m, 5 H, *Ar*-H), 7.65 (s, 1 H, C_2 – H), 8.15 (d, J=9 Hz, C_5 – H).

2-Methyl-7-(3-phenyl-2-propenyloxy)-3-phenyl-(4 H)-1-benzopyran-4-one (**2 b**)

A mixture of **1 b** (2.5 g, 0.01 mol), cinnamyl chloride (2.0 g, 0.013 mol), anhydrous potassium carbonate (10 g) and few crystals of potassium iodide was refluxed in dry acetone (300 ml) for 10 h. The reaction mixture was added to cold water, the separated solid was filtered and washed with dilute alkali to remove any unreacted compound. The crude product was dried and titurated with petroleum ether to remove unreacted reagent, if any. It crystallized from benzene (2.2 g, 60.3%); m.p. 153 – 154°C; found C 81.6, H 5.7; $C_{25}H_{20}O_3$ requires C 81.5, H 5.4%.

7-Hydroxy-2-methyl-8-(1-phenyl-1-propenyl)-3-phenyl-(4 H)-1-benzopyran-4-one (**4 b**) *and 3,5-Dimethyl-2,6-diphenyl-2,3-dihydro-(7 H)furo[2,3-h]-1-benzopyran-7-one* (**7 b**)

2 b (1 g, 0.0027 mol) was refluxed with N,N-dimethylaniline (10 ml) for 8 h. The reaction mixture was cooled and poured into cold conc. hydrochloric acid. The separated solid was filtered and dissolved in ether. The etheral layer was washed with dil. alkali solution. On acidification with conc. hydrochloric acid, a solid separated which was filtered, dried and crystallized from benzene + alcohol to furnish **4 b** (0.2 g, 20%); m.p. 135 – 138°C; found C 81.7, H 5.8; $C_{25}H_{20}O_3$ requires C 81.5, H 5.4%. The etheral layer gave on evaporation a solid which crystallized from benzene to give **7 b** (0.6 g, 60%); m.p. 150°C; found C 82.0, H 5.6; $C_{25}H_{20}O_3$ requires C 81.5, H 5.4%.

2,5-Dimethyl-3,6-diphenyl-(7 H)furo[2,3-h]-1-benzopyran-7-one (**10 b**)

4 b (1.0 g, 0.0027 mol) was refluxed with a mixture of glacial acetic acid (5 ml) and hydrobromic acid (9 ml, 48%) for 8 h. The reaction mixture was poured over crushed ice, the solid obtained was washed with dil. alkali solution to remove unreacted compound. It crystallized from benzene (0.5 g, 50.5%); m.p. 185°C; found C 81.6, H 4.7; $C_{25}H_{18}O_3$ requires C 81.9, H 4.9%.

8-Methyl-7-(3-phenyl-2-propenyloxy)-3-phenyl-(4 H)-1-benzopyran-4-one (**12**)

A mixture of **11** (2.5 g, 0.01 mol), cinnamyl chloride (2.0 g, 0.013 mol), anhydrous potassium carbonate (10 g) and few crystals of potassium iodide was refluxed in dry acetone (300 ml) for 10 h. The reaction mixture was added to water, the solid separated was filtered and washed with dil. NaOH solution

to remove any unreacted compound. The solid was dried and scratched with light petroleum ether to remove any unreacted reagent. It crystallized from benzene (2.0 g, 54.8%); m.p. 145°C; found C 81.6, H 5.7; $C_{25}H_{20}O_3$ requires C 81.5, H 5.4%.

7-Hydroxy-8-methyl-6-(1-phenyl-2-propenyl)-3-phenyl-(4H)-1-benzopyran-4-one (**13**)

12 (1.5 g, 0.004 mol) was refluxed in N,N-dimethylaniline (7 ml) for 8 h. The reaction mixture was poured into cold conc. hydrochloric acid and the solid obtained was dissolved in ether. The etheral solution was washed with dil. alkali solution. On acidification with conc. hydrochloric acid it gave **13** which crystallized from benzene (1 g, 66.6%); m.p. 101°C; found C 81.3, H 5.3; $C_{25}H_{20}O_3$ requires C 81.5, H 5.4%.

7,9-Dimethyl-3,6-diphenyl-6,7-dihydro-(4H)furo[3,2-g]-1-benzopyran-4-one (**14**)

1 g, 0.0027 mol of **13** was refluxed with a mixture of glacial acetic acid (12 ml) and hydrobromic acid (8 ml, 48%) for 8 h. The reaction mixture was poured over crushed ice and the solid obtained was washed with dilute alkali solution to remove any unreacted compound. It was purified by column chromatography using benzene as eluent and crystallized from benzene + petroleum ether (0.45 g, 45%); m.p. 190°C; found C 81.8, H 5.3; $C_{25}H_{20}O_3$ requires C 81.5, H 5.4%.

7,9-Dimethyl-3,6-diphenyl-(4H)furo[3,2-g]-1-benzopyran-4-one (**15**)

A mixture of **14** (0.7 g, 0.002 mol) and palladium on carbon (0.6 g, 10%) was refluxed in diphenyl ether (5 ml) for 20 h. The reaction mixture was filtered hot, excess of solvent was removed and the product was crystallized from benzene (0.25 g, 35.9%); m.p. 195°C; found C 82.4, H 4.9; $C_{25}H_{18}O_3$ requires C 82.0, H 4.9%.

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