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Electron Transfer Oxidation of Enol Derivatives of 2,3-Dihydrobenzopyran-4-ones

M. Consuelo Jiménez, Miguel A. Miranda,* Juan Soto and Rosa Tormos

Departamento de Química/Instituto de Tecnología Química UPV-CSIC, Universidad Politécnica de Valencia, Camino de Vera s/n, Apartado 22012, E-46071-Valencia, Spain.

Abstract: Dihydrobenzopyrones **1a-c** and their enol acetates **3a-c** have been submitted to oxidation under single electron transfer (SET) conditions, using three alternative ways of activation: chemical oxidation with cerium(IV) ammonium nitrate (CAN), photochemical oxidation using triphenylpyrylium tetrafluoroborate (TPT) as sensitizer or electrochemical oxidation. The most significant products obtained are diketones **4**, hydroxyketones **5**, rearranged benzopyrones **6**, enones **9** and, in the case of enol acetate **3c**, 2-methylchromone (**10**) and 1,2-diphenylethane (**13**). These results are rationalized according to three major pathways from the radical cations: i) formation of the α-carbonyl radicals **I** (through deprotonation of the enols $2^{+\cdot}$ or cleavage of the carbonyl-oxygen bond of their acetates $3^{+\cdot}$), eventually followed by secondary oxidation to the carbenium ions **II**, ii) breaking of the bond linking C_2 with one of the substituents and iii) ring opening.

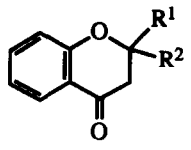
INTRODUCTION

The benzopyran ring system can be found in a wide variety of compounds with interesting biological properties, including several classes of natural products. Among them, the flavonoids are one of the largest families of polyphenols. Their widespread occurrence in higher plants, associated to diverse biological functions, their structural assignment and the reactions involved in their synthesis and interconversion have contributed to the development of the chemistry of flavonoids as a very important area of organic chemistry.[1]

In this framework, oxidation of the C_3-fragment linking the A and B rings allows one to progress in the oxidation level from the 2-hydroxychalcone-flavanone state to the flavonol state. Such processes appear to be enzymatically catalyzed in nature, although they are not completely understood.[2] This explains the interest devoted to model oxidation experiments using benzopyrans and related compounds as substrates.

In the last years, photosensitized SET oxidation has been performed on 2-hydroxychalcones,[3] flavanones[4] and their enol acetates,[5] being formation of flavones the most general result reported. To gain a deeper insight into the mechanistic aspects involved in SET oxidation of benzopyrans and related compounds, we have examined the reactivity of 2,2-disubstituted analogues under electron transfer conditions, using chemical, photochemical and electrochemical methods to achieve the desired activation. This pattern of substitution was

expected to prevent direct dehydrogenation to flavone-like products, therefore providing alternative pathways to divert the behavior and chemical fate of the intermediate radical cations or other short-lived chemical entities generated in the course of the reaction. Since enols are known to undergo SET oxidation much better than ketones,[6] we selected for our study the enol derivatives **3a-c** in addition to the corresponding dihydrobenzopyrones **1a-c**. Our results show that the major types of cleavage occurring in the species **3a-c**$^{+\cdot}$ are those affecting the carbonyl-oxygen bond (i), the bond linking C_2 with one of the substituents (ii) and/or ring opening (iii). Processes i and ii lead to products of functionalization at C_3, dehydrogenation with migration of a substituent and fragmentation.



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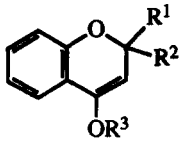


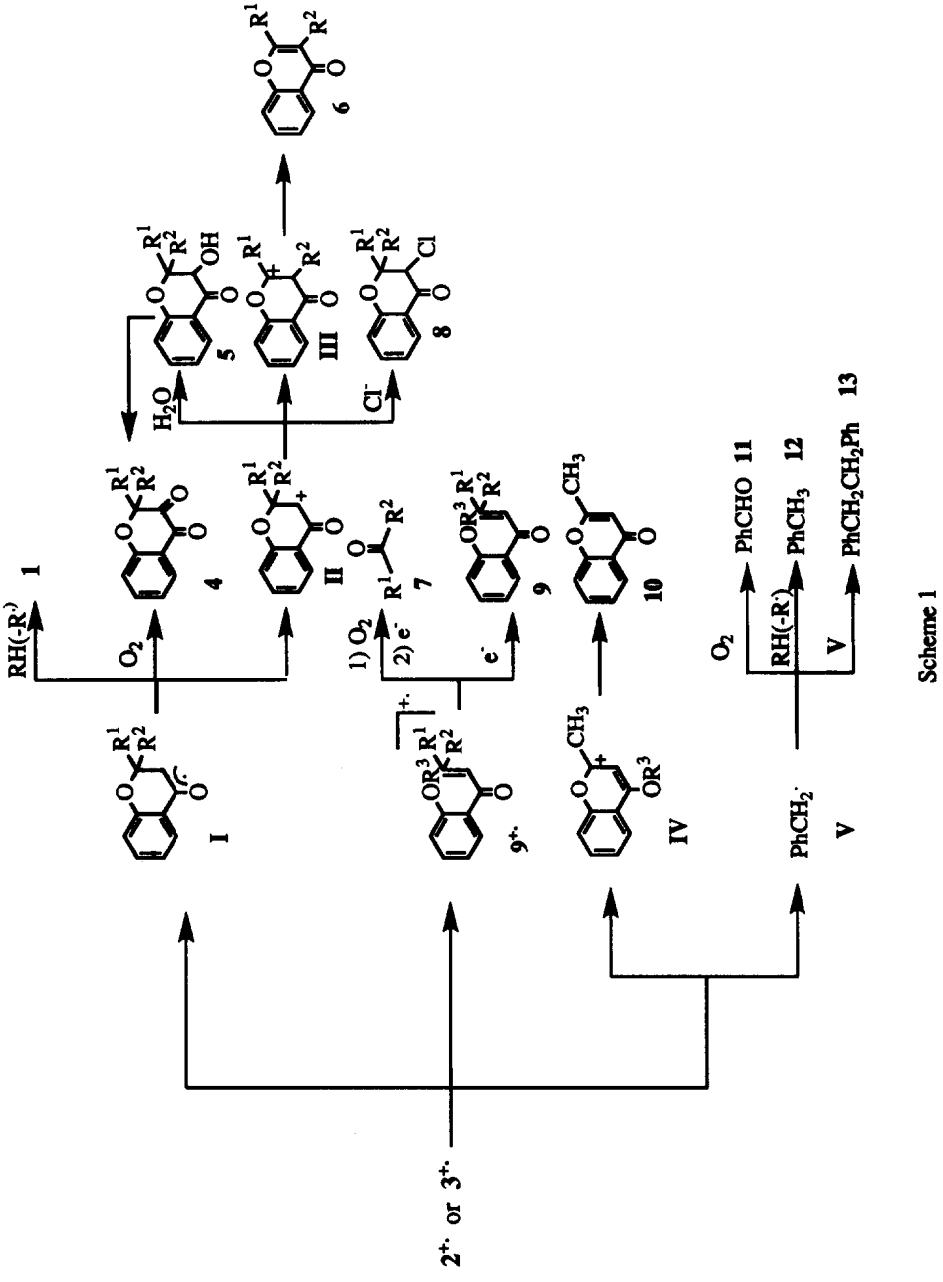
2 $R^3 = H$

3 $R^3 = COCH_3$

	R^1	R^2
a	CH_3	Ph
b	Ph	Ph
c	CH_3	CH_2Ph

RESULTS AND DISCUSSION

The required dihydrobenzopyrones **1a-c** were prepared by condensation of 2-hydroxyacetophenone with acetophenone,[7,8] benzophenone[9,10] or benzyl methyl ketone,[8] according to literature procedures.[11] Their enol acetates **3a-c** were obtained by treatment with isopropenyl acetate, in the presence of catalytic amounts of *p*-toluenesulfonic acid.[5] Attempts to perform direct oxidation of the dihydrobenzopyrones **1a,c** failed, but the 2,2-diphenyl derivative **1b** gave rise to reaction mixtures, whose composition depended upon the type of activation (chemical oxidation with cerium(IV) ammonium nitrate,[12,13] or photochemical oxidation using triphenylpyrylium tetrafluoroborate as sensitizer[4,5,14]). The results are summarized in Table 1. Taking into account the redox properties of **1a-c** ($E_{\mathbf{1a\text{-}c}} > 1.9$ V vs SCE, as measured by cyclic voltammetry), the observed oxidation of **1b** must have occurred through its enol tautomer,[6] by deprotonation or ring opening of the radical cation. The former process justifies formation of the diketone **4b**, through trapping of the intermediate radical **Ib** by oxygen. Further oxidation of this radical to the corresponding cation **IIb**, followed by 1,2-phenyl migration and subsequent deprotonation would afford the benzopyrone **6b**. Ring opening of **1b** would lead to the unsaturated hydroxyketone **9b** and ultimately to benzophenone (**7b**) through a well-established oxidative cleavage of the olefin moiety.[12] The above results are interesting in the framework of enzyme-mediated oxidation of flavanones, which is thought to operate on the enolic form and allows to formulate the formation of dihydroflavonols, flavones and isoflavones as occurring from a common intermediate (*a*-carbonyl carbocation), by way of nucleophilic trapping, deprotonation or 1,2-phenyl migration, respectively. Moreover, the highest oxidation level of the C_3-fragment of flavonoids corresponds to the flavonols, which are the enol tautomers of 3,4-diketones (in the case of compound **4b** enolization is prevented by 2,2-disubstitution). It is also worth mentioning that the fragmentation pattern of the radical cation **1b**$^{+\cdot}$ in the gas phase (EI-MS) reproduces to a



Scheme 1

Table 1. Electron Transfer Oxidation of Dihydrobenzopyrones and/or their Enol Acetates.

Substrate	Conditions[a]	Products (Yield, %)											
		1	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**
1b	A	6	-	10[b]	-	6[c]	23	-	43[d]	-	-	-	-
	B	81	-	-	-	-	3	-	10[d]	-	-	-	-
3a	A	20	2	56	-	-	5	-	-	-	-	-	-
	B	17	7	-	-	-	1	-	50[e]	-	-	-	-
	C	-	6	7	78[f]	-	-	-	-	-	-	-	-
3b	A	-	7	60[b]	-	-	23	-	7[d]	-	-	-	-
	B	-	-	-	-	-	-	-	98[g,h]	-	-	-	-
	C	20	-	-	-	-	25	42[h]	-	-	-	-	-
3c	A	-	2	56	-	-	-	-	-	32	5	-	-
	B	-	5	-	-	-	7	-	-	40	9	4	23
	C	24	3	-	-	-	12	-	-	41	-	-	-

[a] A: chemical oxidation with CAN, B: photochemical oxidation, using TPT as photosensitizer, C: electrochemical oxidation.
[b] Ref. 20. [c] Refs. 21 and 22. [d] R^3= H. [e] R^3= $COCH_3$. [f] Mixture of *E* and *Z* isomers (66 % and 12 %, respectively). [g] R^3= H: 96%, R^3= $OCOCH_3$: 2 %. [h] Ref. 23.

certain extent the behavior of the same species in solution. Thus, 1,2-phenyl migration to the cation **IIIb** (m/z 299) can be detected through the typical set of peaks corresponding to the system stilbene-phenanthrene (m/z 180-178), while ring opening to the hydroxyketone **9b** can be monitored by means of the peak corresponding to the saliciloyl cation (m/z 121).

In view of the lack of reactivity of the dihydrobenzopyrones **1a,c** under our experimental SET conditions, and the fact that the diphenyl derivative **1b** reacts *via* the enol tautomer, we decided to undertake an analogous study on the enol acetates **3a-c**. In a first stage we performed a cyclic voltammetric study on the three substrates **3a-c** and confirmed that they are much more easily oxidizable than the corresponding dihydrobenzopyrones, as expected (E_{3a}=1.58 V; E_{3b}=1.65 V; E_{3c}= 1.45 V *vs.* SCE).

Oxidation of the acetates **3a-c** was performed in three ways: i) chemically, by means of cerium(IV), ii) photochemically, using TPT as sensitizer and iii) electrochemically.[15] The results are summarized in Table 1. The diketones **4a,c** and the ketol **5a** (*Z* and *E*) were unknown. Confirmation of their structures was achieved by alternative synthesis: treatment of the corresponding dihydrobenzopyrones **3a,c** with lead tetraacetate, followed by acid-catalyzed methanolysis of the resulting α-acetoxy derivatives.[16] A part of the ketols thus obtained was oxidized by means of copper acetate/ammonium nitrate,[17] affording the diketones **4a,c.** An analytical sample of **4a** was obtained by treatment with *o*-phenylenediamine, wich led to the corresponding benzopyrano [3,4-b] quinoxaline.

The formation of the obtained products can be explained by breaking of the initially formed radical cations $3^{+\cdot}$, to give radicals **I** or carbenium ions **II**. The involvement of related species has been discussed above to justify the results obtained upon SET oxidation of dihydrobenzopyrone **1b**. Trapping of these intermediates by oxygen, adventitious water, chloride anion, or alternatively hydrogen abstraction (by **I**) from the solvent, would lead to the diketones **4**, the α-functionalized ketones **5** or **8** and the dihydrobenzopyrones **1**. The unsaturated ketones **9** are obviously generated by electrocyclic opening of the pyran ring, followed by transacylation and/or hydrolysis.[5,18] This process is analogous to the above mentioned transformation of **1b** into **9b** under similar conditions. Again, further oxidative cleavage of the double bond justifies the presence of acetophenone and benzophenone in the reaction mixtures.

The behavior of enol acetate **3c**, with a benzyl substituent at C_2, deserves a separate comment. Some of its products followed the general pattern (**4c, 7c**). A minor amount of 2-acetoxy-1-phenylpropene (**14**)[19] was also found among the SET products of **3c**, its origin being attributable to transesterification between the starting enol acetate and benzyl methyl ketone. This hypothesis is supported by the fact that when this ketone was treated with isopropenyl acetate, to obtain an authentic sample of **14** for comparison purposes, an appreciable degree of acyl exchange was observed at room temperature. Be this as it may, the most relevant SET products of enol acetate **3c** were those arising from fragmentation of the bond linking C_2 with the benzyl substituent, to give 4-acetoxybenzopyrylium ion (**IVc**) plus benzyl radical (**V**). Subsequent loss of acetyl cation (eventually trapped by traces of water, to give acetic acid) would lead from intermediate **IVc** to 2-methylchromone (**10**). On the other hand, benzyl radical must be the source of benzaldehyde (**11**), toluene (**12**) and 1,2-diphenylethane (**13**), through alternative pathways involving trapping by oxygen, hydrogen abstraction or dimerization, respectively. It is noticeable that further oxidation of the benzyl radical to the corresponding cation occurs to a low extent during anodic oxidation, as evidenced by the obtention of small amounts of benzyl acetate, the product of nucleophilic trapping by acetic acid.

As in the case of dihydrobenzopyrone **1b**, fragmentation of the radical cations **3a-c**$^{+\cdot}$ in the gas phase presented some analogies with the behavior in solution. Thus, cleavage of the carbonyl-oxygen bond can be detected in the MS through the acetyl cation (m/z 43) and the α-carbonyl cation (m/z 237, 299 or 251), while fragmentation of the bond linking C_2 with its substituents is observable through the 4-acetoxybenzopyrylium ions (m/z 203 or 265). The latter process occurs in the MS experiments with the three enol acetates, due to the high energy contents of the generated radical cations; however, in solution this cleavage only occurs in the case of the compound with a 2-benzyl substituent, due to the stability of the benzyl radical.

The results obtained in this work can be summarized as follows: i) dihydrobenzopyrones such as **1b** can undergo SET oxidation via their enol tautomers **2**, as suggested by thermodynamic considerations, as well as by comparison of the products with those obtained starting from the enol acetates, ii) under electron transfer conditions, a series of transformations have been observed to occur in compounds **3a-c**, analogous to processes of biosynthetic interest in the field of flavonoids, iii) cleavage of the radical cation, with loss of the substituent at C_2, is expected to occur when this substituent is able to stabilize a radical center, as in the case of the enol acetate **3c**, and iv) fragmentation of the radical cations **3a-c**$^{+\cdot}$ in the gas phase (MS) presents some analogies with the behavior of the same species in solution.

ACKNOWLEDGEMENTS

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EXPERIMENTAL SECTION

General.

Melting points are uncorrected. IR-Spectra were obtained by means of a GC-FTIR instrument; ν_{max} (cm^{-1}) is given only for the carbonyl absorption bands. ^1H NMR Spectra were measured in $CDCl_3$ at 400 MHz: chemical shifts are reported in δ (ppm) values, using TMS as internal standard. Mass spectra were determined under electron impact (or in the case of **3c**, by chemical ionization with methane as reactant gas); the ratios m/z and the relative intensities (%) are indicated for the significant peaks. UV Spectra were recorded in methanol; λ_{max} (nm) and log ε values (in brackets) are given for each absorption band. The combustion analyses and the exact mass of the compound **4c** were performed at the CSIC in Barcelona. Cyclic voltammograms were obtained with a programmable function generator, connected to a potentiostat. The working electrode was platinum, with a saturated calomel reference electrode separated from the test solution by a salt bridge containing the solvent/supporting electrolyte. The auxiliary electrode was platinum wire. The electrochemical cell used for controlled potential electrolysis was a conventional H-type design with separated anodic and cathodic compartments by a porous glass frit. Tetra-n-butylammonium hexafluorophosphate and methylene chloride were used as supporting electrolyte and solvent respectively in the electrochemical experiments. Isolation and purification of the products were done by flash column chromatography on silica gel Merck 60, using methylene chloride as eluent unless otherwise stated.

Preparation of dihydrobenzopyrone 1b

To a well stirred refluxing mixture of benzophenone (56.42 g, 310.0 mmol), anhydrous benzene (200 mL), sodium t-butoxide (23.52 g, 210.0 mmol) and t-butyl alcohol (80 ml), was slowly added o-hydroxyacetophenone (4.39 g, 32.2 mmol) in benzene (100 ml) . The resulting mixture was refluxed for 20 hours and then it was filtered under vacuum. The solid was suspended in 30% hydrochloric acid and subsequently extracted with methylene chloride, dried ($MgSO_4$) and concentrated. The yellowish solid (**9b**) was purified by means of a silica gel column. Part of this compound (1.00 g, 3.3 mmol) was cyclized in a two-phase system consisting of benzene (100 ml) and 25% aqueous ammonium hydroxide containing tetraethylammonium hydroxide 40% (5 ml, 13.6 mmol) as phase transfer catalyst. The reaction was monitored by GC and led to completion. After 7 days, the yield was nearly quantitative (overall yield 71%, lit[9] 36%). The product was purified in a silica gel column.

Preparation of dihydrobenzopyrones 1a and 1c

The required 2,3-dihydrobenzopyran-4-ones **1a** and **1c** were prepared from o-hydroxyacetophenone (4.90 g, 36.0 mmol) and the corresponding ketone (44.0 mmol) in the presence of pyrrolidine (0.71 g, 10.0 mmol), using toluene as solvent. The reaction mixture was allowed to stand for 24 h and then refluxed for 4 h, using a Dean-Stark device to facilitate the removal of water. The desired products were isolated by evaporation of the solvent at reduced pressure and further purification by means of a silica gel column, using hexane/methylene chloride mixtures as eluent. The yield obtained for **1a** and **1c** was 21 and 53% respectively (lit[8] 14 and 35%).

Preparation of cyclic enol esters 3a, 3b and 3c

The required enol esters **3a**, **3b** and **3c** were prepared by heating 2.0 mmol of the corresponding 2,3-dihydrobenzopyran-4-ones with 20.00 g (200.0 mmol) of isopropenyl acetate and 0.03 g (0.2 mmol) of p-toluenesulfonic acid during 2 h, under continuous removing of the resulting acetone by distillation. Isolation and purification of these products were done by flash column chromatography on silica gel.

General irradiation procedure

Solutions of 0.2 mmol of the substrates in 2 ml of methylene chloride were placed into pyrex test tubes surrounding a centrally positioned quartz cooling jacket containing a 125 W medium pressure Hg lamp, and irradiated for 4 h. A series of parallel experiments were carried out in the presence of catalytic amounts (10% molar ratio) of TPT. These reaction mixtures were filtered though silica gel before their analyses by GC-MS.

General procedure for oxidations with cerium(IV) ammonium nitrate

To a suspension of the substrates (0.2 mmol) and tetra-n-butylammonium hydrogen sulfate (10% molar ratio) in methylene chloride (15 ml) was added cerium(IV) ammonium nitrate (CAN) (0.33 g, 0.6 mmol). The mixtures were refluxed for 4 hours and filtered through a silica gel column before being analyzed by GC-MS.

General procedure for anodic oxidation

A solution of 0.2 mmol of substrate in methylene chloride (25 ml) was introduced in the anodic compartment of the above described electrochemical equipment and kept at room temperature under magnetic

stirring. A suitable potential (selected according to the peak potential previously established by CV) was applied by means of a potentiostat. The reaction was followed by plotting the current intensity *vs* time and stopped after 2F/mol of substrate had passed. The resulting solution was withdrawn from the anodic compartment, concentrated in vacuo and extracted with cold ethyl ether to remove the supporting electrolyte. The mixture was analyzed by GC-MS as in the previous cases.

Alternative syntheses of the ketols 5

The corresponding dihydrobenzopyrones **1** (5.0 mmol) were heated with lead tetracetate (2.21 g, 5.0 mmol) at 90 °C for 2 h. The crude reaction mixtures were solvolyzed with boiling methanol (20 ml) and concentrated hydrochloric acid (2 ml) for 1 h. After addition of water (100 ml), the mixture was extracted with methylene chloride. The organic phase was dried over $MgSO_4$ and concentrated under reduced pressure. Purification by column chromatography allowed to isolate the ketols **5**.

Alternative synthesis of the diketones 4

The corresponding ketols **5** (3.0 mmol), togheter with ammonium nitrate (0.24 g, 3.0 mmol) and cupric acetate (10% molar ratio), were heated at reflux temperature in 80% aqueous acetic acid (20 ml) for 90 min. After addition of water (100 ml), the mixture was extracted with methylene chloride. The organic phase was dried ($MgSO_4$) and concentrated under reduced pressure. Purification by column chromatography allowed to isolate the diketones **4**. In the case of **4a**, in order to obtain satisfactory elemental analysis, the diketone (1.3 mmol) was condensed with o-phenylenediamine (0.14 g, 1.3 mmol) in ethanol (50 ml) by refluxing the solution during 1 h. Then, water was added until a slight cloudiness persisted and the mixture was allowed to cool. The resulting benzopyrano [3,4-b] quinoxaline precipitated and was further purified by recrystallization from petroleum ether.

Alternative synthesis of the unsaturated ketone 9b (R^3=Ac)

A solution of 0.50 g (1.6 mmol) of 3,3-diphenyl-1-(2-hydroxyphenyl)-2-propen-1-one in 10 ml of acetic anhydride was refluxed for 2 h in presence of pyridine. The reaction mixture was poured onto ice/water (100 ml) and extracted with ether. The organic phase was dried ($MgSO_4$), concentrated and purified through a silica gel column.

Spectral and analytical data of the compounds.

4-Acetoxy-2-methyl-2-phenylbenzopyran (3a). 40%. Viscous oil; FTIR ν 1787; ^{1}H NMR δ 1.9 (s, 3H, -CH_3), 2.2 (s, 3H, -$OCOCH_3$), 5.8 (s, 1H, -CH=), 6.6-7.6 (m, 9H, aromatic H); MS m/z (%) 280 (3), 265 (17), 238 (1), 237 (5), 223 (100), 220 (2), 203 (1), 161 (17), 121(11), 77 (6), 43 (24); UV λ_{max} (log ε) 309 (3.5), 263 (3.7), 224 (4.3); Anal. Calcd for $C_{18}H_{16}O_3$: C 77.12; H 5.75. Found: C 77.08; H 5.78.

4-Acetoxy-2,2-diphenylbenzopyran (3b). 60%. Crystals, mp 83-84 °C; FTIR ν 1787; ^{1}H NMR δ 2.2 (s, 3H, -$OCOCH_3$), 6.0 (s, 1H, -CH=), 6.6-7.6 (m, 14H, aromatic H); MS m/z (%) 342 (13), 300 (12), 299 (16), 282 (10), 265 (8), 223 (100), 178 (18), 121 (15), 77 (6), 43 (23); UV λ_{max} (log ε) 310 (3.4), 265 (3.7), 230, sh (4.4); Anal. Calcd for $C_{23}H_{18}O_3$: C, 80.68; H, 5.30. Found: C, 80.58; H, 5.30.

4-Acetoxy-2-benzyl-2-methylbenzopyran (3c). 60%.Viscous oil; FTIR ν 1787; ^{1}H NMR δ 1.4 (s, 3H, -CH_3), 2.2 (s, 3H, -$OCOCH_3$), 3.0 (s, 2H, -CH_2Ph), 5.4 (s, 1H, -CH=), 6.7-7.3 (m, 9H, aromatic H); MS m/z (%) 234 (1), 203 (13), 161 (100), 121 (5), 91 (9), 43 (9); CIMS 295 (3); UV λ_{max} (log ε) 310 (3.6), 263 (3.8), 228 (4.4); Anal. Calcd for $C_{19}H_{18}O_3$: C, 77.53; H, 6.16. Found: C, 77.63; H, 6.11.

2-Methyl-2-phenyl-2,3-dihydrobenzopyran-3,4-dione (4a). Oil; FTIR ν 1751 , 1710; ^{1}H NMR δ 1.9 (s, 3H, -CH_3), 7.0-7.9 (m, 9H, aromatic H); MS m/z (%) 252 (4), 224 (80), 223 (35), 195 (48), 121 (87), 105 (35), 104 (61), 103 (100), 94 (96), 77 (54), 76 (35). 6-Methyl-6-phenylbenzopyrano [3,4-b] quinoxaline. Crystals, mp 120-121 °C. Anal. Calcd for $C_{22}H_{16}N_2O$: C, 81.46; H, 4.93; N, 8.64. Found: C, 81.40; H, 4.93; N, 8.66.

2-Benzyl-2-methyl-2,3-dihydrobenzopyran-3,4-dione (4c). Oil. FTIR ν 1745, 1707; ^{1}H NMR δ 1.6 (s, 3H, -CH_3), 3.1 (d, J=13.6 Hz, 1H, -CH_2-), 3.4 (d, J=13.6 Hz, 1H, -CH_2-), 7.0-7.9 (m, 9H, aromatic H); MS m/z (%) 266 (5), 160 (9), 147 (14), 121 (6), 117 (5), 115 (10), 91 (100), 76 (6), 65 (6). Exact mass 266.0948, Calcd for $C_{17}H_{14}O_3$ 266.0942.

Z-3-Hydroxy-2-methyl-2-phenyl-2,3-dihydrobenzopyran-4-one (Z-5a). Crystals, mp 105-106 °C ; FTIR ν 1710; ^{1}H NMR δ 1.9 (s, 3H, -CH_3), 4.0 (s, 1H, -CHOH), 4.8 (s, 1H, -CHOH), 6.9-7.7 (m, 9H, aromatic H); MS m/z (%) 254 (7), 225 (25), 147 (27), 134 (20), 121 (100), 105 (28), 103 (18), 92 (11), 91 (10), 77 (23), 65 (10); Anal. Calcd for $C_{16}H_{14}O_3$: C 75.57; H. 5.55. Found C 75.59 ; H 5.56.

E-3-Hydroxy-2-methyl-2-phenyl-2,3-dihydrobenzopyran-4-one (E-5a). Crystals, mp 84-85 °C; FTIR ν 1710; ^{1}H NMR δ 1.6 (s, 3H, -CH_3), 3.9 (s, 1H, -CHOH), 4.7 (s, 1H, -CHOH), 6.9-7.9 (m, 9H, aromatic H); MS m/z (%) 254 (9), 225 (32), 147 (34), 134 (26), 121 (100), 105 (28), 103 (22), 92 (11), 91 (10), 77 (24), 65 (8); Anal. Calcd for $C_{16}H_{14}O_3$: C 75.57; H 5.55. Found C 75.60 ; H 5.56.

E-2-Benzyl-3-hydroxy-2-methyl-2,3-dihydrobenzopyran-4-one (E-5c). Crystals, mp 76-77 °C; FTIR ν 1710; ^{1}H NMR δ 1.3 (s, 3H, -CH_3), 3.2 (m, 2H, -CH_2Ph), 3.8 (s, 1H, -CHOH), 4.3 (s, 1H, -CHOH), 6.9-7.8 (m, 9H, aromatic H); MS m/z (%) 268 (8), 177 (77), 176 (72), 149 (54), 121 (100), 103 (29), 92 (26), 91 (67), 77 (28), 65 (34); Anal. Calcd for $C_{17}H_{16}O_3$: C 76.10; H 6.01. Found C 76.31; H 6.10.

3-Phenyl-1-(2-acetoxyphenyl)-2-buten-1-one (9a). Oil; FTIR ν 1787, 1677: ^{1}H NMR δ 2.2 (s, 3H, -$OCOCH_3$), 2.6 (s, 3H, CH_3), 6.9 (s, 1H, -CH=), 7.1-7.8 (m, 9H, aromatic H); MS m/z (%) 280 (1), 265 (15), 266(3), 223 (100), 161 (26), 121 (14), 120 (5), 115 (12), 91 (6), 77 (4), Anal. Calcd for $C_{18}H_{16}O_3$: C 77.12; H 5.75. Found C 77.14; H 5.77.

3,3-Diphenyl-1-(2-acetoxyphenyl)-2-propen-1-one (9b). Crystals, mp 81-82 °C; FTIR ν 1787, 1678: ^{1}H NMR δ 2.2 (s, 3H, -$OCOCH_3$), 6.9 (s, 1H, -CH=), 7.0-7.7 (m, 14 H, aromatic H); MS m/z (%) 342 (11), 300 (17), 299 (23), 265 (10), 223 (100), 178 (50), 165 (28), 152 (20), 121 (14), 43 (49); Anal. Calcd for $C_{23}H_{18}O_3$: C 80.68; H 5.30. Found C 80.66; H 5.33.

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