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REGIOSELECTIVE SYNTHESIS OF 2-ARYLIDENE COUMARAN-3-ONES BY DYE-SENSITIZED PHOTOOXYGENATION OF 2-HYDROXYPHENYL-STYRYLKETONES IN THE PRESENCE OF SODIUM DODECYL SULPHATE

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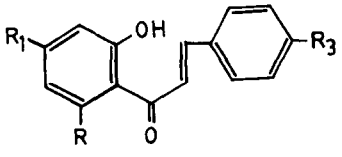
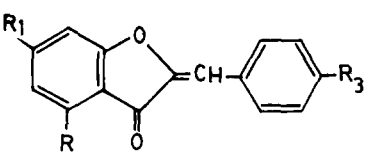
Abstract 2'-Hydroxyphenylstyrylketones when subjected to dye- sensitized photooxygenation in the presence of sodium dodecylsulphate (8×10^{-3}M) in methanol, yielded the corresponding oxidatively cyclized products, i e , 2-aryl idenecoumaran-3-ones and 2-phenyl-3-hydroxy-4H-benzopyran-4- ones It has been observed that the nature of the substituents on the styryl moiety plays an important role in determining the preponderance of 2-arylidene coumaran-3-ones over 2-aryl-3-hydroxy- 4H-benzopyran-4-ones The reaction has been observed to be affected by the hydrophobic environment created by anionic micelles A plausible mechanism of the reaction is described.

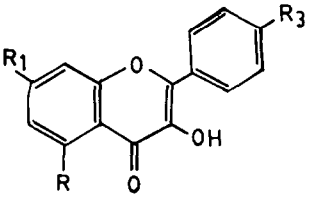
INTRODUCTION

Though synthetic organic chemistry has traditionally been confined to reactions in the homogeneous media, there have been increasing awareness about the utility of heterogeneous conditions for effecting difficult transformations in recent years.[1,2] Heterogeneity offers microenvironment that allows the organization of reactants and products in some specific ways which may be regioselective, regrospecific or enantioselective depending upon the type of heterogeneous system undertaken.[1] Organised molecular assemblies offer a clear cut advantage over random heterogeneity and such molecular organisation can be achieved by employing inorganic constrained systems or organic molecular assemblages [3-5] It has been observed that surfactants are the most readily available molecules which aggregate to form molecular ensembles capable of concentrating or orienting the reagents and substrates in a specific way [2,6-8] Though surfactant aggregates are structurally poorly defined and are dynamic in nature, they can be employed to selectively functionalize, oxidise or photolyse the reactants to achieve

desired targets with enhanced selectivity and rates of reactions [1,2] In this paper, we describe over synthetically useful results on the photooxygenation of 2'- hydroxyphenyl styryl ketones in the presence of anionic and cationic surfactants which has led to a new synthesis of 2-arylidene-Coumaran-3-ones Though several syntheses of these compounds are available,[10-16] this is the first report of their visible light induced photochemical synthesis







1 R_1 = OCH_3, R_2=R_3=H

2. R_1=R_2=H, R_3=OCH_3

3 R_1=R_2=OCH_3, R_3=H

4 R_1=R_3=OCH_3=OCH_3, R_2=H

5. R_1=R_2=R_3=OCH_3

6 R_1=OCH_3,R_2=H, R_3=NO_2

7. R_1=OCH_3, R_2=R_3=H

9 R_1=R_2=H, R_3=OCH_3

10. R_1=R_2=OCH_3, R_3=H

12 R_1=R_3=OCH_3, R_2=H

13 R_1=R_2=R_3=OCH_3

8. R_1=OCH_3, R_2=R_3=H

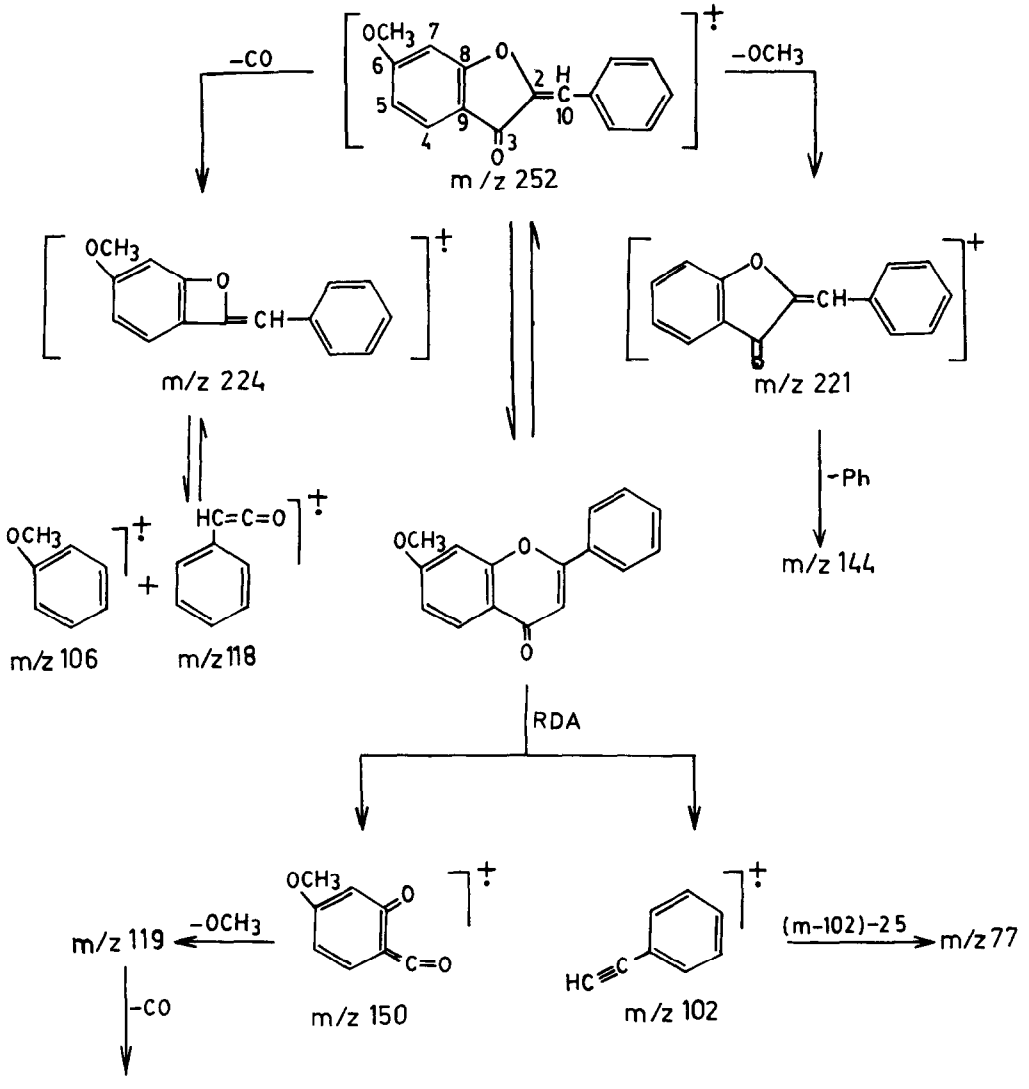
11 R_1=R_2=OCH_3, R_3=H

14 R_1=OCH_3, R_2=H, R_3=NO_2

RESULTS AND DISCUSSION

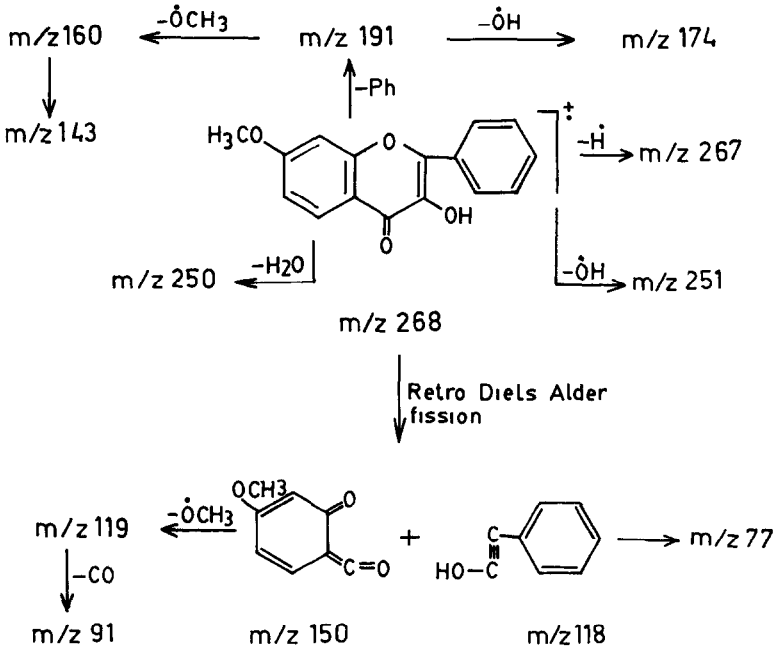
When 2'-hydroxy-4'-methoxyphenylstyrylketones, 1 was subjected to dye sensitized photooxygenation according to the procedure given in the experimental section, a mixture of two compounds A and B were obtained which could be resolved by column chromatography over silica gel. Compound A showed strong absorption bands at ν_{max} 1710 (C=O) and 1170 (-O-) cm^{-1} in its IR spectrum while its PMR spectrum exhibited a three proton singlet at δ 3 76 which could be assigned to the methoxy protons and a singlet at δ6 59 (1H) which could be attributed to the C-10 proton The singals for the aromatic protons at position, C-10, C-4 and C-7 appeared at 6 59(s,1H,=CH), 7 49(dd,1H, J=3.0 and 8 6 Hz, C-4-H) and 7.81 (1H,d, J=8.6 Hz) as a singlect, double doublet and a doublet respectively The other aromatic protons appeared as a multiplet appearing between 6 45 to 7 42 (5H) In its mass spectrum, it showed a molecular ion peak at m/z 252 which successively lost a methoxyl and a phenyl radical to give intense fragments at m/z 221 and 144 The peak at

m/z 224 could be observed due to the loss of a carbon monoxide from the M^+ ion. The ion peaks at m/z 106 and 118 could be explained due to the cleavage of $[M-CO]^+$ ion. The retro-Diels-Alder fragments at m/z 150 and m/z 102 along with other prominent fragments depicted in scheme-1 confirmed the structure of **A** as 2-benzylidene-6-methoxycoumaran-3-one (**7**), which was further confirmed by its direct comparison with an authentic sample



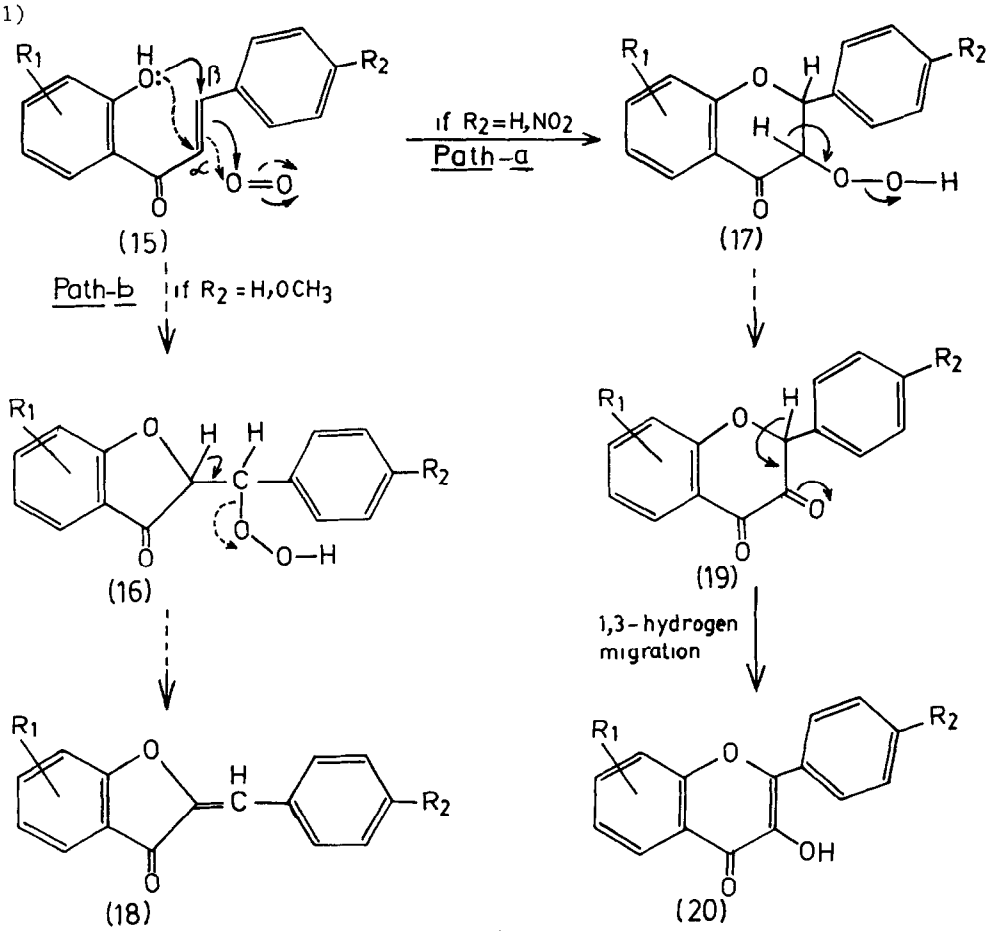
Scheme-1

Compound B recrystallized from methanol as light yellow needles, analyzed for $C_{16}H_{12}O_4$ and showed strong absorption bands at ν_{max}(KBr) 3400 (OH), 1610 (C=C) and 1170 (-O-) cm^{-1} in its IR spectrum. Its PMR spectrum showed a three proton-singlet at 3.85 for the methoxyl protons and a deuterium exchangeable singlet at δ 9.23 (1H) which could be accounted for by the hydroxyl proton The singlet for the C-5, C-6 and C-8 protons could be observed at δ 7 95 (d,1H,J=8.6 Hz, C-5-H), 7 58 (dd, 1H, C-6-H, J=3 1 Hz and 8.6 Hz) and 7.25 (d, 1H, J=3.1 Hz, C-8-H)) as a doublet, a double doublet and a doublet respectively. In its mass spectrum, it showed a molecular ion peak at m/z 286 which lost a hydroxyl radical to give intense peak at m/z 251. The peaks at m/z 220 and 143 could be attributed to the successive loss of a methoxyl and phenyl radical respectively Two retro Diels- Alder fragments were observed at m/z 150 and 118, whereas the intense peak at m/z 119 and 91 could be assigned to the successive loss of a methoxyl radical and a CO molecule from the fragment at m/z 150. The other intense fragments as shown in scheme-2 confirmed the structure of compound B as 2-phenyl-3-hydroxy-4H-1- benzopyran-4-one, 8.



Scheme-2

Similar experiments with 2'-hydroxyphenyl-4-methoxy-styrylketone 2 yielded 2-(4'-methoxybenzylidene)-coumaran-3-one, 9 in 72% yield, while 2'-hydroxy-4',6'-dimethoxy phenylstyrylketone, 3 gave a mixture of two compounds, i e , 2-benzylidene-4,6-dimethoxycoumaran-3-one, 10 and 2-phenyl-3-hydroxy-5,7-dimethoxy-4-H-1-benzopyran-4-one, 11 in 30% and 43% yield respectively. 2'-Hydroxy-4'-methoxy-phenyl-4-methoxy styrylketone, 4 and 2'-hydroxy-4,6'-dimethoxy-phenyl-4-methoxystyrylketone, 5 gave the corresponding 2-(4'-methoxybenzylidene)-4-methoxycoumaran-3-one, 12 and 2-(4'-methoxy-benzylidene)-4,6- dimethoxy coumaran-3-one, 13 in 76% and 63% yield respectively In the case of 2'-hydroxy-4'-methoxyphenyl-4-nitrostyrylketone, 6 only 2-(4'-nitrophenyl)-3-hydroxy-7-methoxy-4H-1-benzopyran-4H-1-benzopyran-4-one, 14 in 63% yield was obtained (Table 1)



Scheme-3

Table 1 Reaction products from the photooxygenation of 2'-hydroxyphenyl styryl ketones

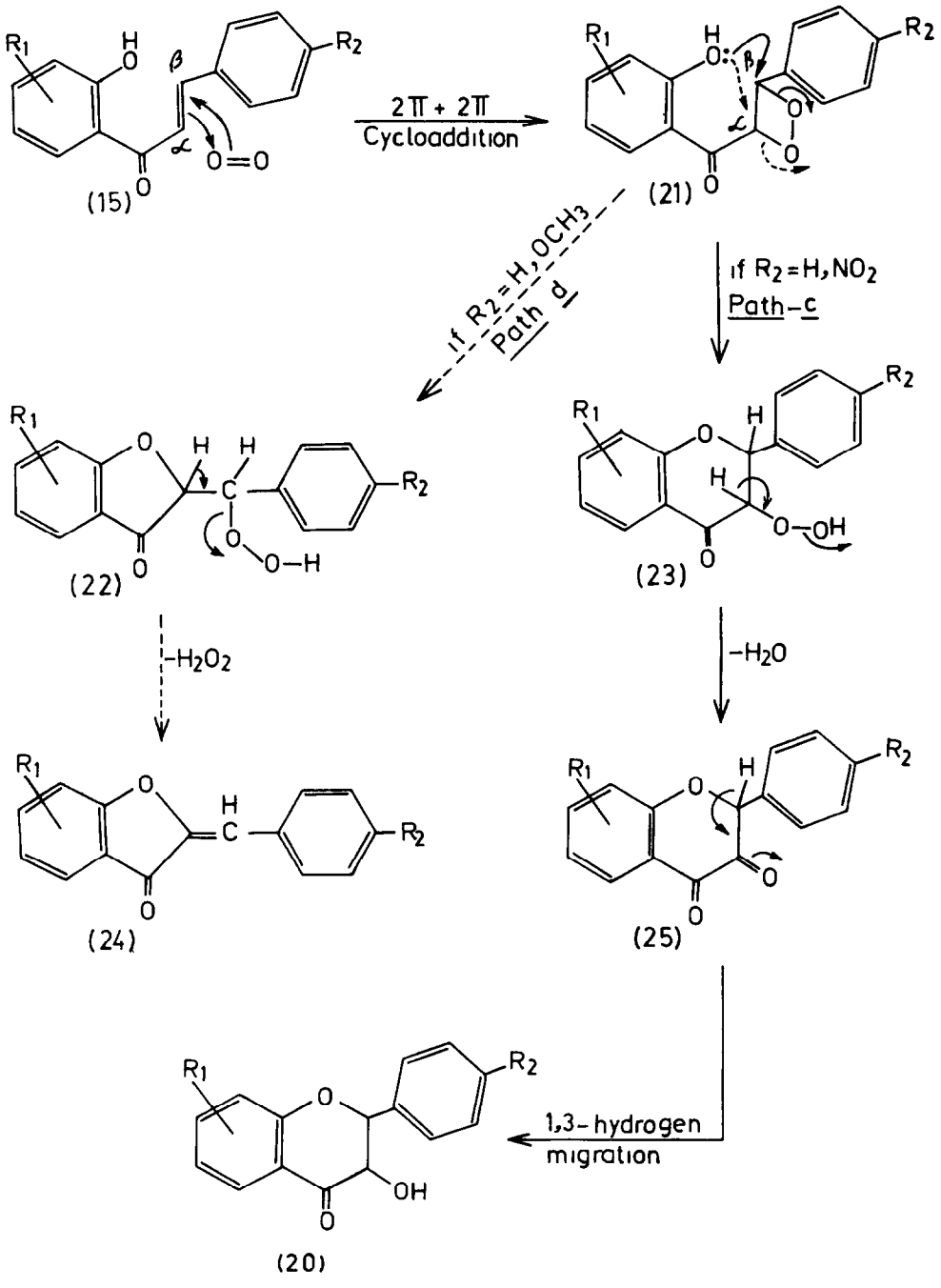
Substrate	Reaction Time (hr)	Products Obtained[a-d] 2-arylidene coumaran-3-ones m.p (°C)	Yield (%)	2-phenyl-3-hydroxy-4H-1-benzopyran-4-one m.p (°C)	Yield (%)
1	53	7 143-4	36	8 137	32
2	43	9 134-5	73	- -	
3	47	10 156	31	11 178	42
4	36	12 132	76	- -	-
5	48	13 158	79	- -	-
6	41	- -	-	14 172	72

a. All the reactions were carried out in methanol using sodiumdodecylsulphate ($x10^{-3}M$) for creating hydrophobic environment. The yields of products were lower at lower concentrations of sodium dodecyl sulphate (SDS) while at higher concentrations of SDS, the products were difficult to isolate from the reaction mixture at room temperature.

b All the compounds were completely characterized by their physical, chemical and spectroscopic (IR, PMR and mass data)

c The yields are unoptimized and are based upon the concentration of phenylstyryl ketones consumed

d The melting points are uncorrected and taken in open capillaries


2π + 2π
Cycloaddition
(15)
(21)
if R2=H, OCH3
Path d
if R2=H, NO2
Path-c
(22)
(23)
-H2O2
-H2O
(24)
(25)
1,3-hydrogen
migration
(20)

Scheme-4

That these reactions may be taking place via singlet oxygen was inferred from repeat experiments in the absence of a sensitizer (methylene blue) when the starting materials (phenylstyrylketones) were recovered unchanged and also carrying out the reaction in the presence of catalytic amount of 1,4-diaza(2,2,2) bicyclooctane (DABCO, a well known singlet oxygen quencher)[17-19], when 2-arylidene coumaran- 3-ones and 2-phenyl-3-hydroxy-4H-1-benzopyran-4-ones could not be detected in the reaction mixture even after 120 h (as revealed by TLC)

The formation of 2-arylidenecoumaran-3-ones and 2-aryl- 3-hydroxy-4H-1-benzopyran-4-one from 2'-hydroxyphenyl- styrylketones can be explained by two possible mechanisms as depicted in schemes-3 and 4 Scheme-3 envisages the attack of the 2'-hydroxyl group either at the -carbon (as shown in path-a) or on the -carbon atom (as shown in path-b) of 2'-hydroxyphenylstyrylketone (15) to give a hydroperoxide in termediate (16 and 17) which eliminates a hydrogen peroxide or a water molecule to give 2-arylidene-coumaran-3-ones (18) and 2-aryl-hydroxy-4H-1-benzopyran-4-ones (20) respectively. We were unsuccessful to isolate any free hydroperoxide and 2-aryl-3-hydroxy-4H-1-benzopyran-4-ones, and 2-arylidenecoumaran-3-ones (or both) were formed directly under the experimental conditions The hydroperoxide intermediate, however, could be inferred from the positive KI-AcOH test carried out on residue obtained after evaporation of solvent of different intervals of reaction

In scheme-4, the formation of a dioxetane intermediate 21 via 2 +2 -cycloaddition of singlet molecular oxygen has been suggested which being unstable can open up according to two pathways or c and d to give the hydroperoxides 22 and 23 respectively which lead to the 2-arylidene coumaran-3-one (24) and 2-aryl-3-hydroxy-4H-1-benzopyran-4- ones (20)

Though mechanistic details are not yet unambiguous, it has been observed that formation of 2-arylidene coumaran-3-ones and 2-aryl-3-hydroxy-4H-1-benzopyran-4-ones from 2'-hydroxyphenylstyrylketones mainly depend upon the substituents on the styryl moiety. For instance when the styryl moiety was unsubstituted as in the case of 2'-hydroxy-4'-methoxy phenylstyrylketones and 2'-hydroxy-4,5'-dimethoxyphenyl-styryl ketone, both types of products, i e., 2-arylidene-coumaran-3-ones and 2-aryl-3-hydroxy-4H-1-benzopyran-4-ones were obtained

The reasons for such a marked dependence of products on the styryl substituents can be many and some of these are being investigated in our laboratories. Since it is well known that singlet oxygen reacts only with electron rich olefins and its reactions with olefins containing electron withdrawing substituents (such as the aroyl group in the present case) are rare, it seems possible that the aryl group at -position is compensating for the electron deficiency on the double bond[9] If this is so then we would see a very profound effect of the substituent at position ortho and para in the styryl part of the reactants. In fact such effects have been observed as is evident from the data presented in Table 1. The intramolecular attack by the 2'-hydroxyl group can in principle take place either on the α- or β-carbon of the arylstyrylketones to yield the 2-arylidene-coumaran-3-ones or 2-aryl-3-hydroxy -4H-1-benzopyran-4-ones respectively. However, if one considers selectivity, this attack is governed by the electron density at the -carbon atom. The particular mode of attack is facilitated by the inductive and resonance effects of substituent present at position 4 the α-position preferably suffers a nucleophilic attack by the 2'-hydroxyl group and therefore leads to the 2-arylidenecoumaran-3-ones This is further supported by the fact that when the styryl moiety is substituted by electron withdrawing functionality (as in the case of 2'-hydroxy-4-nitrostyrylketone), there is a preponderance of 2-aryl-3-hydroxy-4H-1-benzopyran-4-ones Alternatively (may be more plausibly) the mechanism of the reaction may involve electron transfer processes sensitized by methylene blue Details of this possibility however are being washed out and conclusions will be reported later

It has been observed that the reaction of 2'-hydroxyphenlstyryl-ketones with singlet molecular oxygen in the presence of anionic sodium dodecyl sulphate in methanol does not lead to the degradation products as observed previously in the absence of this surfactant [18,19] This obsrervation supplements the notion that the hydrophobic environment created by the surfactant is helpful in concentrating the intermediates in a hydrophobic and restricted small volume created by aggregation of surfactant molecules so as to allow them to cyclise rather than allowing them to drift away to yield degradation products This is borne out by the fact that the maximum yields of cyclised products are obtained when surfactant concentration was of the order of 8×10^{-3} M. This concentration

is within the critical micelle concentration (cmc) range of SDS which is known to form micelle like anionic aggregates in polar solvents It is also likely that the reactant itself is embedded in the hydrophobic micellar core in a specific way. Singlet oxygen generated outside the micellar core by interaction of oxygen with excited state of dye (as a result of absorption of light) can then diffuse into the hydrophobic core and react with the substrate to yield the products The increase in yield of cyclised products in surfactants than in simple solvent systems may be due to the increased life time of singlet oxygen in hydrophobic solvents as compared to that in polar solvents The variation in nature of the products with type of substituents on the styryl moeity of hydroxyphenylstyryl- ketones may also be due to the stabilization of the preferred conformation of intermediates in the micellar core This is supported by the observation that at lower concentrations of SDS, the yield of cyclized products was much less while at higher concentrations of SDS the products were difficult to isolate. It has also been observed that the cationic surfactant such as cetyltrimethylammonium bromide (CTAB) do not yield the cyclized products and starting materials could be recovered from the reaction mixture even after 80 h of the reaction.

Though, the detailed study on the orientational and other effects of micellization in these dye-sensitized photooxygenation reactions are a subject of further work in our laboratory, it is obvious from our results that regioselectivity can be achieved in singlet oxygen reactions by using appropriate hydrophobic environment and this can be fruitfully exploited to achieve synthetic targets Further work on dye-substrate surfactant-oxygen interactions is in progress and will be reported separately

EXPERIMENTAL SECTION

Melting points were taken in open capillaries on an electric melting point apparatus (Adair Dutt) and are uncorrected IR spectra were recorded on 5-DX-Nicolet FT-IR spectrophotometer on KBr discs PMR spectra were taken on Nicolet-99 55 Mz Jeol-FT NMR spectrometer in solution form in $CDCl_3$ using tetramethyl silane as an internal standard and the values are reported in scale The mass spectra were recorded on JMS-D-300 Jeol mass spectrometer while uv spectra were obtained on Hitachi-330 spectrophotometer using

methanol as a reference solvent. The time allowed for completion of the reaction and purity of the compounds were controlled by means of TLC performed on silica gel (BDH, Bombay) plates using iodine for visualizing the spots. Column chromatography was performed on silica gel and organic solvents were usually dried over anhydrous sodium sulphate. The solvents used were freshly distilled and purified before use. Petroleum ether refers to the one with the boiling range of (60-80)°C.

GENERAL REACTION PROCEDURE

2'-Hydroxyphenylstyrylketones 1-6 (0.3 mM) were dissolved in a standard solution of sodium dodecyl sulphate (20 ml, $8x10^{-3}$M) in methanol and a catalytic amount of methylene blue (5 mg) was added to it The reaction mixture was irradiated with tungsten filament lamps (4x100 watt) while a stream of oxygen gas was continuously passed through the solution A potassium chromate screen (3% solution) was placed in between the lamps and the solution to be photooxygenised to filter off the possible U V radiations from the lamp The progress of the reaction was monitored by TLC using different solvent systems as described under each compound When the reaction was complete (as revealed by TLC), it was stopped and the mixture was distilled under reduced pressure The residue was extracted with chloroform (3x50 ml) and ethyl acetate (3x25 ml) In order to remove a small amount of methylene blue which came along with the extracts, silica gel (0.2 g) was added to the total extract The organic extracts were combined and concentrated under reduced pressure and the residue was subjected to column chromatography over silica gel (30 g) and eluted with solvents with increasing polarity either alone or in combination as mentioned for particular compounds The isolated compounds were further crystallized from an appropriate solvent as mentioned against each compound before subjecting them to physical, chemical and spectroscopic (IR, UV, PMR and mass) analysis

REACTION PRODUCTS FROM 2'-HYDROXY-4'-METHOXYPHENYL STYRYL KETONE

2-Benzylidene-7-methoxycoumaran-4-one,7 (36%) was eluted from benzene-chloroform (4 3) and crystallized from methanol as yellow prisms, m.p. 133-4°C, (Lit m.p 135°C) IR(KBr) ν_{max} 1710 (C=O), 1600 (C=C) and 1170 (-O-) cm^{-1} PMR($CDCl_3$, δ) 3 76(s, 3H, OCH_3),

6.59(s, 1H, C-10-H), 7.81(d, 1H, J=8.6 Hz, C-4-H), 6.45-7 42(m, 5H, Ar-H), 7.23(d, 1H, J=3.0 Hz, C-7-H), 6.45-7.42(m, 5H, Ar-H). MS, m/z (% abundance). 252 (16.2), 251 (32.7), 224 (71.2), 221 (53.8), 150 (100), 149 (32.6), 144 (36.6), 120 (25 0), 199 (32 7), 118 (11 2), 106 (51.9), 102 (18.2), 91 (25.0), 77 (71 2) Analysis (Found. C, 75.91; H, 4.68; $C_{16}H_{12}O_3$ requires, C, 76.19 and H, 4 76%)

2-Phenyl-3-Hydroxy-7-methoxy-4H-1-benzopyran-4-one, 8 (32%) was eluted from chloroform-methanol (5·2) and crystallized from methanol as light yellow needles, m.p 137°C (Lit m.p 137°C). IR(KBr)· ν_{max} 3400(-OH), 1670 (C=O), 1610 (C=C), 1170 (-O-) cm^{-1}, PMR ($CDCl_3$,δ). 9 23(s, 1H, exchangeable with D2O, OH). 3 85(s, 3H, OCH_3), 7 95 (d, 1H, J=8 6 Hz, C-5- H), 7.58 (dd, 1H, J=3.1 and 8.6 Hz, C-6-H), 7 25 (d, 1H, J=3.1 Hz, C-8-H), 76 90-7 83 (m, 5H, Ar-H). MS. m/z (% abundance) 268 (13.2), 251 (52 4), 250 (14.4), 220 (13 4), 191 (68 2), 174 (15.2), 160 (10.1), 151 (65 2), 150 (100), 143 (13.7), 120 (15.6), 119 (32 4), 118 (62 4), 91 (15.2), 77 (71.6). Anal. Calcd (Found C, 71 23, H, 4 37, $C_{16}H_{12}O_4$ requires C, 71.64 and H, 4 47%)

REACTION PRODUCTS OF 2'-HYDROXYPHENYL-4-METHOXYSTYRYL KETONE

2-(4'-methoxybenzylidene)-coumaran-3-one, 9 (73%) was crystallized from methanol as yellow needles, m.p. 134-5°(Lit m p. 134°C) IR (KBr) ν_{max} 1695 (C=O), 1610 (C=C), 1170 (-O-) cm^{-1}, PMR ($CDCl_3$,δ) 3 94 (S, 3H, OCH_3). MS. (% abundance) 252 (17 7), 251 (43.5), 224 (32 3), 221 (75 0), 120 (100), 107 (50 2), 92 (62.7), 91 (31.7), 77 (41.7), 76 (15.3) Anal. Calcd (Found C, 75.91, H, 4.72; $C_{16}H_{12}O_4$) requires C, 76.19 and H, 4 7%).

REACTION PRODUCTS OF 2'-HYDROXY-4'-METHOXYPHENYL-4-STYRYL KETONE

2-(4'-methoxybenzylidene)-6-methoxy coumaran-3-one, 12 (76%) was crystallized from benzene-methanol (4 1) as yellow needles, m p 132° (Lit m p 133°C) IR(KBr) ν_{max} 1690 C=O), 1620 (C=C), 1170 (-O-), PMR ($CDCl_3$, δ) 3 81(bs, 6H, 2xOCH_3) 6.65 (s, 1H, C-1H), 6.54 (m, 7H, Ar-H) MS m/z (% abundance) 282 (32.5), 281 (29.4), 254 (19 4), 251 (34.9), 175 (32.6), 151 (100), 150 (15.0), 148 (14.6), 144 (32.4), 132 (15 6), 120

(24 6), 119 (39 4), 106 (32 4), 101 (12.3), 91 (39.4), 77 (51 6), 76 (64.4), Anal. Calcd (Found C, 71.84, H, 4 81, $C_{17}H_{14}O_4$ requires C, 72.34 and H, 4.96%).

REACTION PRODUCTS OF 2'-HYDROXY-4'-METHOXYPHENYL-4-METHOXY STYRYL KETONE

2-(4'-methoxybenzylidene)-6-methoxy coumaran-3-one, 12 (76%) was crystallized from benzene-methanol (4 1) as yellow needles, m.p 132°C (Lit m p 133°C) IR KBr. ν_{max} 1690 (C=O), 1620 (C=C) and 1170 (-O-), PMR ($CDCl_3$, δ) 3 81 (bs, 6H, 2xOC$\underline{H}_3$), 6.65 (s, 1H, C-1$\underline{H}$), 6 54-7 (m, 7$\underline{H}$, Ar-$\underline{H}$) MS m/z (% abundance) 282 (32.5), 281 (29.4), 254 (19 4), 251 (34 9), 175 (32 6), 151 100), 150 (15.0), 148 (14.6), 144 (32.4), 132 (15.6), 120 (24 6), 119 (39.4), 106 (32 4), 101 (12 3), 91 (39 4), 77 (51.6), 76 (64 4), Anal. Calcd. (Found C, 71.80, H, 4 78, $C_{17}H_{14}O_4$ requires C, 72 34 and H, 4 96%)

REACTION PRODUCTS OF 2'-HYDROXY-4',6'-DIMETHOXYPHENYLSTYRYL KETONE

2-Benzylidene-4,6-dimethoxycoumaran-3-one, 10 (31%) was eluted from benzene-chloroform (9 2) and crystallized from methanol as light yellow needles, m.p 156°C (Lit m p. 157°C), IR (KBr) ν_{max} 1690 (C=O), 1590 (C=C) and 1170 (-O-) cm^{-1}, PMR ($CDCl_3$),δ3.93 (bs, 6$\underline{H}$, 2xOC$\underline{H}_3$), 6 72 (s, 1$\underline{H}$, C-10-$\underline{H}$), 7 45 (d, 1H, J=2.5 Hz, C-5-$\underline{H}$), 7.26 (d, 1H, J=2.5 Hz), 6 69-7.29 (m, 5H, Ar-$\underline{H}$), M.S m/z (% abundance) 282 (23.7), 281 (52.8), 254 (71 7), 251 (14 2), 221 (23 1), 205 (72 0), 180 (100), 174 (32.4), 152 (18 2), 151 (33 8), 149 (60 4), 136 (39.6), 121 (18.0), 119 (23.4), 102 (50 6), 77 (88 6). Anal Calcd (Found C, 72 03, H, 4 82, $C_{17}H_{14}O_4$ requires C, 72 34 and H, 4 96%)

2-Phenyl-3-hydroxy-5,7-dimethoxy-4H-1-benzopyran-4-one, 11 (42%) was eluted from a mixture of chloroform-methanol (3 1) and crystallized from methanol as light yellow needles, m p 178°C (Lit. m p. 179-80°C) IR (KBr) ν_{max} 3420 (-OH), 1670 (C=O), 1620 (C=C), and 1170 (-O-) cm^{-1} PMR ($CDCl_3$,δ) 3 86 (bs, 6H, 2xOC$\underline{H}_3$), 7 26 (d, 1H, J=2 5 Hz, C-8$\underline{H}$), 4 46-7 62 (m, 5H, Ar-$\underline{H}$) Anal Calcd (Found C, 68 02, H, 4 60, $C_{17}H_{14}O_5$ requires C, 68 45 and H, 4 69%)

REACTION PRODUCT OF 2'-HYDROXY-4',6'-DIMETHOXYPHENYL-4- METHOXY STYRYL KETONE

2-(4'-methoxybenzylidene)-4,6-dimethoxycoumaran-3-one, 13 (79%) was crystallized from benzene-methanol (4 1) as yellow needles, m p 158°C (Lit m p 157-8°C) IR (KBr) ν_{max}.

1720 (C=O), 1605 (C=C), and 1170 (-O-) cm^{-1} PMR ($CDCl_3$, δ) 3.62-3.84 (bs, 9H, 3xOC<u>H</u>$_3$), 7.51 (dd, 1H, J=2.6 Hz, C-5<u>H</u>), 6.72-7.18 (m, 4H, Ar-<u>H</u>) Anal. Calcd (Found C, 68.45, H, 5.01, $C_{18}H_{16}O_5$ requires C, 69.23 and H, 5 13%)

REACTION PRODUCT OF 2'-HYDROXY-4'-METHOXY PHENYL-4-NITRO- STYRYL KETONE

<u>2 - (4-nitrobenzylidene (- 3- hydroxy- 7 -methoxy- 4H - 1 -benzopyran-4-one</u>, <u>14</u> (72%) was crystallized from methanol as light yellow needles, m.p 172°C, IR (KBr) $\nu_{max.}$ 3400 (-OH), 1665 (C=O), and 1600 (C=C), 1540, 1350 (-NO_2) and 1170 (-O-) cm^{-1} PMR ($CDCl_3$, δ), 3 83 (s, 3H, OC<u>H</u>$_3$), 9.41 (bs, 1H, exchangeable with D_2O, C<u>H</u>) 7.25 (d, 1H, J=2 8 Hz), C-8-<u>H</u>) 7 40 (dd, 1H, 2 8 and 9 4 Hz, C-6-<u>H</u>), 7.91 (d, 1H, J=9.4 Hz, C-5-<u>H</u>), 6.65-7 77 (m, 4H, Ar- <u>H</u>) Anal Calcd (Found C, 60 82, H, 3.47, H, 4 39 requires, C, 61 34, H, 3 51 and N, 4 47%).

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