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# DYE SENSITIZED PHOTOOXYGENATION OF IMIDAZOLIN-2-ONES

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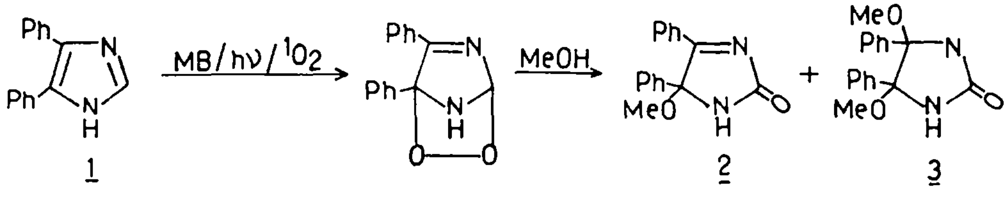
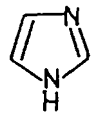
**ABSTRACT:** Imidazolin-2-ones(13-18) on photooxygenation in the presence of methylene blue yielded the corresponding diacylureas as the only products isolated at room temperature. The rate of photooxygenation followed the order 16>17>18>13>14>15. The reaction was also studied at pH 4.4, 6.0 and 9.2 as well as in solvents of varying dielectric constants to explore the nature of the intermediates. It appears that the reaction involves the formation zwitterionic perepoxides leading to dioxetanes which decompose to yield diacylureas.

Photoinactivation of enzymes and other biomolecules is a subject of intense research activity. One of the approaches adopted to understand such inactivation is the study of reactions of singlet oxygen with heterocyclic compounds and heterocyclic adjunct in complex biologically active macromolecules[1,2]. The study of destruction of histidine and guanine residues in enzymes and nucleic acids has prompted investigations into the reactions of singlet oxygen with substituted imidazoles which have indicated that they behave very similar to furans[3] and pyrroles[4]. They have been determined to be prone to cleave at their enamine double bond and the reaction is sensitive to the substitution pattern at position 2,4 and 5[1]. The presence of substituents at 2 or 5 permits the β-elimination type of decomposition of 1,4-endoperoxide leading to the imidazolone system which may further react with the solvent alcohol to yield 2 and 3



Scheme 1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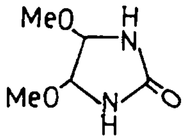
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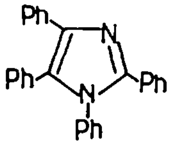
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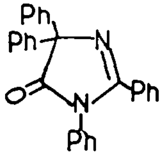
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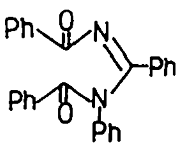
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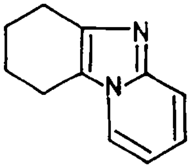
(Scheme 1)[5]. Similarly when 4 is subjected to reaction with singlet oxygen, it yielded compound 5 while 6 gives compound 7 and 8 via the dioxetane or hydroperoxide intermediates[6]. Fused ring imidazoles such as 9 yield the corresponding diamide 10 presumably via the dioxetane intermediates. The involved dioxetane 11 may also break down by a β-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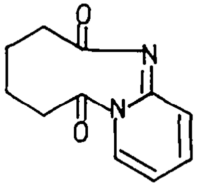
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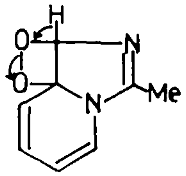
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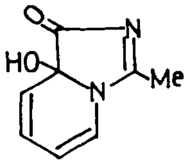
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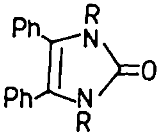
elimination process to give compound 12. In contrast, 2-methyl-1,2-dimethylimidazole gives degraded products[7]. Recently Wasserman et al. have observed that the reaction either takes place via the dioxetane or via the zwitterionic perepoxide intermediate[7]. For example, when 4,5-diphenylimidazolin-2-one 13 was treated with singlet oxygen, it gave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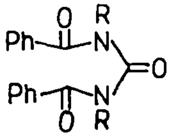
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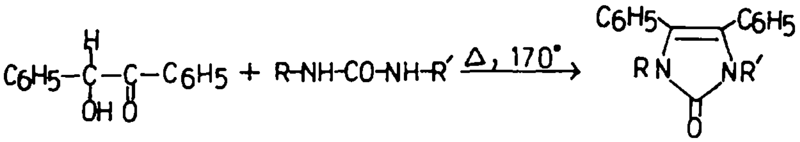
dibenzoylurea 19 as the major product but not much has been stated about the mechanism of photooxygenation[8]. The formation of variety of products in the reaction of imidazoles with singlet oxygen indicates the complexity of the reaction. In an attempt to study the reaction in detail and the effect of substituents on the imidazole nitrogens, we have subjected imidazolin-2-ones (13-18) to dye sensitized photooxygenation at different pH's and solvents of varying dielectric constants and report our prime results in this paper.

SYNTHESIS OF IMIDAZOLIN-2-ONES:

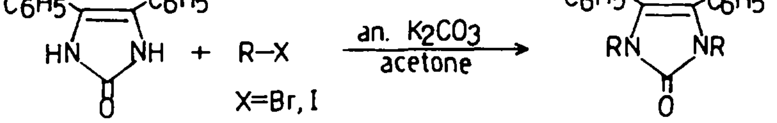
Imidazolin-2-ones (13,14 and 15) were synthesized by the thermal condensation of benzoin with urea in their molar ratio (Scheme 2). The desired compounds were isolated from the reaction mixture by the method described in the experimental section.



13. $R = R' = H$
14. $R = H$ , $R' = C_6H_5$
15. $R = R' = C_6H_5$

Scheme 2

The above 4,5-diphenylimidazolin-2-one could be alkylated with different alkyl halides in the presence of anhydrous $K_2CO_3$ and acetone to yield different N-substituted-4,5- diphenylimidazolin-2-ones (16,17 and 18 Scheme 3)[9].

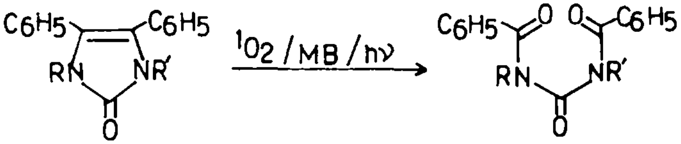


16. $R = CH_3$
17. $R = CH_2CH{=}CH_2$
18. $R = (CH_2)_3CH_3$

Scheme 3

## PHOTOOXYGENATION OF IMIDAZOLIN-2-ONES

The synthesized imidazolin-2-ones (13-18) were dissolved in a mixture of $CHCl_3$ and $CH_3OH$ (1:1 v/v) and a dye sensitizer, methylene blue was added to it. The reaction mixture was subjected to photooxygenation by a minor modification of the procedure described earlier[10] and the progress of the reaction was monitored by TLC. The products obtained after completion of the reaction were characterised as diacylureas (Scheme 4) by analysis of their UV, IR, NMR and mass spectra.



| | | | |
|---|---|---|---|
| 13. | R= R'= H | 19. | R=R'=H |
| 14. | R=H, R'=$C_6H_5$ | 20. | R=H, R'=$C_6H_5$ |
| 15. | R=R'=$C_6H_5$ | 21. | R=R'=$C_6H_5$ |
| 16. | R=R'=$CH_3$ | 22. | R=R'=$CH_3$ |
| 17. | R=R'=$CH_2$-CH=$CH_2$ | 23. | R=R'=$CH_2$-CH=$CH_2$ |
| 18. | R=R'=$(CH_2)_3CH_3$ | 24 | R=R'=$(CH_2)_3CH_3$ |

Scheme 4

The reaction was repeated in the absence of light, oxygen or sensitzer alone or in combination of any two, when no reaction could be observed. The reaction also failed to yield any isolable product when catalytic amount of 1,4-diazabicyclo[2,2,2]octane (DABCO) and 2,6-di-t-butylphenol (DTBP, also used as radical scavenger) were added to the reaction mixture[10,11], thereby confirming the involvement of singlet oxygen in the reaction.

## EFFECT OF pH ON PHOTOOXYGENATION OF 4,5-DIPHENYLIMIDAZOLIN-2-ONE

The reaction when carried out at pH 4.4, 6.0 and 9.2 in $CH_3OH$, indicated that the yield of the product is affected markedly. At pH 4.4 and pH 9.2 the yield of dibenzoylurea was determined to be decreased while at pH 6.0 the maximum yield of dibenzoylurea was obtained. The percentage yields at pH 4.4, 6.0 and 9.2 were recorded as 35.1%, 54.3% and 34.9% respectively (Fig.1).

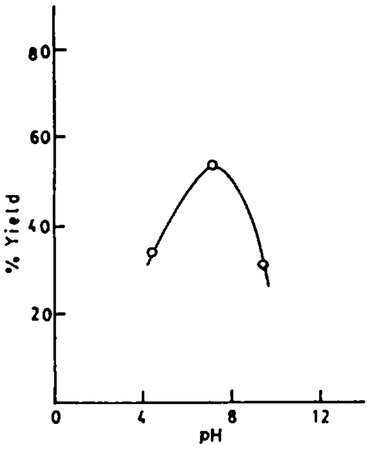


Fig.1 Effects of pH on the yield of dibenzoylurea.

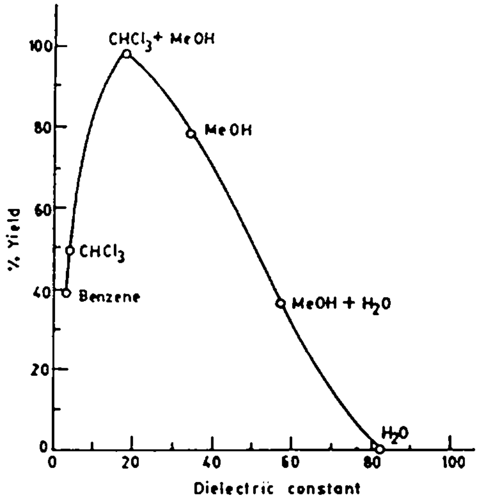


Fig.2 Variation of the yield of dibenzoylurea with dielectric constant of the solvent.

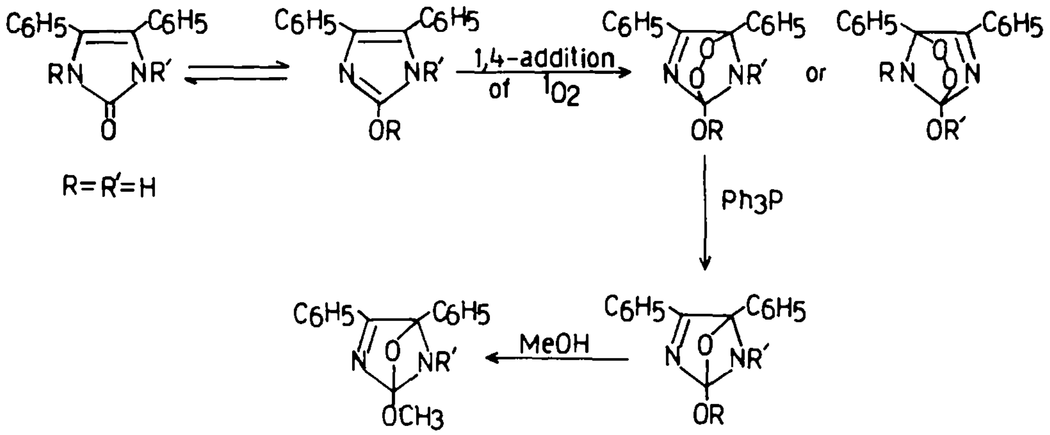
## EFFECT OF SOLVENT ON PHOTOOXYGENATION OF 4,5-DIPHENYLIMIDAZOLIN-2-ONE

The formation of the same dibenzoylureas was observed when 4,5-diphenylimidazolin-2-one was subjected to sensitized photooxygenation whether the solvents used were benzene, $CHCl_3$, $CH_3OH$, water or the mixture of any two, but the yield of the products varied markedly. For example, the yield of the product during first 30 minutes of the reaction was less in non-polar solvents like benzene and $CHCl_3$ as well as in polar solvents such as $CH_3OH$ and water (Fig.2). The yield of the product 19 from 13 was found to be maximum when the mixture of $CHCl_3$ and $CH_3OH$ (1:1 v/v) was used for photooxygenation experiments. The lower rates of reaction may be due to decreased life time of singlet oxygen in polar solvents as compared to the non-polar solvents or due to the differences between solubility of the used dye in different solvents. That it is not the solubility of dye was proved by using another dye (haematoporphyrin) in place of methylene blue which is soluble in non-polar solvents as well;and also by adsorbing methylene blue on silica gel and using adsorbed silica gel for photosensitization.

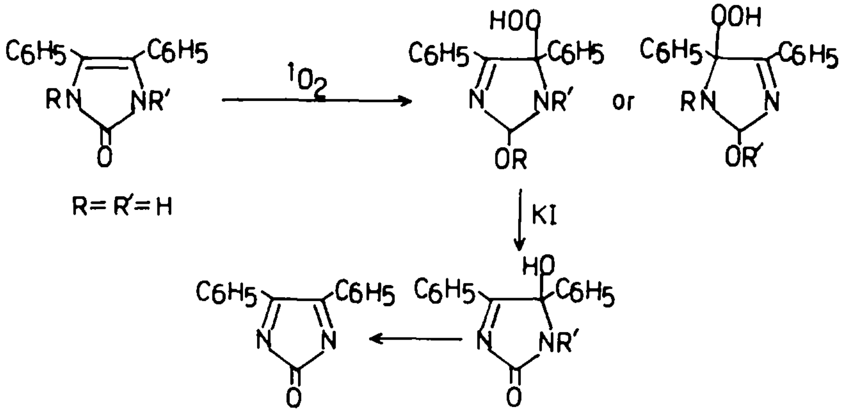
## MECHANISM OF PHOTOOXYGENATION OF IMIDAZOLIN-2-ONES

If one recapitulates the general reactions of singlet oxygen with alkenes, one can easily see that it can react with N-substituted-4,5-diphenylimidozolin-2-ones in three ways as depicted in Scheme 5, Scheme 6 and Scheme 7.

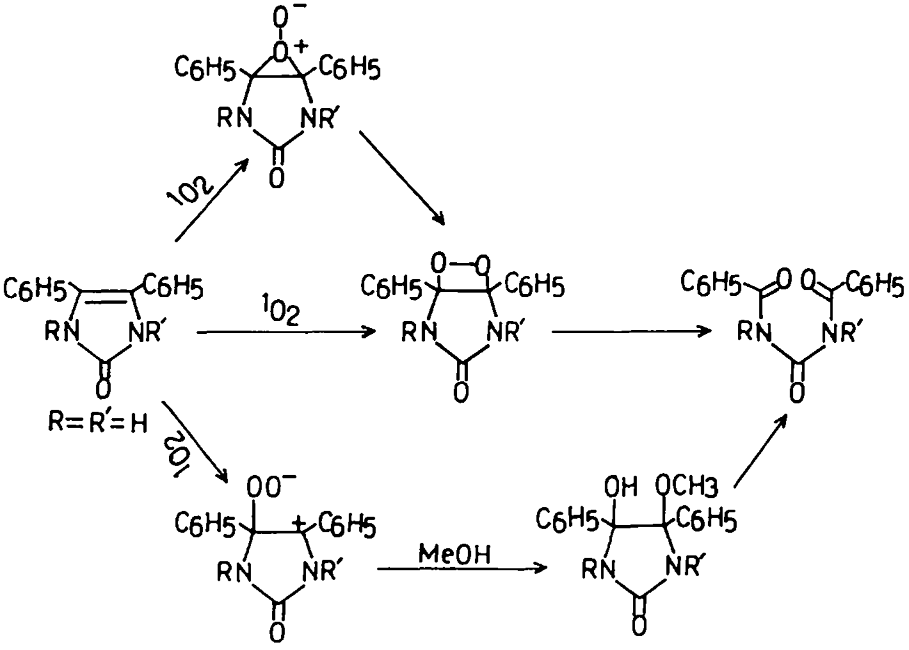
Scheme 5 envisages the attack of singlet oxygen on 4,5-diphenylimidazolin-2-one in a 4π+2π cycloaddition fashion leading to the endoperoxide which if formed in the reaction may result in epoxides. This type of mechanism requires tautomerization of the substrate prior to an attack by singlet oxygen. The phototautomerism of 4,5-diphenylimidazolin-2-ones is



Scheme 5



Scheme 6



Scheme 7

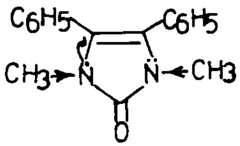
possible due to the presence of labile hydrogen on nitrogen. This hydrogen can migrate to more electronegative oxygen in the presence of polar solvents[12]. Since the hydrogen present at α-position is labile in the reactant, the involvement of hydroperoxide as an intermediate giving rise to products may be another possibility by which the reaction can occur (Scheme 6). This type of hydroperoxides have been accepted as intermediates in photooxygenation of certain heterocycles having a -C=C-NH- moiety, i.e., imidazoles[13], pyrroles[14] and indoles[15]. Singlet oxygen can also react with electron rich olefins and substrates having enaminic double bonds by a 2π+2π addition to give dioxetane as an intermediate which may decompose to yield diacylureas.

Since we were unable to isolate any hydroperoxide, the possible involvement of this species in the reaction was considered to be less likely. Further in the event of involvement of hydroperoxide intermediates, the reaction should be expected to be favoured by the polar solvents[16]. However, since in our experiments the percentage yield of the product was found to decrease in polar solvent like $CH_3OH$ and water (Fig.2) this intermediate may be of less significance. Moreover the reaction failed to give a positive KI-AcOH test for hydroperoxides when carried out on the residue obtained after evoporation of solvent under reduced pressure. On the basis of the above observations the mechanism depicted in Scheme 6 was ruled out.

The alternative mechanism (Scheme 5) requires tautomerized form of imidazolin-2-one and the endoperoxide formed by the addition of singlet oxygen should further decompose to give plausibly stable epoxides[17]. Since none of these epoxides could be detected in the reaction mixture for any of the six substrates, the involvement of endoperoxide as an intermediate seems to be less importance. This was further supported by carrying out the reaction at various pH's when the yield of the product was found to decrease at lower or higher pH (4.4 and 9.2) although there was no effect on the nature of the product. The yield of the product was maximum at pH 6.0-7.0 (Fig.1).

The above discussion leaves the possibility of the reaction of these compounds with singlet oxygen via the formation of a dioxetanes (Scheme 7). The presence of dibenzoylurea as the only major product in the reaction can be best explained by the involvement of dioxetane intermediates. This conclusion was further supported by (a) studying the effect of substituents and (b) effect of dielectric constant of the medium[18,19].

a) Effect of Substituents: It has been observed that the facility with which the photooxygenation proceeds was 16>17>18>13>14>15. For instance it was found that 1,3-dimethyl-4,5-diphenylimidazolin-2-one 16 reacted faster with singlet oxygen than 1,3,4,5- tetraphenylimidazolin-2-one 15. The higher rate of reaction for compound 16 is probably due to the participation of lone pair of electrons present on the nitrogen atom attached to the double bond to ehnance the nucleophilicity of a double bond so as to interact with electrophilic singlet oxygen in a better way. The presence of electron donating groups such as $CH_3$ and $(CH_2)_3CH_3$ increase such a possibility. The presence of phenyl rings in compound 15 reduce the nucleophilicity of a double bond primarily due to the attraction of lone pair of nitrogen towards the benzene rings. Such a situation increases the stability of compound 15 towards singlet oxygen.



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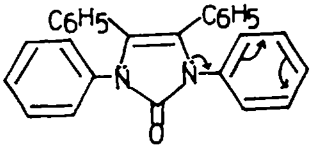

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b) Effect of Solvents: Since the presence of polar solvent such as $CH_3OH$ along with $CHCl_3$ was always required for the reaction to go, dioxetane intermediates cannot be unambiguously postulated for they should have been highly favoured when photooxygenation was carried out in non-polar solvents; a phenomenon not observed in our reactions (For example, the reaction when carried out in $C_6H_6$ using haematoporphyrin as the sensitizer does not give better yields of diacylureas). This gives credence to the idea that some polar effects are operative in the reaction (e.g., zwitterionic intermediates) at least in the transitory state leading to the dioxetanes which may give diacylureas as products on decomposition.

Imidazolin-2-one---->[Zwitterionic perepoxide]--->Dioxetane--->Diacylurea

The participation of zwitterionic perepoxide leading to dioxetanes is being studied by carrying out the reaction in surface active compounds. It has been determined that the yield of the products are affected markedly by the presence of surfactants at their critical micelle concentrations. The cationic surfactants like CTAB are more effective in enhancing the rate of the reaction than anionic surfactants (SDS) and neutral surfactants (ethoxylated sterols). How the micellar core affects the mechanism will be reported in a separate paper.

## EXPERIMENTAL

All the melting points of the compounds were taken on electric melting point apparatus (Adair Dutt and Co. Calcutta, India) and are uncorrected. UV spectra were obtained on Perkin Elmer [Lambda-3B] spectrophotometer and the IR spectra were recorded on FT-IR Perkin Elmer spectrometer. The NMR spectra were obtained using [Jeol-FX100] FT-NMR spectrometer while mass spectra were taken on GC-MS [JNM-D300] spectrometer at 70 eV. The solvents used were of L.R.Grade and were obtained from Merck, Bombay. They were dried before use by the published procedures[9]. Pet. ether used for chromatography refers to the fraction having boiling point range 60-80°C. Methylene blue used was metal free and was purchased from BDH Chemicals, Bombay.

a) Synthesis of 4,5-Diphenylimidazolin-2-one (13)

A mixture of benzoin (3.18g, 15mM) and urea (3.6g, 60 mM) was heated on an oil bath for 12 h at 170°C. After the completion of the reaction, the mixture was cooled and the residue obtained was suspended in $CH_3OH$ (25 ml). The solution was filtered and the filtrate obtained was mixed with water (50 ml), when a white precipitate appeared which was again filtered and the residue left was collected and dried. It was found to be homogeneous on TLC (silica gel, $CHCl_3$ -EtOAc 5:5 v/v, $R_f$=0.40). Compound 13 was isolated in 85.0% yield and crystallised from the mixture of $CHCl_3$ and $CH_3OH$ (2:8) as fine white needles, m.p. > 280°C; UV ( $\lambda_{max}$) 238 and 304 nm; IR (KBr,$cm^{-1}$) 3150, 1700,1450,1232,1210,920; $^1$HNMR ($CDCl_3$)$\delta$ 7.72 (m,10H, ArH), 9.8 (s,2H,NH).

### b) Synthesis of 1,4,5-Triphenylimidazolin-2-one(14)

Benzoin (3.15g, 5mM) and N-phenylurea (4.5g, 30 mM) were heated an oil bath for 7 h at 170°C and the residue obtained was extracted with $CHCl_3$ (100 ml). Evoporation of the solvent under reduced pressure gave a white powder in 70% yield, m.p 265°C, $R_f$=0.44 ($CHCl_3$ - EtOAc 7:3 v/v); UV ($\lambda_{max}$) 236 and 303nm IR (KBr, $cm^{-1}$) 3270, 1720, 1503, 1436, 1319, 920; ${}^1$HNMR ($CDCl_3$) δ 7.23 (m, 15H, ArH), 9.37 (s, 1H, NH).

### c) Synthesis of 1,3,4,5-Tetraphenylimidazolin-2-one (15)

Benzoin (3.15g, 15mM) was mixed with diphenyl urea (3.36g, 15mM) and the mixture was heated in an oil bath for 8h at 170°C. The residue was extracted with $CHCl_3$ and compound 15 was obtained on evoporation of solvent in 55.0% yield; m.p. 215°C, $R_f$=0.45 ($CHCl_3$ - EtOAc; 7:3 V/V), UV ($\lambda_{max}$) 240nm. IR (KBr, $cm^{-1}$) 1730,1433,1373,1277,1015; ${}^1$HNMR ($CDCl_3$)δ7.1-7.37 (m, 20H, ArH).

### d) Synthesis of 1,3-Dimethyl-4,5-diphenylimidazolin-2-one(16)

4,5-Diphenylimidazolin-2-one (.5g, 2mM) was dissolved in dry acetone (20ml), anhydrous $K_2CO_3$(1.5 g) and methyl iodide (.8g, 6mM) were added and the reaction mixture refluxed for 30 min. The solution was cooled poured over crushed ice and extracted with $CHCl_3$. Evoportion of the solvent gave a yellow coloured powder which was recrystallised from the $CHCl_3$ as light yellow needles; yield 45%; m.p. 205°C; $R_f$=0.48 ($CHCl_3$ - EtOAc, 7:3 v/v), UV ($\lambda_{max}$) 241 nm. IR (KBr, $cm^{-1}$) 1690, 1495, 1400, 1205, 1070, 940; ${}^1$HNMR($CDCl_3$)δ 3.24 (s, 6H, $CH_3$), 7.16-7.69 (m, 10H, ArH).

### e) Synthesis of 1,3-Diallyl-4,5-dipenylimidazolin-2-one (17)

A mixture of 4,5-diphenylimidazolin-2-one (.5g, 2mM), anhydrous $K_2CO_3$ (1.5g) and allyl bromide (.802g, 6mM) was taken in dry acetone (20ml) and refluxed for 20 min. The reaction mixture was extracted with $CHCl_3$ and the organic extract was concentrated when a light yellow coloured liquid was obtained in 40% yield which was further purified by column chromatography over silica gel (50g) using a mixture of $CHCl_3$ and EtOAc (9:1, v/v) for elution. $R_f$=0.53 ($CHCl_3$ - EtOAc, 7:3 v/v); UV ($\lambda_{max}$) 240nm.; IR (KBr, .$cm^{-1}$) 1725, 1452, 1350, 1200, 1150, 1110, 980; ${}^1$HNMR ($CDCl_3$) δ 4.25 (d, J=9Hz, 4H, $CH_2$), 5.05-5.31(d,J=9Hz, 4H,=$CH_2$), 5.6-5.9 (m,2H,CH ), 7.02-7.69(m,10H, ArH).

### f) Synthesis of 1,3-Dibutyl-4,5-diphenylimidazolin-2-one(18)

A mixture of 4,5-diphenylimidazolin-2-one (.5g, 2mM), anhydrous $K_2CO_3$ (1.5g) and *n*-butyl iodide (1.2g, 6mM) in acetone (20 ml) was refluxed for 30 min. The reaction mixture was poured over crushed ice and extracted with $CHCl_3$. A colourless liquid was obtained after evoporation of the $CHCl_3$ which was purified by passing through a column of silica gel (50g) and eluting with $CHCl_3$ and EtOAc (9:1 v/v). $R_f$ = 0.51 ($CHCl_3$-EtOAc, 7:3 v/v); UV ($\lambda_{max}$) 244 nm; IR (KBr, $cm^{-1}$) 1680, 1600, 1460, 1390, 1116, 922; ${}^1$HNMR($CDCl_3$)δ 0.95(t,J=9Hz, 6H,$CH_3$); 1.68-1.8(m,8H,$CH_2$), 3.5(t, 4H, $CH_2$), 7.17-7.9 (m, 10H, ArH).

### g) Sensitized Photooxygenation of 4,5-Diphenylimidazolin-2-one

Compound 13 (.1g, 4 mM) was dissolved in a mixture of $CHCl_3$ and $CH_3OH$ (100 ml, 1:1 v/v) and dye senstizer methylene blue (5mg) was added to it. The reaction mixture was irradiated with tungsten filament lamps (2x200 watt) while oxygen gas was bubbled through the solution for 40 min.

A potassium chromate filter was used to avoid possible U.V. radiations from the lamp. The progress of the reaction was monitored by TLC ($CHCl_3$-EtOAc, 7:3 v/v) and chromatograms were developed with iodine vapours to visualize the spots.

When the reaction was complete, the solution was mixed with ice cold water (50ml) and then extracted with $CH_2Cl_2$ (2x50 ml). The small amount of dye which came along with the extract was removed by passing the solution through silica gel column (50 g). The eluate was then concentrated under reduced pressure. Evoporation of the solvent gave a white powder which was further purified on silica gel column (50g) by eluting it with a mixture of benzene and EtOAc (9:1 v/v). The solvent when evoporated yielded compound 19 (.106g, 96.5%). It was recrystallised from the mixture of $CHCl_3$ and pet. ether (3:7 v/v) as small white needles, m.p. 218°C (Lit[8].m.p. 218°C), $R_f$ = 0.59 ($CHCl_3$-EtOAc, 9:3 v/v), and analysed for $C_{15}H_{12}N_2O_3$ [Anal: C, 67.3%; H, 5.0%; N, 10.2% cal: C, 67.1%; H, 4.9%; N, 10.4%]; UV ($\lambda_{max}$) 245 nm; IR (KBr, $cm^{-1}$) 3150, 1720, 1680, 1282, 934; $^1$HNMR ($CDCl_3$)$\delta$ 7.52-8.07 (m, 10H, ArH), 10.84 (s, 2H, $D_2O$ exchangeable, NH); MS (m/z, %abundance) 268(35), 147(10),134(51), 121(15), 119(7.5), 106(51), 105(100).

### (h) Photooxygenation of 1,4,5-Triphenylimidazolin-2-one

When a solution of 1,4,5-triphenylimidazolin-2-one (.1g, 3mM) in $CHCl_3$ and $CH_3OH$ (100 ml, 1:1 v/v) was subjected to sensitized photooxygenation for 30 min. as described earlier. Compound 20 was obtained in 95% (.103g) yield on usual workup of the reaction mixture and purified by column chromatography over silica gel ($CHCl_3$-EtOAc, 9:1 v/v). It was crystallised as offwhite needles from $CHCl_3$ and pet. ether (2:8 v/v); m.p 120°C. $R_f$=0.66 ($CHCl_3$-EtOAc, 7:3 v/v). It analysed for $C_{21}H_{16}N_2O_3$ [Anal: C, 73.31%; H, 4.57%; N, 8.26%; Cal. 73.25%; H, 4.65%; N,8.13%]; UV ($\lambda_{max}$) 240 and 303 nm; IR (KBr, $cm^{-1}$) 3255, 1746 1655, 1603, 1397, 1192, 922; $^1$HNMR ($CDCl_3$)$\delta$ 7.86-7.08 (m, 15H, ArH), 8.37 (s, 1H, $D_2O$ exchangeable, NH); MS (m/z, % abundance), 344(30.4) 224(10), 196(96.5), 147(10), 119(45), 106(20), 105(97.5).

### (i) Photooxygenation of 1,3,4,5-Tetraphenylimidazolin-2-one

1,3,4,5-Tetraphenylimidazolin-2-one (.1g, 2.5mM) was dissolved in a mixture of $CHCl_3$ and $CH_3OH$ (100ml, 1:1 v/v) and photooxygenated for 48 h according to the procedure described above. On completion of the reaction compound 21 was obtained in 50% (.05g) yield,which was purified on silica gel column using a mixture of $CHCl_3$ and EtOAc (9:1 v/v) as an eluant. The compound was recrystallised from $CHCl_3$ as white needles; m.p. 165°C; $R_f$=0.65 ($CHCl_3$-EtOAc, 7:3 v/v) and analysed for $C_{27}H_{20}N_2O_3$ [Anal: C, 77.3%, H, 4.72%; N, 6.65%; Cal: C,77.1%, H, 4.75%; N, 6.66%]. UV($\lambda_{max}$) 245 nm; IR (KBr, $cm^{-1}$) 1710, 1642, 1577, 1288, 1126, 963; $^1$HNMR ($CDCl_3$)$\delta$ 7.21-7.77 (m,20H,ArH).

### (j) Photooxygenation of 1,3-Dimethyl-4,5-diphenylimidazolin-2-one

1,3-Dimethyl-4,5-diphenylimidazolin-2-one (.1g, 6mM) was taken in a mixture of $CHCl_3$ and $CH_3OH$ (100ml, 1:1 v/v) and subjected to sensitized photoxygenation for 5 min. On usual workup of the reaction mixture compound 22 was obtained which was purified by using silica gel column chromatography (50g) and eluted by a mixture of $CHCl_3$ and EtOAc (9:1 v/v). It was recrystallised from $CHCl_3$ and pet. ether (5:5 v/v) as white needles in 90.0% (.119g) yield, m.p. 149°C; $R_f$=0.66 ($CHCl_3$-EtOAc, 7:3 v/v). The compound was analysed for $C_{17}H_{16}N_2O_3$ [Anal: C, 68.88%; H,5.5%; N, 9.43%, Cal: C, 68.9%; H, 5.4%; N, 9.45%); UV ($\lambda_{max}$) 247 nm; IR (KBr, $cm^{-1}$) 1729, 1660,1180,1128,950; $^1$HNMR ($CDCl_3$)$\delta$ 2.98 (s, 6H, $CH_3$), 7.26-7.49 (m, 10H, ArH); MS (m/z, % abundance) 296(12) 192(10), 191(40), 178 (32.5), 134(10), 106(75), 105(97.5).

### (k) Photooxygenation of 1,3-Diallyl-4,5-dipheynlimidazolin-2-one

The reaction was carried out by irradiating a soultion of 1,3-diallyl-4,5-diphenylimidazolin-2-one (.1g, 3mM) and methylene blue (5mg) in a mixture of $CHCl_3$ and $CH_3OH$ (100 ml, 1:1 V/V) for 8 min. by a procedure as described above. The residue obtained after the completion of the reaction was subjected to column chromatography (silica gel, $CHCl_3$-EtOAc, 9:1 v/v). Evoporation of the solvent yielded a light brown semisolid (23) (.105g, 95.5%) $R_f$=0.76 ($CHCl_3$-EtOAc, 7:3 v/v). The compound was analysed for $C_{21}H_{20}N_2O_3$ [Anal; C, 72.24%; H, 5.71%; N, 7.94%, Cal: C, 72.44%; H, 5.7%; N, 8.04%), UV ($\lambda_{max}$) 246 nm, IR (KBr, cm$^{-1}$) 1720, 1660, 1645, 1210, 1180; $^1$HNMR ($CDCl_3$) $\delta$ 4.01 (d, J=9Hz, 4H, $CH_2$), 5.25 (d, J=9Hz, 4H,=$CH_2$), 5.72-5.89(m,2H,CH),7.42(m,10,ArH);MS (m/z, %abundance) 348(20.5), 160 (17.5), 121 (7.5), 166 (25), 105(100).

### (l) Photooxygenation of 1,3-Dibutyl-4,5-diphenylimidozolin-2-one

A solution of 1,3-dibutyl-4,5-diphenylimidazolin-2-one (.1g, 3mM) in a $CHCl_3$ and $CH_3OH$ (100 ml, 9:1 v/v) was photooxygenated in the presence of methylene blue (5mg) for 15 min. On completion of the reaction and usual workup, compound 24 was obtained as a colourless liquid in 92.0% (.101g) yield. It was further purified on silica gel column (50g) using a mixture of $CHCl_3$ and EtOAc (9:1 v/v) as an eluant, $R_f$=0.69 ($CHCl_3$-EtOAc, 7:3 v/v). The compound was analysed for $C_{23}H_{28}N_2O_3$ [Anal: C, 72.66%; H,7.53%, N, 7.21%, Cal; C, 72.63% ; H, 7.36%; N, 7.36%]; UV ($\lambda_{max}$) 252 nm, IR (KBr, cm$^{-1}$) 1705, 1642, 1057, 922; $^1$HNMR ($CDCl_3$) $\delta$ 0.095 (t,6H,$CH_3$), 1.82 (m, 8H, $CH_2$), 3.49-3.62 (t, 4H, $CH_2$), 7.17-7.62 (m, 10H, ArH); MS (m/z, %abundance) 380(20), 177(80), 162(12.5), 149(27.5), 148(25), 135(99.8), 134(87.5), 122(45.2), 121(99.8), 106(100), 105(99.8).

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