ABSTRACT
The photocyclization reaction is highlighted in this review. The two main aspects of this reaction are explored; namely photocyclization under oxidative conditions and under non-oxidative condition. Also, several examples of stilbenoid photochemistry are discussed. The synthesis and photochemistry of a series of 2,3,4,5-tetraphenyldihydrophenanthrene, 2,3,5-triarylfuran and 2,3-di-(3,4-methylenedioxyphenyl) furan have also been mentioned in this review.

KEYWORDS: photocyclization, stilbenes, stilbenoids, dihydrophenanthrene, phenanthrene, triarylfuran, non-oxidative conditions

INTRODUCTION
The discovery of the oxidative photocyclization reaction of stilbenes and stilbenoids around 50 years ago opened the door to an enormous amount of work in this field of chemistry. It was discovered by Mallory during studies of the photochemical isomerization of stilbenes [1, 2]. However, this reaction became a very useful method in synthetic organic chemistry when it was discovered in 1964 that iodine could catalyze the reaction [3, 4]. This reaction was reviewed by several authors who discussed various aspects and applications. This review will focus on the reaction as a useful tool in synthesis, using oxidative and non-oxidative conditions [5-13].

Oxidative cyclization
The Mallory-reaction is illustrated in Scheme 1. The photochemical isomerization of the double bond in stilbene has been very well studied [14-16]. Since the cis/trans-isomerization occurs rapidly under the reaction conditions in such a way that different ratios of cis- and trans-stilbenes can exist to give the same products. Therefore, the stilbenes 1 can be used as isomeric mixtures in the photocyclization reactions; however, only the cis-isomer 2 is able to undergo further cyclization reactions. The intermediate dihydrophenanthrene 3 or 4 is unstable and can be trapped by oxidation to form a phenanthrene 5, or by elimination given a suitable substituent in the ortho-position on one of the aromatic rings to give the corresponding stilbene 6. In 1984 Mallory et al., reported examples of hydrogen-shifts at this stage under “nonoxidative conditions” [8].

It was found that in more concentrated solutions stilbenes can form dimers in a [2+2] cycloaddition as well [17, 18]. It was also proven that “oxidative trapping” occurs much faster when traces of iodine were used together with O₂ [3], but increased concentrations of iodine did not affect the reaction rate. It has been suggested [17] that iodine is photochemically cleaved into radicals that react in a chain reaction causing the oxidative trapping. Concentrations of iodine were found to be optimal at around 0.01 mole/litre of stilbene [4]. [2+2] Cycloaddition between two stilbenes occurred when higher concentrations of iodine were used. It seems obvious that the concentration of iodine has a great effect on both the yield and selectivity of the required product. Noller et al. [19] discovered that a 1/1 molar ratio of iodine per cyclization can prevent elimination of methanol but greatly affected the product selectivity (Scheme 2).
Scheme 1. Proposed reaction pathways for the photocyclization reaction of stilbenes.

Scheme 2. The effect of iodine concentration on product yield and product selectivity.
Martin et al. [23] and Laarhoven et al. [24] synthesised 4,16-dibromobenzo[5,6]phenanthro[3,4-c]hexahelicene 12 from the photolysis of 2-bromo-3-((Z)-2-{6-[(Z)-2-(2-bromo-3-phenanthryl)ethenyl]-2-naphthyl}ethenyl)phenanthrene in the presence of iodine (11, cis and trans) Scheme 3. The bromine atoms were introduced to prevent the cyclisations taking place on the 2-positions of the phenanthrene system 11.

A double photocyclisation of 2-((E)-2-{2-bromo-3-[(E)-2-(2-naphthyl)ethenyl]phenyl}ethenyl)naphthalene (13) afforded 9-bromodinaphtho[1,2-a:2,1-j]anthracene (14, Scheme 4) [25]. Again a bromine atom was incorporated into this system to prevent cyclisation from occurring at C2.

The role of methyloxirane

The presence of a high concentration of hydrogen iodide causes many undesirable by-products and this leads to a reduction in the final yield of the required product. It was reported by Katz that methyloxirane can be used to scavenge any hydrogen iodide formed during the photochemical reaction [20-22].

The iodide could not then be reoxidized by oxygen and therefore one equivalent of iodine was needed. The reaction could then be carried out under an inert atmosphere preventing the formation of any undesirable product (Table 1).

Arisvaran et al. [28] reported the synthesis of benzo[k]phenanthridin-6(5H)-one (16) in 84% yield; from the irradiation of 3-[(E)-2-phenylethenyl]-2(1H)-quinolinone (15) at 253.7 nm in methanol containing a small amount of iodine (Scheme 5).

It was also found [29] that irradiation of 1,3-diphenylbenzo[f]quinoline (17) in an acidic ethanol solution gave rise to 2-phenylanthrantho[9,10,1-def]quinoline (18) (Scheme 6). However, when the same reaction was performed without the acid, no product was obtained.

Irradiation of (E)-1-mesityl-2-phenyldiazene (19, Scheme 7) in 10.25M sulfuric acid proceeded rapidly to give 2,4-dimethylbenzo[c]cinnoline (20) as the major component [30]. However, a small amount of (21) was also isolated, having been formed by migration of a methyl group from one of the ortho-positions. This isolation of 1,2,4-trimethylbenzo[c]cinnoline (21) was of considerable interest as it provides the first clue to the fate of the ortho-methyl groups in such cyclizations.

Stilbene photocyclization under non-oxidative conditions

Horspool et al. [6, 7] reported the synthesis of 2,3,4,5-tetraphenyl-2,4-cyclopentadien-1-one
<table>
<thead>
<tr>
<th>Starting material</th>
<th>Product</th>
<th>Cat. I$_2$</th>
<th>Katz’s conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1" alt="Structure" /></td>
<td><img src="image2" alt="Structure" /></td>
<td>51% (8h)</td>
<td>95% (8)</td>
</tr>
<tr>
<td><img src="image3" alt="Structure" /></td>
<td><img src="image4" alt="Structure" /></td>
<td>61% (4h)</td>
<td>100% (1h)</td>
</tr>
<tr>
<td><img src="image5" alt="Structure" /></td>
<td><img src="image6" alt="Structure" /></td>
<td>&lt;8% (3.5h)</td>
<td>61% (13h)</td>
</tr>
<tr>
<td><img src="image7" alt="Structure" /></td>
<td><img src="image8" alt="Structure" /></td>
<td>66% (1.2h)</td>
<td>87% (1.2h)</td>
</tr>
<tr>
<td><img src="image9" alt="Structure" /></td>
<td><img src="image10" alt="Structure" /></td>
<td>&lt;4% (4.5h)</td>
<td>71% (4.5h)</td>
</tr>
<tr>
<td><img src="image11" alt="Structure" /></td>
<td><img src="image12" alt="Structure" /></td>
<td>64% Ref [26]</td>
<td>71% Ref [27]</td>
</tr>
</tbody>
</table>
The main feature of the phenanthrene system which had been obtained by photolysis was the low field absorptions in the NMR spectra. They showed a typical phenanthrene system and these absorptions were between $\delta_{7.5-10.0}$. Phenanthrene itself showed an absorption at $\delta_{8.65}$.

Photolysis of the adduct (23 c, Scheme 8) gave an inseparable mixture of (24 c and e) in a ratio of 1:2. From this ratio it could be seen that the electronic and steric factors had their effects in the

(a) R = H, (b) R = Cl, (c) R = CH$_3$

Scheme 5. Photolysis of 3-[(E)-2-phenylethenyl]-2(1H)-quinolinone (15a) in methanol containing iodine.

Scheme 6. Irradiation of 1,3-diphenylbenzo[f]quinoline (17) in an acidic ethanol solution.

Scheme 7. Irradiation of (E)-1-mesityl-2-phenyldiazene (19) in acidic medium provided (20) and (21).

(22, 25, 28) (Scheme 8) by adapting standard literature procedures [31-33]. The synthesis of the adducts was achieved by refluxing the substituted 2,3,4,5-tetraphenyl-2,4-cyclopentadien-1-one and 3,4,5,6-tetrachlorobenzo-1,2-quinone in benzene for a few hours. The photodehydrocyclization of the adducts in scheme (8) in propan-2-ol under non-oxidative conditions, using Pyrex filtered light, gave the corresponding 2,3-diphenyl-1H-cyclopenta[f]phenanthren-1-one.
formed as a yellow solid in good yield. Reaction of (27) with hydrazine hydrate gave rise to (28, Scheme 9) 3,6-diphenyl-4,5-di(2-pyridinyl)pyridazine in quantitative yield. Similarly, Bikales and Becker [34, 35] found the photolysis of 2,3,4,5-tetraphenyl-2,4-cyclopentadien-1-one (31) in the presence of oxygen produced cis and trans (2Z)-1,2,3,4-tetraphenyl-2-butene-1,4-dione (32, 33) and 3,4,5,6-tetraphenyl-2H-pyran-2-one (34, Scheme 11).

**Mechanism of the photochemical reaction:**

Horspool [36, 37] reported that there are two possible mechanisms for the formation of the substituted 2,3-diphenyl-1H-cyclopenta[l]
explained that the reaction could involve elimination of tetrachloro-1,2-benzquione to phenanthren-1-one from the photolysis of the corresponding adducts. The first mechanistic route

\[
\text{hv} \quad \text{O} \quad \text{N} \quad \text{N} \quad \text{N}_2\text{H}_4
\]

\[
\text{hv/O}_2
\]

\[
\text{N}_2\text{H}_4
\]

Scheme 9. Synthesis of \((2Z)-1,4\)-diphenyl-2,3-di(2-pyridinyl)-2-butene-1,4-dione (27) and 3,6-diphenyl-4,5-di(2-pyridinyl)pyridazine (28).

\[
\text{hv} \quad \text{O} \quad \text{N} \quad \text{N} \quad \text{N}_2\text{H}_4
\]

\[
\text{hv/O}_2
\]

\[
\text{N}_2\text{H}_4
\]


\[
\text{hv/air}
\]

\[
\text{hv/air}
\]

\[
\text{hv/air}
\]

Scheme 11. Photolysis of 2,3,4,5-tetraphenyl-2,4-cyclopentadien-1-one (31) in the presence of air.

phenanthren-1-one from the photolysis of the corresponding adducts. The first mechanistic route explained that the reaction could involve elimination of tetrachloro-1,2-benzquione to
produce an exited tetracyclone, which might cyclise to form the dihydrophenanthrene (35). Oxidation of (35) could be affected by the quinone. This mechanism was eventually eliminated by showing that it was essential to have a stilbene portion in the adducts for the photoreaction to take place. The adduct 6,7,8,9-tetrachloro-4b,10a-diphenyl-4b,10a-dihydro-11H-indeno[1,2-b][1,4] benzodioxin-11-one (36) failed to form the expected product 13H-indeno[1,2-f]phenanthren-13-one (37, Scheme 12).

The second mechanistic route illustrated in (Scheme 13) by cyclising of the aryl groups on C2 and C3 of the adduct affords the dihydrophenanthrene (23a, b) which can eliminate tetrachlorocatechole by a thermal process. The involvement of the aryl groups on the enone double bond was verified by the efficient formation of the cyclopentaphenanthrene (24 Scheme 13) by photolysis of adduct (23, Scheme 13) in alcohol. The mechanism depicted in (Scheme 13) should also show some solvent dependency. Thus, in hydroxylic solvents, where proton removal and solvation of the catecholate anion are possible, the reaction is efficient while in cyclohexane no reaction could be detected.

Synthesis and photolysis of compounds (39a-f)

Horspool et al. [6, 7] prepared a series of 2,3,5-triarylfurans and one 2,3-di-(3,4-methylene-dioxyphenyl)furan using standard literature procedures [5-7, 38-40]. Photolysis of compounds (39a-f, Scheme 14) afforded the corresponding phenanthrene (40a-f) (Scheme 13).

They [6, 7] also prepared 2,3,5-triarylur (43 a-h, Table 3) in which two routes were carried out.
Scheme 14. Synthesis and photolysis of compounds (39a-f).

Table 3. $^1$HNMR (CDCl$_3$) spectra of substituted 2,3,5-triaryl furan (43, a-h).

<table>
<thead>
<tr>
<th>Furans</th>
<th>Aryl Protons</th>
<th>Furan Ring Proton</th>
<th>Aryl Ring Substituents</th>
</tr>
</thead>
<tbody>
<tr>
<td>43a</td>
<td>7.0-7.8 (15H, m)</td>
<td>6.70 (1H, s)</td>
<td>------</td>
</tr>
<tr>
<td>b</td>
<td>6.7-7.6 (14H, m)</td>
<td>6.50 (1H, s)</td>
<td>3.60 (3H, s, OMe)</td>
</tr>
<tr>
<td>c</td>
<td>7.0-7.7 (14H, m)</td>
<td>6.65 (1H, s)</td>
<td>2.30 (3H, s, Me)</td>
</tr>
<tr>
<td>d</td>
<td>6.9-7.8 (13H, m)</td>
<td>6.70 (1H, s)</td>
<td>2.30 (6H, 2xMe)</td>
</tr>
<tr>
<td>e</td>
<td>7.0-7.8 (12H, m)</td>
<td>6.70 (1H, s)</td>
<td>2.20-2.40 (6H, 2xMe)</td>
</tr>
<tr>
<td>f</td>
<td>7.0-7.7 (14H, m)</td>
<td>6.70 (1H, s)</td>
<td>------</td>
</tr>
<tr>
<td>g</td>
<td>7.1-7.7 (14H, m)</td>
<td>6.75 (1H, s)</td>
<td>3.80 (3H, s, OMe)</td>
</tr>
<tr>
<td>h</td>
<td>7.1-7.8 (14H, m)</td>
<td>6.85 (1H, s)</td>
<td>------</td>
</tr>
</tbody>
</table>

Scheme 15. Synthesis of 2,3,5-triaryl furan.
The fact that the phenanthrene system had been formed in the photolysis was confirmed by inspection of $^1$H-NMR spectrum of each product. All of them contained low field resonances between $\delta 7.0-8.7$. This is typical for phenanthrene systems; phenanthrene itself showing a resonance at $\delta 8.65$. The details of the $^1$H-NMR spectra of the substituted 2-phenylphenanthro[9,10-$b$]furan ($46a$-$h$, Scheme 16) are contained in Table 4.

ACKNOWLEDGEMENT
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REFERENCES

Table 4. $^1$HNMR ($CDCl_3$) spectra of substituted 2-phenylphenanthro[9,10-$b$]furan.

<table>
<thead>
<tr>
<th>Furans</th>
<th>Aryl Protons</th>
<th>Aryl Ring Substituents</th>
</tr>
</thead>
<tbody>
<tr>
<td>46a</td>
<td>7.0-7.8 (14H, m)</td>
<td>----</td>
</tr>
<tr>
<td>b</td>
<td>7.1-8.8 (13H, m)</td>
<td>2.40 (3H, s, Me)</td>
</tr>
<tr>
<td>c</td>
<td>6.7-8.7 (14H, m)</td>
<td>3.80 (3H, s, OMe)</td>
</tr>
<tr>
<td>d</td>
<td>7.1-8.5 (12H, m)</td>
<td>2.5 (6H, s, 2xMe)</td>
</tr>
<tr>
<td>e</td>
<td>7.2-8.5 (11H, m)</td>
<td>2.6 (6H, 2xMe)</td>
</tr>
<tr>
<td>f</td>
<td>7.0-8.7 (13H, m)</td>
<td>----</td>
</tr>
<tr>
<td>g</td>
<td>6.7-8.7 (13H, m)</td>
<td>3.90 (3H, s, OMe)</td>
</tr>
<tr>
<td>h</td>
<td>7.0-8.7 (13H, m)</td>
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</tr>
</tbody>
</table>

The first route was using hydriodic acid and (2Z)-1,2,4-triphenyl-2-butene-1,4-dione (41) under reflux for a few minutes. The excess of the iodine was removed by treating the mixture with sodium hydrogen sulfate. The second route to prepare the furans was carried out using 1,2,4-triphenyl-1,4-butanedione (42, Scheme 15) and cooled sulfuric acid at room temperature.

Irradiation of (45a-g) afforded a single product from each adduct in around 70% yield. The irradiation of (45h) afforded the phenanthrene in low yield (~7%).