Background
Synthetic organic photochemistry has made impressive strides during the past two decades. The technique has been utilized for the synthesis of a wide variety of carbocyclic as well as heterocyclic compounds utilizing precursors like stilbenes, stilbazoles, azobenzenes, Schiff bases, anilides, enamides etc.* It is considered that a review outlining their synthesis would provide the necessary background to the discussion on the synthesis of benzo(k)phenanthridines, which we have accomplished based on the photolysis of 4-phenyl-3-vinylquinolines.

Photochemical reactions of stilbenes and stilbene like compounds.

Mallory and co-workers\textsuperscript{19} - \textsuperscript{21} have done considerable work on the photolysis of stilbenes which in the presence of oxidants like oxygen, iodine etc., gave rise to phenanthrenes. Subsequent to their work, a spate of similar observations were made on the other related systems mentioned above and they have been reviewed by two authors.\textsuperscript{22}
The mechanistic interpretation given by them for the photocyclization of stilbene is as follows.

\[
\text{The formation of the phenanthrene (12) is assumed to proceed through the trans-dihydro intermediate 11 which according to Woodward - Hoffmann rules should result from the conrotatory ring closure of the cis-stilbene (10),}
\]
followed by the stripping of the allylic hydrogens by the oxidant. Attempts to isolate the proposed intermediate dihydrophenanthrene (11) were not successful because of its ready revertibility to the starting stilbene. But its presence as the intermediate has been identified spectroscopically.

The isolation of a true dihydrophenanthrene intermediate (16) was however reported in the photolysis of diethylstilbesterol (13).

\[ \text{11} \quad \text{10} \]
The 'stilbene to Phenanthrene' conversion under oxidative photolysis has been realized in the case of several stilbenes and stilbene like compounds. Among them the following may be mentioned.

Benzo(c)phenanthrene:

\[ \text{h} \nu / J_2 \]

Chrysene:

\[ \text{h} \nu / J_2 \]
Kharasch et al. obtained triphenylene by the oxidative photolysis of o-terphenyl.

The photocyclization of several 2,2′-divinylbiphenyls leading to tetrahydropyrenes was investigated by Padwa and Mazzu.27, 28

R = H, -CN, -COOMe
They have found that in the case of 2,2'-distyrylbiphenyl ($R = \text{Ph}$), irradiation for a shorter duration gave rise to a cyclobutane derivative as the kinetically controlled product. But on prolonged irradiation, tetrahydropyrene was obtained as the thermodynamically controlled product. The formation of the products was mechanistically accounted for as outlined below:
2-vinylbiphenyls have also been reported\textsuperscript{30, 31} to undergo oxidative as well as non-oxidative photocyclization leading to phenanthrenes.

It was observed by Sargeant et al.\textsuperscript{32} that photocyclization of 2'-methoxy substituted stilbenes, for e.g. 17 gave rise to the ring closed product 18 under non-oxidative conditions, the formation of which apparently involves the
loss of elements of methanol. But when the reaction was carried out under oxidative conditions, the product was proved to be 19, in the formation of which the loss of methanol did not occur.

Photocyclizations leading to heterocyclic systems:

There are several reports on the synthesis of heterocycles based on the photolysis of the appropriate precursors. A few of them are catalogued below:
1) **Synthesis of carbazole (21) from diphenylamine (20)**

\[
\begin{array}{c}
\text{H} \\
\text{N} \\
\text{N} \\
\text{Ph} \\
\text{Ph}
\end{array}
\xrightarrow{h \text{ /O}_2}
\begin{array}{c}
\text{H} \\
\text{N} \\
\text{N} \\
\text{Ph} \\
\text{Ph}
\end{array}
\]

2) 1) **Synthesis of benzo(f)isoquinoline (23) from 3-stilbazole (22)**

(ii) **benzo(f)quinoline (25) from 2-stilbazole (24)**

(iii) **benzo(h)isoquinoline (27) from 4-stilbazole (26)**

(iv) **benzo(i)phenanthridine (29) from styrylquinoline (28)**

(v) **benzo(f)quinoxaline (31) from 4-styryl pyrimidine (30)**

\[
\begin{array}{c}
\text{Ph} \\
\text{N} \\
\text{N} \\
\text{Ph}
\end{array}
\xrightarrow{h^\gamma /J_2}
\begin{array}{c}
\text{Ph} \\
\text{N} \\
\text{N} \\
\text{Ph}
\end{array}
\]

\[
\begin{array}{c}
\text{Ph} \\
\text{N} \\
\text{N} \\
\text{Ph}
\end{array}
\xrightarrow{h^\gamma /J_2}
\begin{array}{c}
\text{Ph} \\
\text{N} \\
\text{N} \\
\text{Ph}
\end{array}
\]
\[ \text{26} \xrightarrow{h\gamma / J_2} \text{27} \]

\[ \text{28} \xrightarrow{h\gamma / J_2} \text{29} \]

\[ \text{30} \xrightarrow{h\gamma / J_2} \text{31} \]
3. Naphtho(2,1-b)thiophene (33) from 2-α-styryl thiophene (32) and 11-thia benz(a)fluorene (35) from 3-α-styrylbenzo(b)thiophene (34); (Carruthers & Stewart) \(^3^8\)

4. Naphtho(2,1-b)furan (37) from trans-2-styrylfuran (36), thieno(3,2-c)benzofuran (39) from trans 1-(2-furyl)-2-(2-thienyl)ethylene (38), benzo-(1,2-b; 4,3-b)difuran (41) from trans 1,2-di-(2-furyl)-ethylene (40) and benzo(1,2-b; 4,3-b)dithiophene (43) from trans 1,2-di-(2-thienyl)ethylene (42); (Loader & Timmons) \(^3^9\)
5) (9, 10-b)phenanthrofuran (45) from 2,3-diphenyl-furan (44) (Padwa and Hartman)\textsuperscript{40}

6) Phenanthridone (47) and carbazole (48) from 2-biphenyl isocyanate (46) (Swenton)\textsuperscript{41}
7) Benzo(b)naphtho(2,1-d)furan (50) from o-chlorophenyl-1-naphthyl ether (49). (Henderson and Zweig)\textsuperscript{42, 43}

\[ \begin{align*}
49 & \xrightarrow{h+} 50 \\
\end{align*} \]

8) Benzo(c)cinnolines (52) from azobenzenes: (51).
(Badger and Co-workers)\textsuperscript{44, 46}
This reaction involves a photochemical disproportionation i.e., for every molecule of azobenzene that undergoes cyclodehydrogenation, one molecule is reduced to hydroazo benzene (53) and under the acidic reaction conditions this rearranges to benzidine (54).

An interesting observation made by them was the expulsion of methyl group in the photocyclization reaction of 2-methyl azobenzene (55), 2,2'-dimethyl azobenzene (56), and 2,4,6-trimethyl azobenzene (57).
Such eliminative photocyclization reactions involving substituents such as -Cl, -COOH, -I were also observed by them.

Naphtho(1,2-c)cinnoline (59) was obtained from 1-phenyl azonaphthalene (58).
9) *Dibenz(c,i)phenanthridine from Schiff's bases:*

Cava and Schelesinger\(^{47}\) were the first to report on the photocyclization of Schiff bases. They obtained *dibenz(c,i)phenanthridine* (61) by the photolysis of the Schiff base (60) from 2-naphthylamine and 2-naphthaldehyde.

Prior to this, there was a report\(^{48}\) on the photocyclization of anils but it proceeded by incorporation of a C\(_2\)-fragment from the solvent. It seemed probable that the C\(_2\)-fragment was derived from acetaldehyde formed by photo oxidation of ethanol.
Badger and co-workers$^{49}$ have reported the formation of phenanthridine and benzylaniline from benzalanilines.

Clark and Cox$^{50}$ synthesised calycanine (63) by the irradiation of the anil of 4-formylquinoline (62) in concentrated sulphuric acid in the presence of oxygen.
Recently Kessar et al. have synthesised the benzo(c)phenanthridine alkaloids Sanguilutine (64) and chelilutine (65) by the irradiation of the dihydroanil 66.

They invoked an electron transfer mechanism for this photochemical synthesis as the dihydroanil does not...
constitute a 6 π-electron system and gave the mechanism as follows:

The low ionisation potential of the naphthalene was considered a favourable factor for this transformation.

10) Benzanilides were successfully photocyclized to yield phenanthridone.
Cleveland and Chapman\(^53\) have reported on the non-oxidative photocyclization of the unsaturated anilide \(67\).

\[
\begin{array}{c}
\text{R}^1 \quad \text{O} \\
\text{H} \\
\text{R}^2
\end{array}
\quad \text{h} \gamma 
\quad \begin{array}{c}
\text{R}^1 \\
\text{O} \\
\text{R}^2
\end{array}
\]

Kanaoka and Itoh\(^54\) have made an interesting observation in photolysing benzanilide \(68\) which underwent an eliminative photocyclization to yield phenanthridone \(69\).

\[
\begin{array}{c}
\text{N} \\
\text{O} \\
\text{OCH}_3
\end{array}
\quad \text{h} \gamma 
\quad \begin{array}{c}
\text{N} \\
\text{O}
\end{array}
\]

Kessar\(^55\) has utilized the photocyclization of the ortho-bromo anilides \(70\) as a preliminary step in the synthesis of benzo(c)pheanthridine alkaloids Nitidine and Avicine.
Stermitz et al. and Ninomiya et al. have also adopted this photocyclization technique to synthesise benzoc-phenanthridine alkaloids.

11) **Photocyclization of enamides**

Lenz has made an excellent survey of the photocyclization of enamides. Only the photo reactions of enamides which lead to the synthesis of various benzophenanthridine systems are outlined below:

**Benzo(a)phenanthridine**

Ninomiya et al. have synthesised N-methyl benzo(a)phenanthridone (71) by photolyzing the enamide (72) obtained by the benzoylation of N-methyl imine of 2-tetralone.
The sterochemistry of the resulting compound was shown by NMR spectroscopy to be trans.

Ninomiya et al. have synthesised benzo(c)-phenanthridines as well as a number of benzo(c)phenanthridinium alkaloids by exploiting the photocyclization of enamides.

Ninomiya et al.\textsuperscript{60, 61} have synthesised benzo(c)-phenanthridines as well as a number of benzo(c)phenanthridinium alkaloids by exploiting the photocyclization of enamides.

Corynaline (77) was synthesised by Ninomiya et al.\textsuperscript{62} by utilizing an enamide photocyclization.

\[ R = -\text{CH}_2\text{C}_6\text{H}_5 \]

Corynaline (77) was synthesised by Ninomiya et al.\textsuperscript{62} by utilizing an enamide photocyclization.
From the product structures it is evident that cyclization has occurred at both the substituted ortho positions and that 1,5-methoxy shift has occurred in the formation of (A).

A similar approach was used for the synthesis of the antileukemic alkaloid Nitidine (74).

In the above photocyclization elements of methanol were eliminated under non oxidative conditions.
Based on the photocyclization of dienamides, Ninomiya and co-workers\textsuperscript{64} have synthesised a variety of benzo(i)phenanthridines providing a potential preparative route to 6-aza steroids. The enamides obtained by the acylation of N-cyclohexylidene methylimine with 3,4-dihydro-1-naphthoyl chloride (75) and 1-naphthoyl chloride (76) were photoconverted to yield benzo(i)phenanthridine derivatives.

\[
\begin{align*}
\text{Oxidative \\ & non-oxidative}
\end{align*}
\]