

## Photocyclization of stilbenes and stilbenoids

**Abedawn I. Khalaf**

Department of Pure & Applied Chemistry, WestCHEM, Strathclyde University,  
Thomas Graham Building, 295 Cathedral Street, Glasgow G1 1XL, Scotland, UK

### 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-tetraphenyl-2,4-cyclopentadien-1-one and of 2,3,5-triarylfurans as well as 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

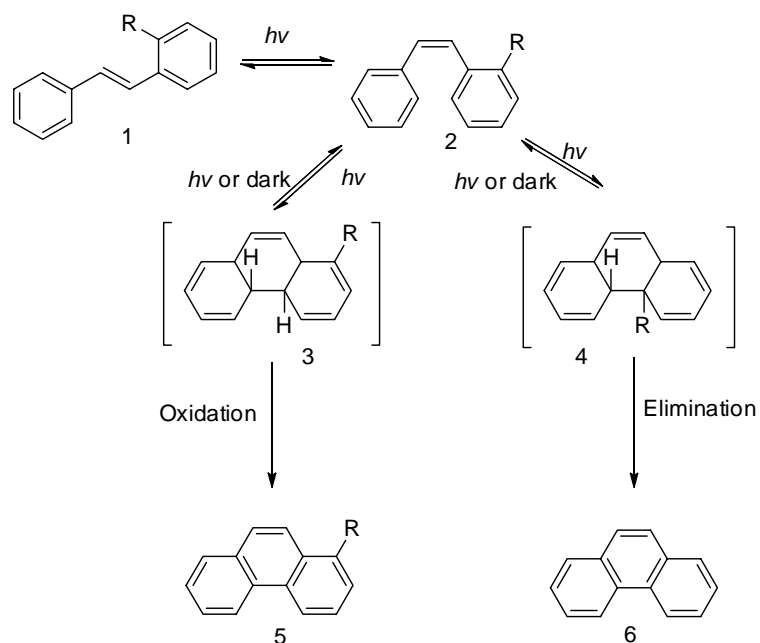
The discovery of the oxidative photocyclization reaction of stilbenes and stilbenoids around 50 years ago opened the door to an enormous amount of work in this field of chemistry. It was discovered by Mallory during studies of the photochemical isomerization of stilbenes [1, 2]. However, this reaction 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

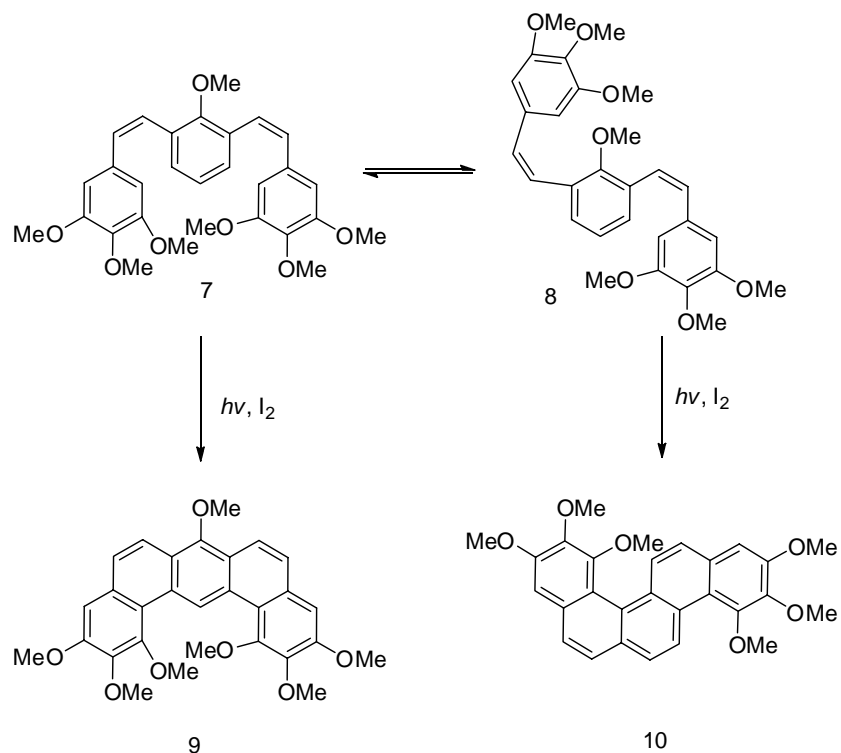
The Mallory-reaction is illustrated in Scheme 1. The photochemical isomerization of the double

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 O<sub>2</sub> [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.



Conditions:	9:10	Yield
1 equivalent of $I_2$	50:50	53%
2 equivalent of $I_2$	97:3	35%

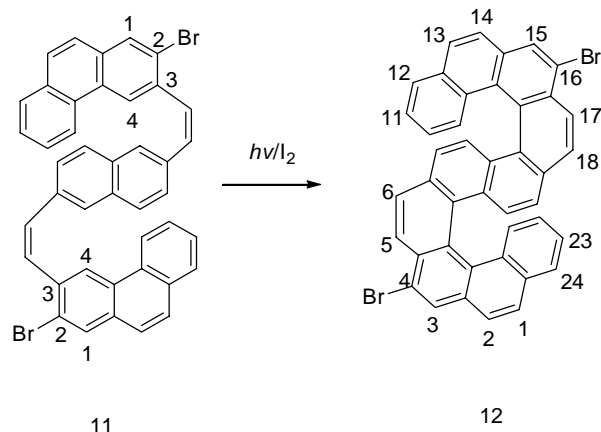
**Scheme 2.** The effect of iodine concentration on product yield and product selectivity.

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-*α*: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



**Scheme 3.** Photolysis of 2-bromo-3-((*Z*)-2-{6-[(*Z*)-2-(2-bromo-3-phenanthryl)ethenyl]-2-naphthyl}ethenyl)phenanthrene **11** in the presence of iodine to give 4,16-dibromobenzo[5,6]phenanthro[3,4-*c*]hexahelicene **12**.

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).

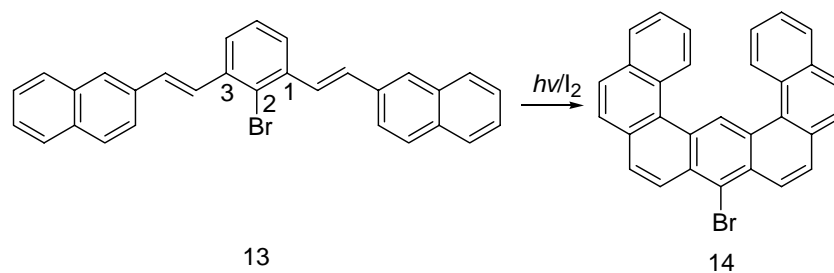
Arisvaran *et al.* [28] reported the synthesis of benzo[*k*]phenanthridin-6(5*H*)-one (**16**) in 84% yield; from the irradiation of 3-[(*E*)-2-phenylethenyl]-2(1*H*)-quinolinone (**15**) at 253.7 nm in methanol containing a small amount of iodine (Scheme 5).

It was also found [29] that irradiation of 1,3-diphenylbenzo[*f*]quinoline (**17**) in an acidic ethanol solution gave rise to 2-phenylphenanthro[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.

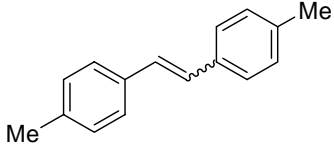
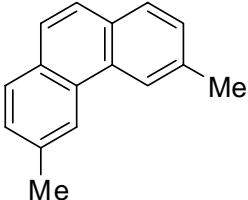
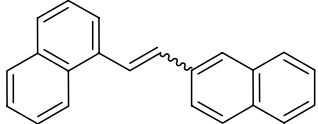
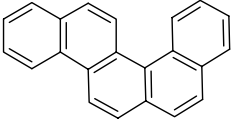
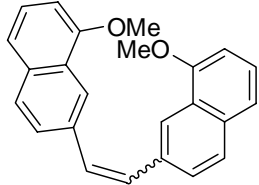
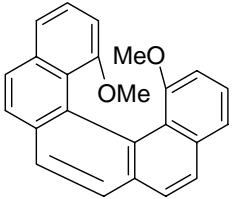
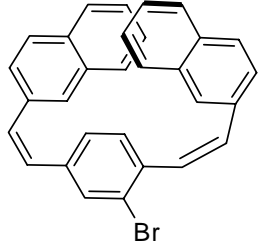
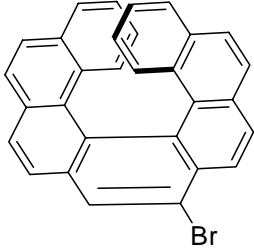
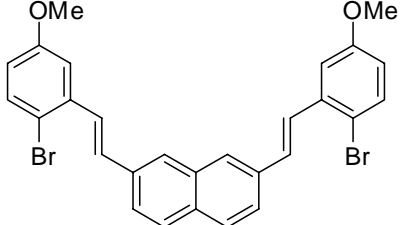
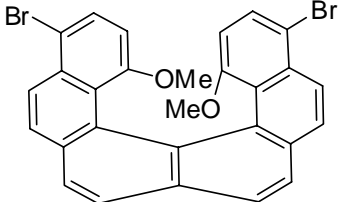
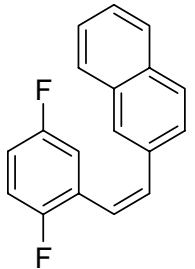
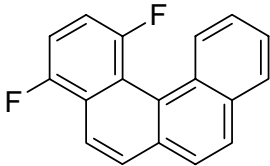
### Stilbene photocyclization under non-oxidative conditions

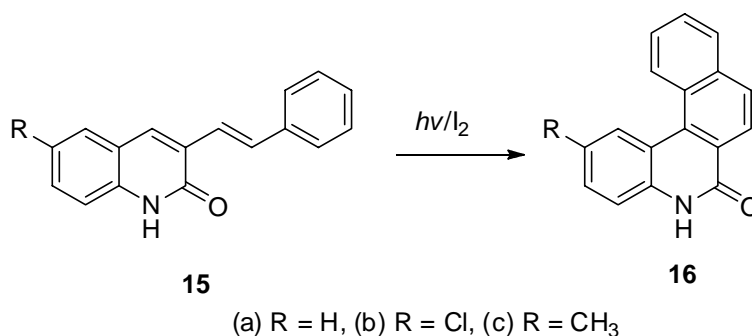
Horspool *et al.* [6, 7] reported the synthesis of 2,3,4,5-tetraphenyl-2,4-cyclopentadien-1-one



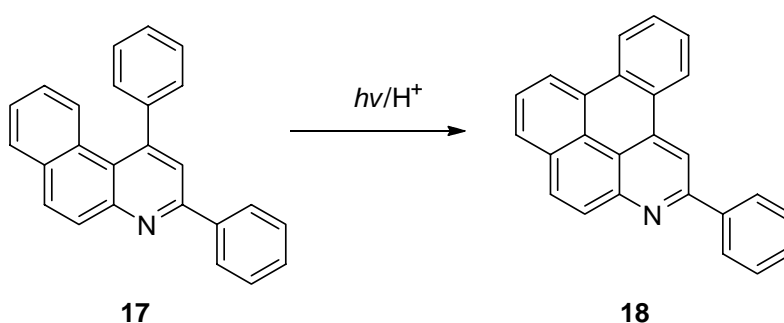
**Scheme 4.** Photolysis of 2-((*E*)-2-{2-bromo-3-[(*E*)-2-(2-naphthyl)ethenyl]phenyl}ethenyl)naphthalene (**13**).

**Table 1.** Comparison of the yields between the use of catalytic amounts of iodine and the Katz-conditions.

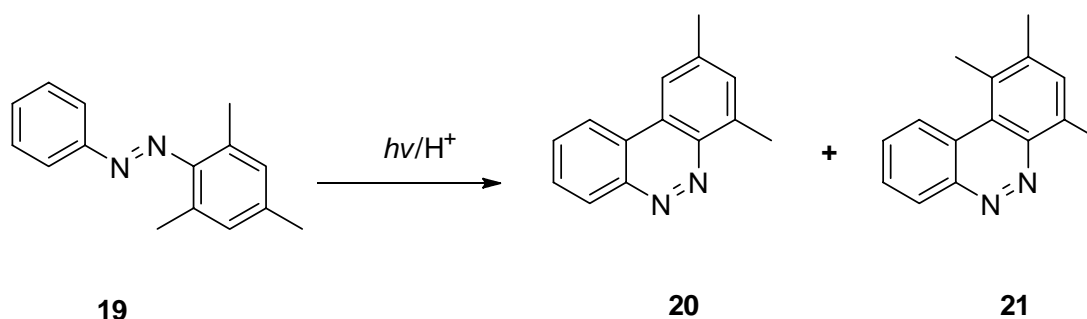
Starting material	Product	Cat. I <sub>2</sub>	Katz's conditions
		51% (8h)	95% (8)
		61% (4h)	100% (1h)
		<8% (3.5h)	61% (13h)
		66% (1.2h)	87% (1.2h)
		<4% (4.5h)	71% (4.5h)
		64% Ref [26]	71% Ref [27]



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



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

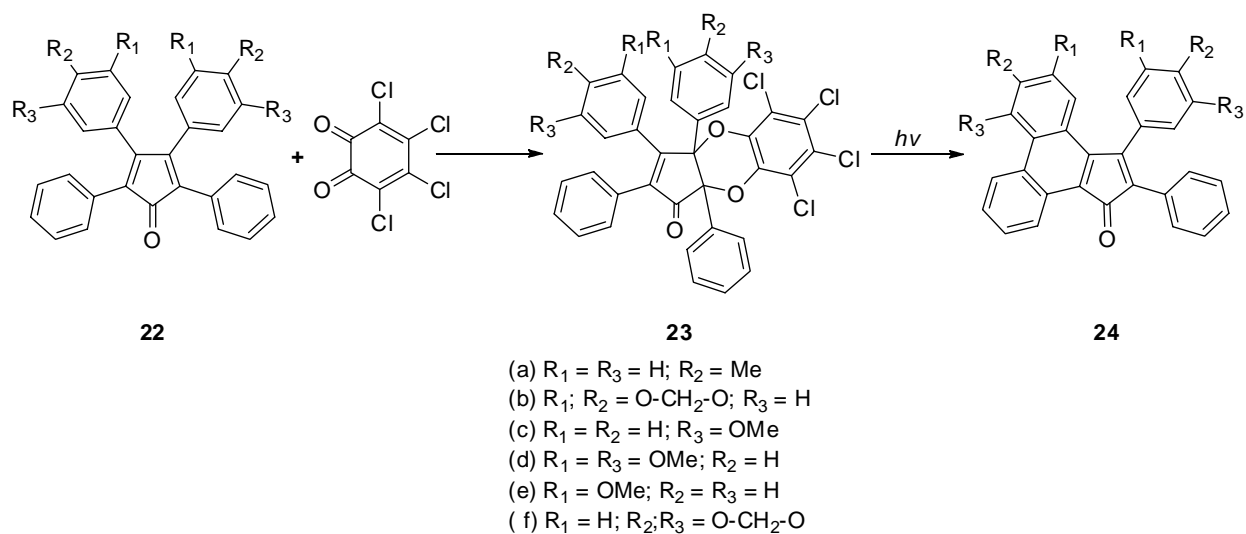


**Scheme 7.** Irradiation of (*E*)-1-mesityl-2-phenyldiazene (**19**) in acidic medium provided (**20**) and (**21**).

(**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-1*H*-cyclopenta[*l*]phenanthren-1-one.

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  $\delta 7.5$ - $\delta 10.0$ . 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



**Scheme 8.** Synthesis of substituted 2,3-diphenyl-1*H*-cyclopenta[*l*]phenanthren-1-one.

**Table 2.** Yield, mp, CHN analysis and IR spectroscopy of compounds 24a-d.

No	Yield %	MP °C	IR (Nujol)/Cm <sup>-1</sup>	CHN/Found	CHN/Calculated
24a	82	197-199	690, 720, 730, 750, 770, 820, 1610, 1700	C, 90.33; H, 5.15	C, 90.70; H, 5.40
24b	76	291-293	670, 690, 720, 730, 740, 760, 770, 1020, 1680	C, 79.28; H, 4.28	C, 79.14; H, 3.86
24c	74	190-195	690, 720, 730, 750, 770, 790, 1030, 1580, 1600, 1700	C, 84.43; H, 5.19	C, 84.14; H, 5.01
24d	75	227-229	690, 720, 730, 750, 790, 1580, 1610, 1700	C, 79.11; H, 5.22	C, 78.86; H, 5.22

photocyclization reaction. However, photolysis of (**23b**) gave (**24f**) as the only isolable product (Table 2). In theory, beside the photoproduct (**24f**) another photoproduct (**24b**) should have been formed. Also, photolysis of (**29**, Scheme 10) gave compound (**30**) as the only isolable photoproduct.

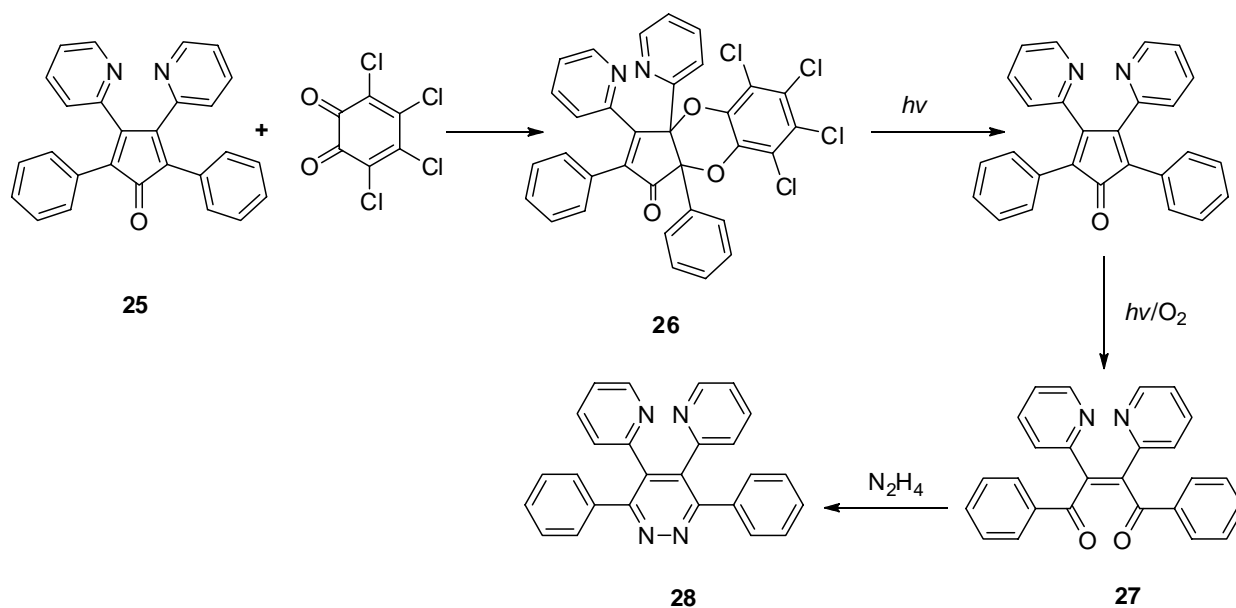
It was reported that adduct (**26**) underwent a retro-Diels-Alder reaction during the photolysis in propan-2-ol, under nitrogen, to give 2,5-diphenyl-3,4-di(2-pyridinyl)-2,4-cyclopentadien-1-one (**25**). An attempt was made to photocyclize (**26**) using iodine as an oxidizing agent, but it failed. Another attempt was made using molecular oxygen as an oxidizing agent, aiming to get a photocyclized product; but (2*Z*)-1,4-diphenyl-2,3-di(2-pyridinyl)-2-butene-1,4-dione (**27**) was

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.

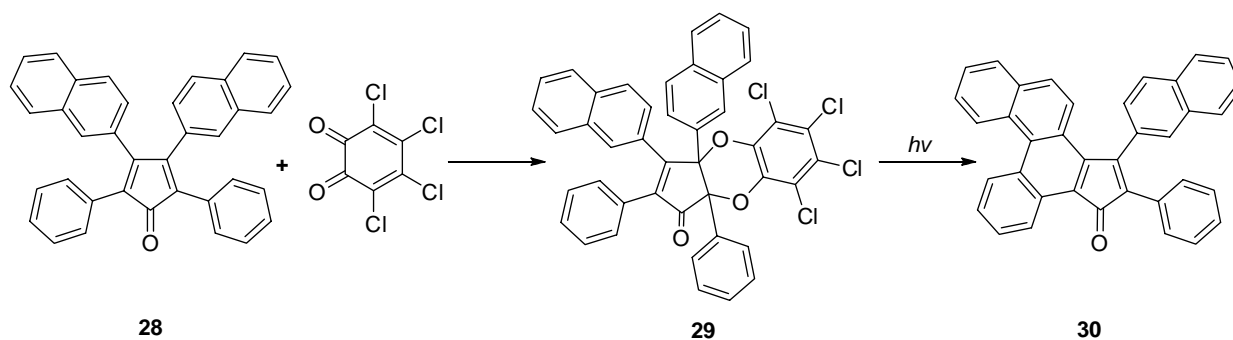
Similarly, Bikales and Becker [34, 35] found the photolysis of 2,3,4,5-tetraphenyl-2,4-cyclopentadien-1-one (**31**) in the presence of oxygen produced *cis* and *trans* (2*Z*)-1,2,3,4-tetraphenyl-2-butene-1,4-dione (**32**, **33**) and 3,4,5,6-tetraphenyl-2*H*-pyran-2-one (**34**, Scheme 11).

#### Mechanism of the photochemical reaction:

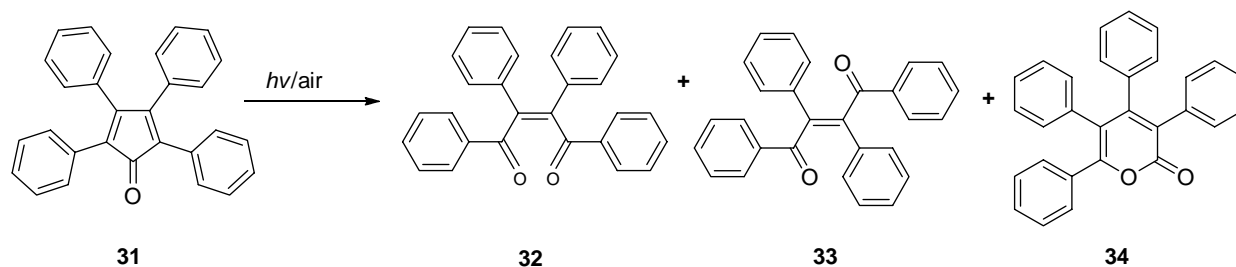
Horspool [36, 37] reported that there are two possible mechanisms for the formation of the substituted 2,3-diphenyl-1*H*-cyclopenta[*l*]



**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**).



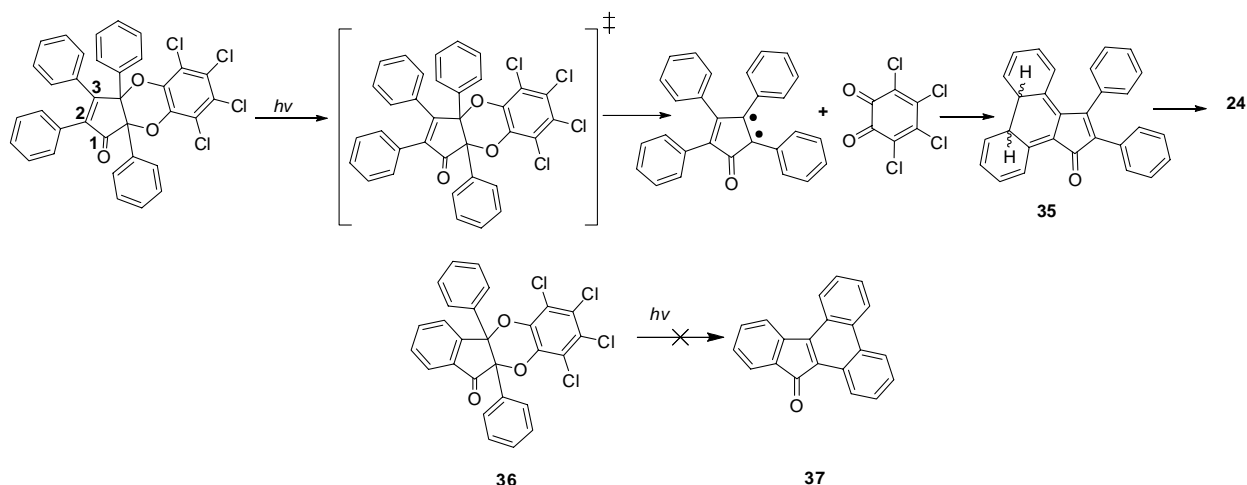
**Scheme 10.** Synthesis of 7-(2-naphthyl)-6-phenyl-5H-benzo[*c*]cyclopenta[*a*]phenanthren-5-one (**30**).



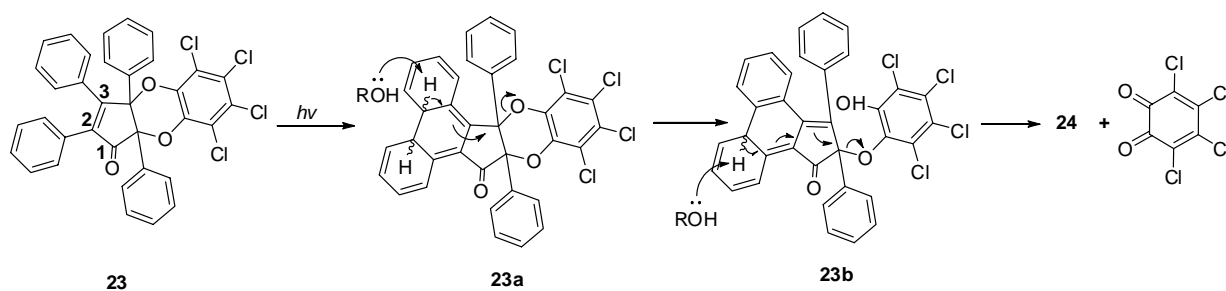
**Scheme 11.** Photolysis of 2,3,4,5-tetraphenyl-2,4-cyclopentadien-1-one (**31**) in the presence of air.

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-benzoquinone to



**Scheme 12.** The first proposed mechanistic route for the formation of the substituted 2,3-diphenyl-1*H*-cyclopenta[*l*]phenanthren-1-one.



**Scheme 13.** The second proposed mechanistic route for the formation of the substituted 2,3-diphenyl-1*H*-cyclopenta[*l*]phenanthren-1-one.

produce an excited 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-11*H*-indeno[1,2-*b*][1,4]benzodioxin-11-one (**36**) failed to form the expected product 13*H*-indeno[1,2-*l*]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 tetrachlorocatechol by a thermal process. The involvement of the aryl groups on the enone double bond was verified by the efficient

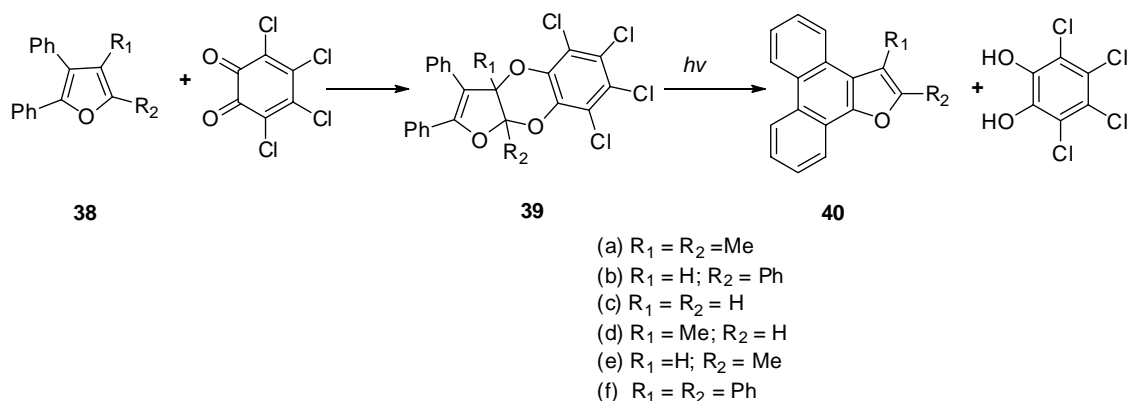
formation of the cyclopentaphenanthrene (**24** Scheme 13) by photolysis of adduct (**23**, Scheme 13) in alcohol. The mechanism depicted in (Scheme 13) should also show some solvent dependency. Thus, in hydroxylic solvents, where proton removal and solvation of the catecholate anion are possible, the 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-triarylfuran (**43 a-h**, Table 3) in which two routes were carried out.

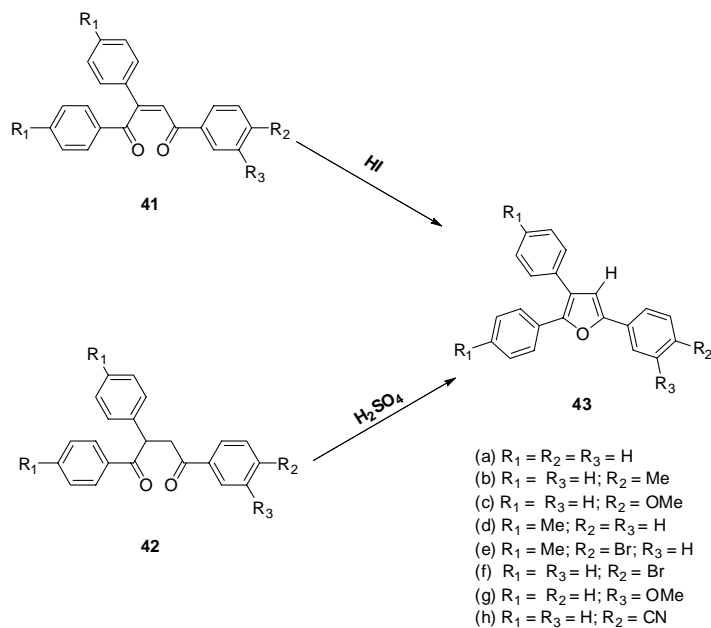




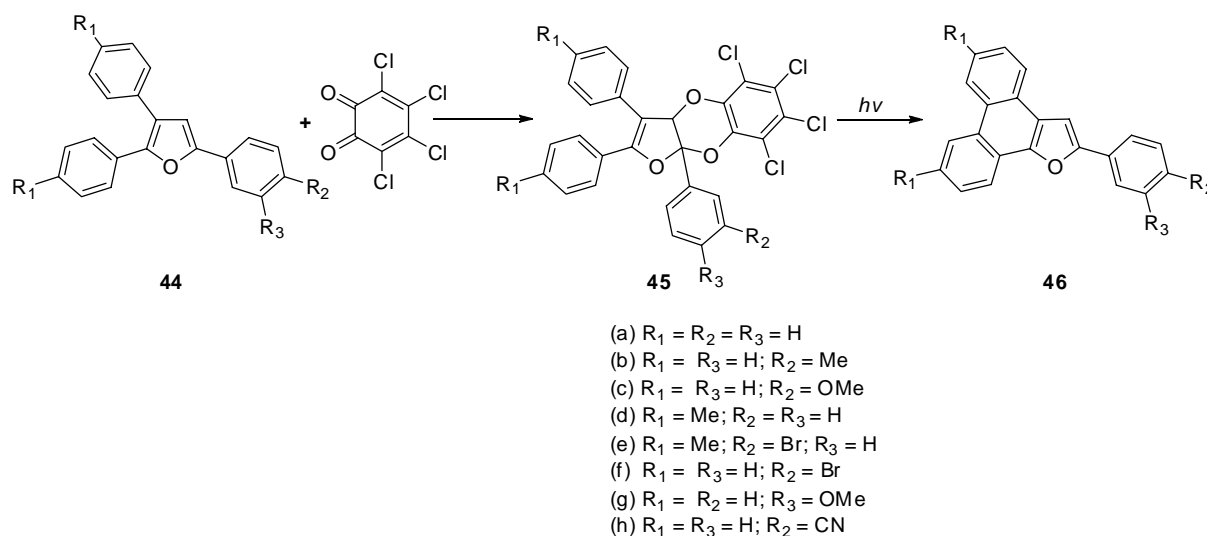
Scheme 14. Synthesis and photolysis of compounds (39a-f).

Table 3.  $^1\text{H}$ NMR ( $\text{CDCl}_3$ ) spectra of substituted 2,3,5-triarylfuran (**43**, a-h).

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



Scheme 15. Synthesis of 2,3,5-triarylfuran.



**Scheme 16.** Synthesis and photolysis of substituted 5,6,7,8-tetrachloro-2,3,9a-triphenyl-3a,9a-dihydrofuro[2,3-*b*][1,4]benzodioxine.

**Table 4.**  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ) spectra of substituted 2-phenylphenanthro[9,10-*b*]furan.

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

The first route was using hydriodic acid and (2*Z*)-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%).

The fact that the phenanthrene system had been formed in the photolysis was confirmed by inspection of  $^1\text{H-NMR}$  spectrum of each product. All of them contained low field resonances between  $\delta 7.0$ - $\delta 8.7$ . This is typical for phenanthrene systems [**6**, Scheme 1]; phenanthrene itself showing a resonance at  $\delta 8.65$ . The details of the  $^1\text{H-NMR}$  spectra of the substituted 2-phenylphenanthro[9,10-*b*]furan (**46a-h**, Scheme 16) are contained in (Table 4).

#### ACKNOWLEDGEMENT

The author would like to thank Mrs. Carol Khalaf for her help, advice and encouragement in the preparation of this article.

#### REFERENCES

- Smakula, A. 1934, *Z. physik. Chem.*, B25, 90-98.
- Buckles, R. E. 1955, *J. Amer. Chem. Soc.*, 77, 1040-1041.
- Mallory, F. B., Wood, C. S., and Gordon, J. T. 1964, *J. Amer. Chem. Soc.*, 86, 3094-3102.
- Mallory, F. B. and Wood, C. S. 1964, *J. Org. Chem.*, 29, 3374-3377.
- Khalaf, A. I. 1983, PhD thesis, Dundee University, Dundee, Scotland, UK.
- Horspool, W. M. and Khalaf, A. I. 1983, *Tetrahedron Letters*, 24(35), 3745-3748.

7. a) Horspool, W. M. and Khalaf, A. I. 1989, *J. Chem. Soc. Perkin Transaction I*, 1147-1152. b) Anderson, D. T. and Horspool, W. M. 1971, *J. Chem. Soc., Chem. Commun.*, 615.
8. Mallory, F. B. and Mallory, C. W. 1984, *Org. React.*, 30, 1-456.
9. a) Laarhoven, W. H., *Recueil*, J. 1983, *Royal Netherlands Chem. Soc.*, 102, 185-204. b) Laarhoven, W. H. and *Recueil*, J. 1983, *Royal Netherlands Chem. Soc.*, 102, 241-254.
10. Hagen, S. and Hopf, H. 1998, *Topics in Current Chemistry*, 196, 45-89.
11. Meier, H. 1992, *Angew. Chem. Int. Ed. Eng.*, 31, 1399-1420.
12. Tominaga, Y. and Castle, R. N. 1996, *J. Heterocycl. Chem.*, 33, 523-538.
13. Laarhoven, W. H. 1989, *Org. Photochem.*, 10, 163-308.
14. a) Meier, H. 1992, *Angew. Chem. Int. Ed. Eng.*, 31, 1399-1420. b) Tominaga, Y. and Castle, R. N. 1996, *J. Heterocycl. Chem.*, 33, 523-538. c) Laarhoven, W. H. 1989, *Org. Photochem.*, 10, 163-308. d) Mori, T. 2005, *Mol. Supramol. Photochem.*, 12, 417-452.
15. Zertani, R. and Meier, H. 1986, *Chem. Ber.*, 119, 1704-1715.
16. Noller, K., Kosteyn, F., and Meier, H. 1988, *Chem. Ber.*, 121, 1609-1616.
17. Meier, H. 1992, *Angew. Chem. Int. Eng.*, 31, 1399-1420.
18. Sudhakar, A. and Katz, T. J. 1986, *Tetrahedron Lett.*, 27, 2231-1134.
19. Sudhakar, A., Katz, T. J., and Yang, B. 1986, *J. Amer. Chem. Soc.*, 108, 2790-2791.
20. Liu, L., Yang, B., Katz, T. J., and Poindexter, M. K. 1991, *J. Org. Chem.* 56, 3769-3775.
21. Sudhakar, A. and Katz, T. J. 1986, *Tetrahedron Lett.*, 27, 2231-2234.
22. Sudhakar, A., Katz, T. J., and Yang, B. 1986, *J. Amer. Chem. Soc.* 108, 2790-2791.
23. Martin, R. H., Eyndels, Ch., and Defay, N. 1972, *Tetrahedron Lett.*, 27, 2731-2734.
24. Laarhoven, W. H. and Cuppen, Th. J. H. M. 1971, *Tetrahedron Lett.*, 2, 163-164.
25. Wilcox, C. F. Jr., Lahti, P. M., Rocca, J. R., Halpern, M. B., and Meinwald, J. 1978, *Tetrahedron Lett.*, 22, 1893-1896.
26. Bae, S., Mah, H., Chaturvedi, S., Jeknic, T. M., Baird, W. M., Katz, A. K., Carrell, H. L., Glusker, J. P., Okazaki, T., Laali, K. K., Zajc, B., and Lakshman, M. K. 2007, *J. Org. Chem.*, 72 (20), 7625-7633.
27. Plater, M. J. 1994, *Tetrahedron Lett.*, 35 (33), 6147-6150.
28. Arisvaran, V., Ramesh, M., Rajendran, S. P., and Shanmugam, P. 1981, *Synthesis*, 821-823.
29. Huisgen, R. 1949, *Justus Liebigs Annalen der Chemie.*, 564, 16-32.
30. Badger, G. M., Drewer, R. J., and Lewis, G. E. 1964, *Australian J. Chemistry*, 17(9), 1036-49.
31. Eistert, B., Fink, G., and El-Chahawi, M. A. 1967, *Justus Liebigs Annalen der Chemie.*, 703, 104-108.
32. Arbuzov, B. A. and Akhmed-Zade, Dzh. A. 1942, *Zhurnal Obshchei Khimii.*, 12, 212-219.
33. Ogliaruso, M. A., Romanelli, M. G., and Becker, E. I. 1965, *Chem. Rev.*, 65(3), 261-367.
34. Bikales, N. M. and Becker, E. I. 1956, *J. Org. Chem.*, 21, 1405-1407.
35. Ogliaruso, M. A., Romanelli, M. G., and Becker, E. I. 1965, *Chem. Rev.*, 65(3), 261-367.
36. Horspool, W. M. 1971, *J. Chem. Soc. (c)*, 400-404.
37. Horspool, W. M. 1969, *Chem. Commun.*, 467-468.
38. Alex Smith. 1890, *J. Chem. Soc. Transactions*, 57, 643-652.
39. Hendrickson, J. B., Rees, R., and Templeton, J. F. 1964, *J. Amer. Chem. Soc.*, 86(1), 107-111.
40. Padwa, A. and Hartman, R. 1966, *J. Amer. Chem. Soc.*, 88(7), 1518-1524.