The Photocyclisation of Stilbene Analogues

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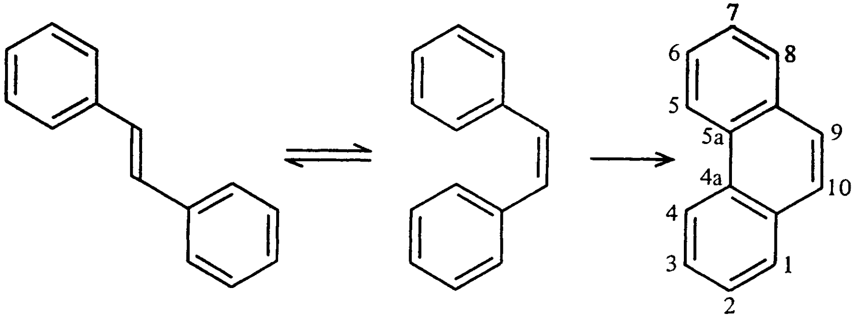
1 Introduction

Stilbene and its analogues undergo many interesting photochemical reactions, *e.g.* photoisomerisation, dimerisation, and intramolecular rearrangements. Two isomers of stilbene are known, *trans*-stilbene (I) and *cis*-stilbene (II), and photochemical interconversion may be effected by direct irradiation or by irradiation in the presence of a sensitiser. A triplet mechanism has been substantiated for the latter case,[1] however the mechanism of the former reaction is still the subject of much controversy.[2, 3]



(I) (II) (III)

The lowest triplet state of stilbene is of considerable interest because of its possible rôle in the *cis-trans* photoisomerisations. Several groups have studied the flash photolysis of *trans*-stilbene in a rigid medium at 77° K and reported the reversible formation of a transient spectrum, with vibrational fine structure which has been attributed to the triplet of *trans*-stilbene.[4, 5]

The photodimerisation[6–10] and mixed photoaddition[11] reactions of stilbene

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[1] J. Saltiel, *J. Amer. Chem. Soc.*, 1968, **90,** 6394.

[2] D. Gegiou, K. A. Muszkat, and E. Fischer, *J. Amer. Chem. Soc.*, 1968, **90,** 3907 and refs therein.

[3] J. Saltiel and E. D. Megarity, *J. Amer. Chem. Soc.*, 1969, **91,** 1265.

[4] G. Heinrich, H. Blume, and D. Schulte-Frohlinde, *Tetrahedron Letters*, 1967, 4693.

[5] W. G. Herkstroeter and D. S. McClure, *J. Amer. Chem. Soc.*, 1968, **90,** 4522.

[6] G. Ciamician and P. Silber, *Ber.*, 1902, **35,** 4128; H. Stobbe, *Ber.*, 1914, **47,** 2701; H. M. Rosenberg, R. Rondeau, and P. Servé, *J. Org. Chem.*, 1969, **34,** 471.

[7] J. D. Dunitz, *Acta Cryst.*, 1949, **2,** 1.

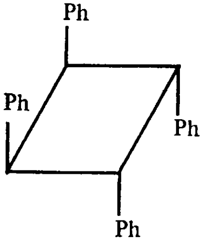
[8] H. Schechter, W. J. Link, and G. V. D. Tiers, *J. Amer. Chem. Soc.*, 1963, **85,** 1601

[9] G. Montaudo, *Gazz. Chim. Ital.*, 1964, **94,** 127.

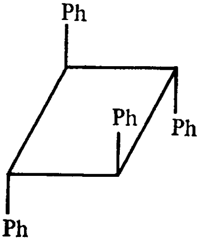
[10] H. Stegemeyer, *Chimia (Aarau)*, 1965, **19,** 536.

[11] D. Bryce-Smith and A. Gilbert, *Chem. Comm.*, 1968, 1701 and 1702.

and its analogues[12–15] are well known and the dimers obtained after irradiation of solutions of *trans*-stilbene have been formulated as (IV) and (V).[7, 8] This dimerisation probably involves a singlet mechanism[9, 10] and the absence of dimerisation from *cis*-stilbene may be caused by the short lifetime of the molecule in the first excited singlet state. *Trans*-stilbene does not dimerise, however, in the crystalline state.[10]



(IV)



(V)

A particularly important photochemical reaction of stilbene is the photocyclodehydrogenation of *cis*-stilbene (II) to give phenanthrene (III). In 1934 Smakula observed that a compound having $\lambda_{max.}$ 247 nm was formed from the irradiation of a solution of *cis*-stilbene.[16] Lewis, Magel, and Lipkin found that a yellow substance was formed immediately upon irradiation of *cis*-stilbene, but only slowly from *trans*-stilbene.[17] This suggested the formation of a secondary product directly from *cis*-stilbene. However, it was not until 1950 that the compound having $\lambda_{max.}$ 247 nm was identified as phenanthrene (III) by Parker and Spoerri.[18] As phenanthrene is colourless, its presence could not account for the yellow colour observed.[17] Buckles confirmed the formation of phenanthrene which he obtained in good yield.[19]

2 Polyhomocyclic Aromatic Compounds

The synthetic potential of the photocyclodehydrogenation reaction of stilbene analogues to polyhomocyclic aromatic compounds is very great and has been extensively studied by Hugelshofer, Kalvoda, and Schaffner.[20] They found that irradiation of 3,3′-dimethoxystilbene in hexane gave a mixture of 2,5-dimethoxyphenanthrene and 2,7-dimethoxyphenanthrene, but detected no 4,5-dimethoxyphenanthrene, probably due to steric effects. Stilboestrol and its dimethyl ether also photocyclised to give the expected phenanthrenes.

Fonken prepared 1-phenylnaphthalene (VII) and chrysene (IX) by the

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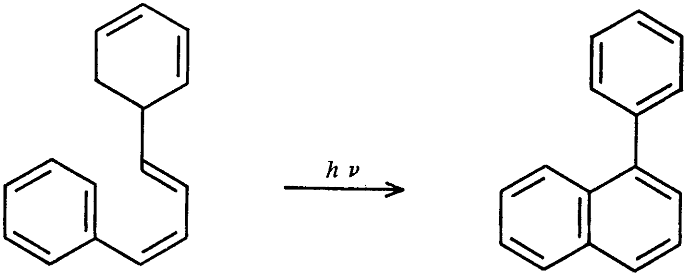
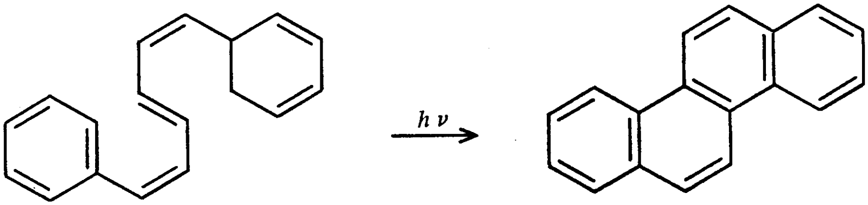
[12] G. Koller, *Ber.*, 1927, **60**, 1920.
[13] J. L. R. Williams, S. K. Webster, and J. A. Van Allan, *J. Org. Chem.*, 1961, **26**, 4893.
[14] M. Henze, *Ber.*, 1937, **70B**, 1273.
[15] H. Erlenmeyer, H. Baumann, and E. Sorkin, *Helv. Chim. Acta*, 1948, **31**, 1978.
[16] A. Smakula, *Z. phys. Chem.*, 1934, **B25**, 90.
[17] G. N. Lewis, T. T. Magel, and D. Lipkin, *J. Amer. Chem. Soc.*, 1940, **62**, 2973.
[18] C. O. Parker and P. E. Spoerri, *Nature*, 1950, **166**, 603.
[19] R. E. Buckles, *J. Amer. Chem. Soc.*, 1955, **77**, 1040.
[20] P. Hugelshofer, J. Kalvoda, and K. Schaffner, *Helv. Chim. Acta*, 1960, **43**, 1322.

irradiation of 1,4-diphenylbuta-1,3-diene (VI) and 1,6-diphenylhexa-1,3,5-triene (VIII) respectively.[21]



(VI) (VII)



(VIII) (IX)

Mallory and his co-workers have studied the synthetic potential of the photocyclodehydrogenation reaction of substituted stilbenes to give phenanthrenes in good yield.[22–25] They found that the most satisfactory conditions for preparative scale conversions involved the irradiation of the stilbene analogue (0·01 mole) and iodine (0·0005 mole) dissolved in cyclohexane (1 1.) under an air atmosphere using an unfiltered 100 watt medium pressure mercury arc. When oxygen was excluded, so that iodine was the only oxidant present, the time required for the conversion of the stilbene was not altered significantly but the yield of phenanthrene was decreased. Chloranil and selenium were also found to be useful oxidants. Yields were generally in the 60—85% range on a scale of 2—3 g. Successful conversions were achieved with stilbenes bearing fluoro, chloro, bromo, methoxy, methyl, trifluoromethyl, phenyl, and carboxyl substituents but the method failed for stilbenes having nitro, acetyl, or dimethylamino substituents.

Iodo substituents were found to be lost owing to the ready photolysis of the

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[21] G. J. Fonken, *Chem. and Ind.*, 1962, 1327.

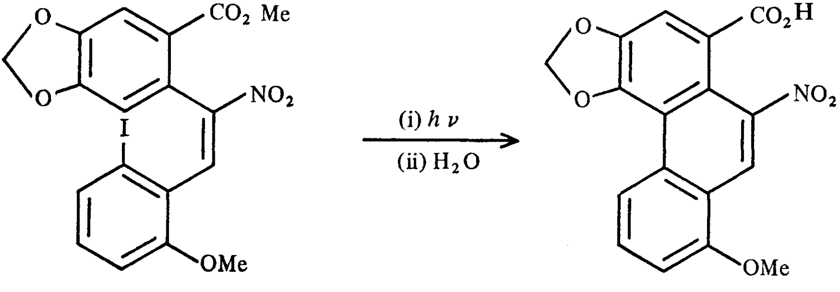
[22] F. B. Mallory, C. S. Wood, J. T. Gordon, L. C. Lindquist, and M. I. Savitz, *J. Amer. Chem. Soc.*, 1962, **84**, 4361.

[23] F. B. Mallory, J. T. Gordon, and C. S. Wood, *J. Amer. Chem. Soc.*, 1963, **85**, 828.

[24] F. B. Mallory, C. S. Wood, and J. T. Gordon, *J. Amer. Chem. Soc.*, 1964, **86**, 3094.

[25] C. S. Wood and F. B. Mallory, *J. Org. Chem.*, 1964, **29**, 3373.

carbon–iodine bond; thus *o*- and *p*-iodostilbene gave phenanthrene in very high yield.[26] Nitro substituted 2-iodostilbenes also photocyclised to provide a useful synthetic route to nitrophenanthrenes as they could not be prepared by irradiation of the corresponding unsubstituted nitrostilbene. This reaction has been utilised in the synthesis of the naturally occurring tumour inhibitor, aristolochic acid (X).[26] A radical mechanism seems likely for this reaction and this photochemical Ullmann reaction has been used to prepare other ring systems.[27]



(X)

The use of copper halides as catalysts in the photocyclisation of some α,α′-disubstituted stilbenes has been reported.[28] Irradiation of 4,4′-dimethoxy-α,α′-dimethylstilbene gave only 0·6% 3,6-dimethoxy-9,10-dimethylphenanthrene on irradiation in ethanol in the presence of iodine. However, addition of cupric chloride or bromide improved the yield to 54%. Irradiation of the stilbene in the presence of iodine in cyclohexane solution gave 11% of the phenanthrene and also 9% of *p*-methoxyacetophenone. The formation of the acetophenone is the first photo-oxidative cleavage to be reported in these systems.

Selenium radicals have been used in the photocyclisation aromatisation of a degassed solution of 3,3′,5,5′-tetramethyl stilbene to 2,4,5,7-tetramethylphenanthrene.[29] However, better yields of the phenanthrene have been reported using iodine and dissolved oxygen as oxidants.[30]

Atomic sulphur has also been utilised as an oxidant.[31] Irradiation of a degassed solution of *cis*-stilbene sulphide (XI) gave phenanthrene. It appears that atomic sulphur generated from (XI) acts as oxidant and that the first stage of the reaction is desulphurisation to give *cis*-stilbene.

A photoexcited carbonyl group has been utilised as the hydrogen scavenger. Thus irradiation of tetraphenyl cyclopentadienone (XII) in solution under a slow stream of nitrogen gave 2,3-diphenyl-1*H*-cyclopentano[*l*]phenanthrene

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[26] S. M. Kupchan and H. C. Wormser, *Tetrahedron Letters*, 1965, 359.

[27] R. K. Sharma and N. Kharasch, *Angew. Chem. Internat. Edn.*, 1968, **7**, 36.

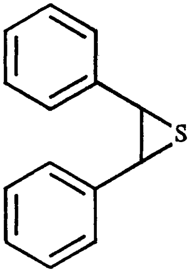
[28] D. J. Collins and J. J. Hobbs, *Austral. J. Chem.*, 1967, **20**, 1905.

[29] E. J. Levi and M. Orchin, *J. Org. Chem.*, 1966, **31**, 4302.

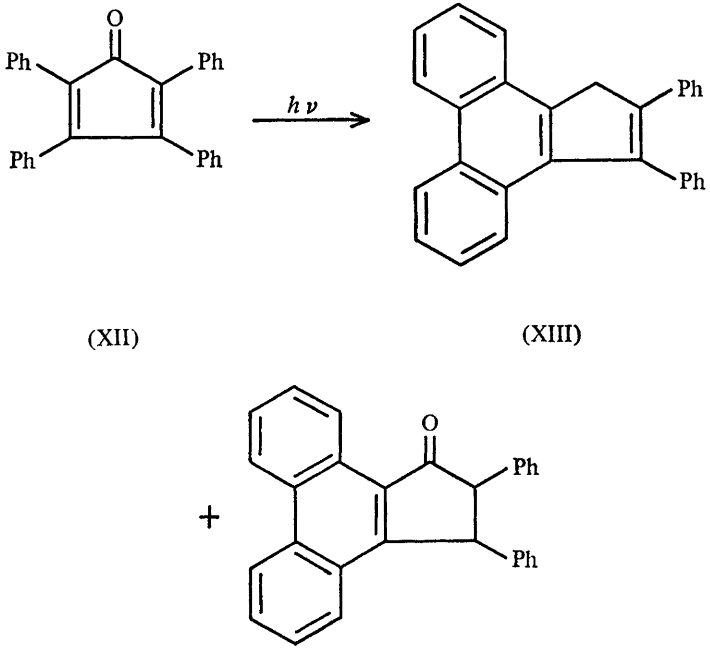
[30] E. V. Blackburn, C. E. Loader, and C. J. Timmons, *J. Chem. Soc.* (*C*), 1968, 1576.

[31] T. Sato, Y. Goto, T. Tohyama, S. Hayashi, and K. Hata, *Bull. Chem. Soc. Japan*, 1967, **40**, 2975.

(XIII) and 1-oxo-2,3-diphenyl-2,3-dihydro-1*H*-cyclopentano[*l*]phenanthrene (XIV) when a protic solvent was used. No phenanthrene was obtained in the absence of such a solvent.[32]



(XI)



(XII) (XIII)

(XIV)

Horspool has reported the irradiation of the adduct (XV) to give the cyclopentenophenanthrene derivative (XVI).[33]

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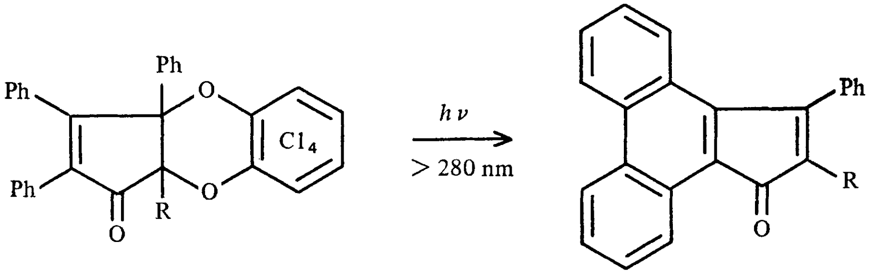
[32] I. Moritani and N. Toshima, *Tetrahedron Letters*, 1967, 467; N. Toshima and I. Moritani, *Bull. Chem. Soc. Japan*, 1967, **40**, 1495.

[33] W. M. Horspool, *Chem. Comm.*, 1969, 467.



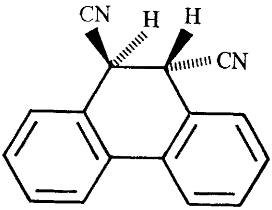
(XV)

(a) R = Ph
(b) R = Me

(XVI)

Stilbenes substituted at the point of cyclisation have been shown to eject the substituents.[30] Irradiation of 2,2′,3,3′-tetramethylstilbene gave 1,2,5,-trimethylphenanthrene, by methyl elimination, as well as 1,2,7,8-tetramethylstilbene.[34] The elimination of methyl and methoxy groups in other stilbenes has been reported.[25, 35] Styrylnaphthalenes substituted by methyl, bromo, or chloro groups at the points of cyclisation also photocyclise with elimination of these substituents.[36]

Sargent and Timmons have photocyclised several α-substituted and α,α′-disubstituted stilbenes to the corresponding 9-mono- and 9,10-di-substituted phenanthrenes.[37] They also found that 9,10-dihydrophenanthrenes could be prepared by the degassed irradiation of stilbenes with electron withdrawing substituents in the α,α′-positions. Thus irradiation of a degassed benzene solution of α,α′-dicyanostilbene gave *trans*-9,10-dicyano-9,10-dihydrophenanthrene (XVII). Irradiation of diphenylmaleimide, however, gave the *cis*-dihydrophenanthrene (XVIII). The mechanistic implications of this reaction are not clear.



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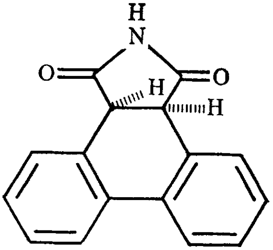

(XVIII)

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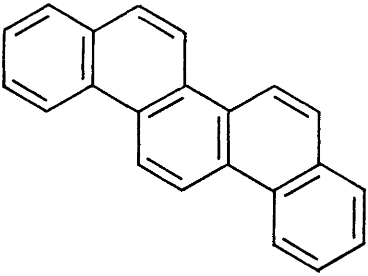
[34] W. Carruthers and H. N. M. Stewart, *J. Chem. Soc.* (*C*), 1967, 556.
[35] K. L. Servis and Kai-Nan Fang, *Tetrahedron Letters*, 1968, 967.
[36] E. V. Blackburn, C. E. Loader, and C. J. Timmons, *J. Chem. Soc.* (*C*), 1969, in the press.
[37] M. V. Sargent and C. J. Timmons, *J. Chem. Soc.*, 1964, 5544.

A substituted anthracene has been isolated from an irradiated solution of 4,4′-diethoxycarbonylstilbene in AnalaR n-butanol. 3,6-Diethoxycarbonylphenanthrene and 2,6-diethoxycarbonylanthracene were formed in a ratio of 4 : 1.[38]

The photocyclisation of the three isomeric distyrylbenzenes has been reported recently.[39] 1,2-Distyrylbenzene gave picene (XIX), the 1,3-distyrylbenzene gave benzo[*c*]chrysene (XX), and 1,4-distyrylbenzene gave benzo[*g*,*h*,*i*]perylene (XXI) on irradiation.



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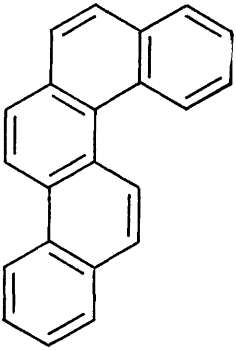

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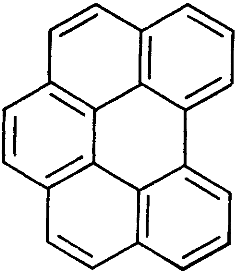

(XXI)

Photocyclisation reactions also occur with the styrylnaphthalenes and provide an excellent synthetic route to chrysene and benzo[*c*]phenanthrene derivatives.[36] Irradiation of solutions of 1-styrylnaphthalene and 2-styrylnaphthalene (XXII) gave chrysene[20] and benzo[*c*]phenanthrene[40] (XXIII) respectively. Cyclisation in the case of 2-styrylnaphthalenes is always to the α-position of the naphthalene nucleus. Picene,[19] benzo[*g*]chrysene,[41] and benzo[*g*,*h*,*i*]perylene[40] have all been prepared in this manner.

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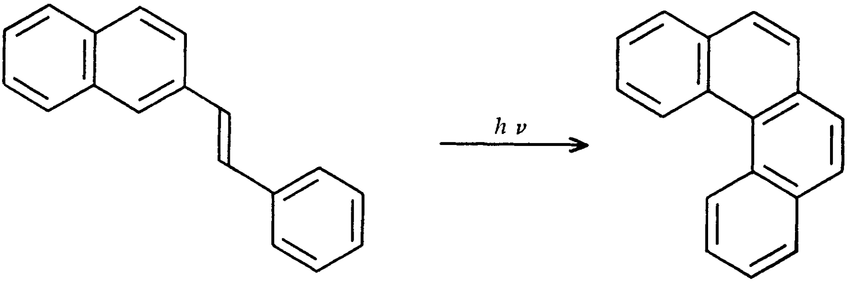
[38] S. D. Cohen, M. V. Mijovic, and G. A. Newman, *Chem. Comm.*, 1968, 722.

[39] F. Dietz and M. Scholz, *Tetrahedron*, 1968, **24**, 6845.

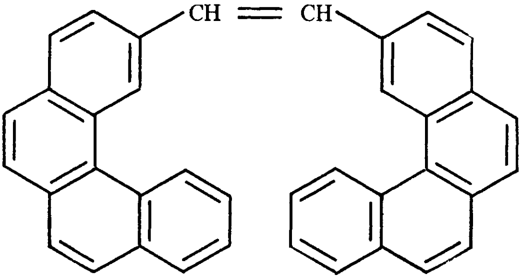
[40] M. Scholz, M. Mühlstädt, and F. Dietz, *Tetrahedron Letters*, 1967, 665.

[41] W. Carruthers, *J. Chem. Soc.* (*C*), 1967, 1525.



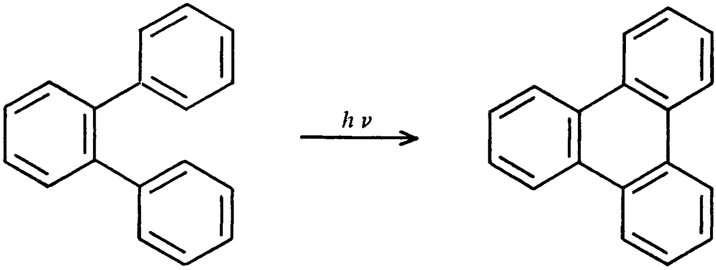
(XXII) (XXIII)

The synthetic potential of this basic reaction has been elegantly exploited in the synthesis of hepta-, octa-, and nona-helicene from the corresponding stilbene analogue.[42] Irradiation of (XXIV) in benzene containing iodine, for example, gave nonahelicene (bisphenanthro[3,4-*c*:4′,3′-*g*]phenanthrene) in 48% yield.



(XXIV)

The ethylenic linkage of the stilbene chromophore may be part of a ring system and in most cases the photocyclodehydrogenation reaction proceeds to give the expected products. Irradiation of a benzene solution of *o*-terphenyl (XXV) in the presence of a large excess of iodine gave complete conversion to triphenylene (XXVI).[43]



(XXV) (XXVI)

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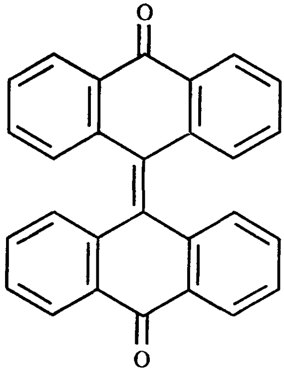
[42] R. H. Martin, M. Flammang-Barbieux, J. P. Cosyn, and M. Gelbcke, *Tetrahedron Letters*, 1968, 3507.

[43] N. Kharasch, T. G. Alston, H. B. Lewis, and W. Wolf, *Chem. Comm.*, 1965, 242; T. Sato, Y. Goto, and K. Hata, *Bull. Chem. Soc. Japan*, 1967, **40**, 1994.

Similarly, *o,p*-quaterphenyl gave 2-phenyltriphenylene. The iodine must play a key part in the reaction which is probably of a free radical nature.

White and Anhalt have reported that irradiation of 1,2,5,6-tetraphenyl-1,5-cyclooctadiene and 1,2-diphenylcyclobutene lead to the development of phenanthrene type spectra. However, no phenanthrene analogues were isolated.[44]

The bianthrone derivatives possess potential stilbene chromophores and the photocyclisation of these compounds has been known for a long time. In 1912 Meyer, Bondy, and Eckert reported that dehydrodianthrone (XXVII) and helianthrone (XXVIII) are converted by irradiation in solution into *meso*-naphthodianthrone (XXIX).[45] Brockmann and Mühlmann have extensively studied this reaction.[46] The photocyclisation will proceed in pyridine and glacial acetic acid and for each mole of photoproduct formed, one mole of oxygen was consumed with liberation of hydrogen peroxide. Brockmann has also extended the scope of this reaction synthetically and this culminated in the synthesis of the *Hypericum* pigment hypericin (XXX). It was suggested that a similar photocyclisation was also likely to be a biosynthetic step in hypericin formation in the plant.[47]



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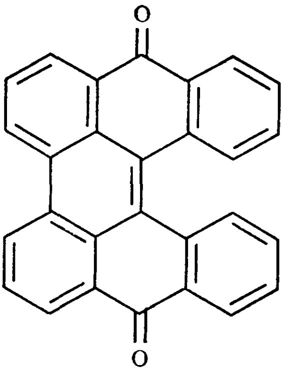

(XXVIII)

3 Polyheterocyclic Aromatic Compounds

The photocyclodehydrogenation of stilbene has been extended to its heterocyclic analogues with considerable success. Styrylpyridines photocyclise in cyclohexane solution to the otherwise relatively inaccessible azaphenanthrenes. Thus benzo[*f*]quinoline (XXXI), benz[*f*]isoquinoline (XXXII), and benz[*h*]-isoquinoline (XXXIII) have been prepared by the photochemical cyclohydrogenation of 2-, 3-, and 4-styrylpyridine respectively.[48] 3-Styrylpyridine has also

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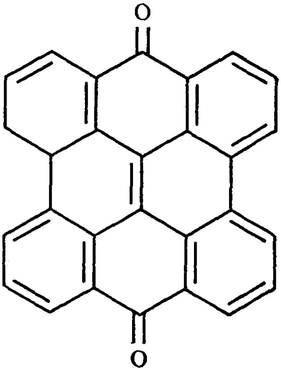
[44] E. H. White and J. P. Anhalt, *Tetrahedron Letters*, 1965, 3937.
[45] H. Meyer, R. Bondy, and A. Eckert, *Monatsh*, 1912, 33, 1447.
[46] H. Brockmann and R. Mühlmann, *Chem. Ber.*, 1949, **82**, 348.
[47] H. Brockmann, *Proc. Chem. Soc.*, 1957, 304.
[48] C. E. Loader and C. J. Timmons, *J. Chem. Soc.* (*C*), 1966, 1078.



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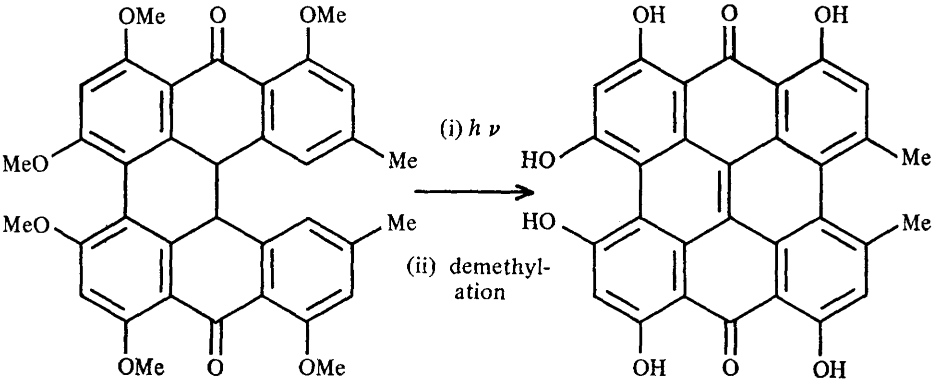

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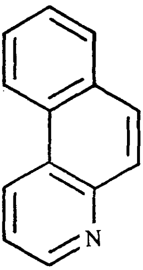

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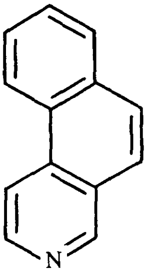

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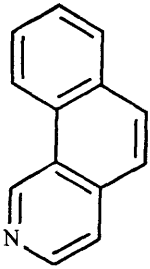

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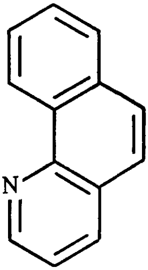

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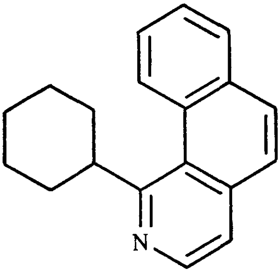

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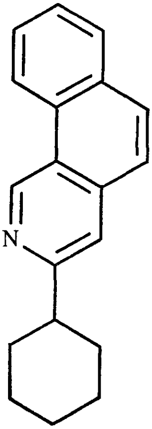
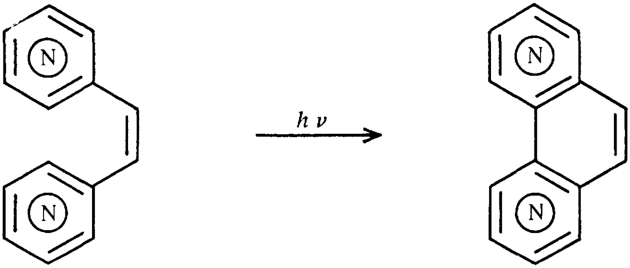


(XXXVI)

been reported to photocyclise to benzo[*h*]quinoline (XXXIV).[49] Loader and Timmons have reported an interesting side reaction on irradiation of 4-styrylpyridine.[50] They isolated 1- and 3-cyclohexylbenz[*h*]isoquinoline (XXXV and XXXVI) in the photocyclodehydrogenation of 4-styrylpyridine to benz[*h*]isoquinoline in cyclohexane solution.

4-Styrylpyrimidines,[51] styrylquinolines, and styrylisoquinolines[52] photocyclise in the expected manner.

Perkampus and Kassebeer have prepared all the isomers of phenanthroline (XXXVIII) by the photocyclisation of 1,2-dipyridylethylenes (XXXVII).[53]



(XXXVII) (XXXVIII)

A route to the benzo[*a*]quinolizinium salt (XL) has been developed by Doolittle and Bradsher.[54] The photocyclisation is performed in ethanol containing iodine and the benzoquinolizinium salt is obtained in good yield (60%).

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[49] P. Bortolus, G. Cauzzo, and G. Galiazzo, *Tetrahedron Letters*, 1966, 3717.

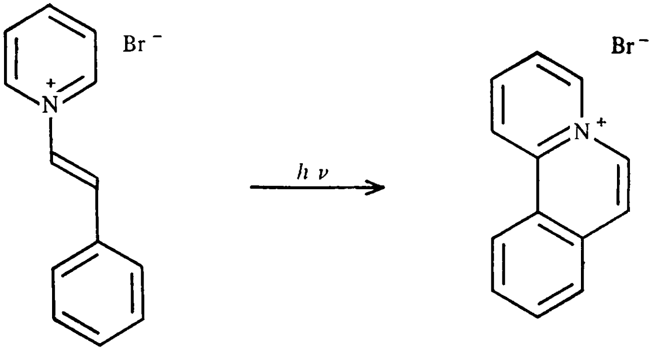
[50] C. E. Loader and C. J. Timmons, *J. Chem. Soc. (C)*, 1967, 1457.

[51] C. E. Loader and C. J. Timmons, *J. Chem. Soc. (C)*, 1967, 1343.

[52] S. F. Dyke and M. Sainsbury, *Tetrahedron*, 1967, **23**, 3161; C. E. Loader and C. J. Timmons, *J. Chem. Soc. (C)*, 1968, 330.

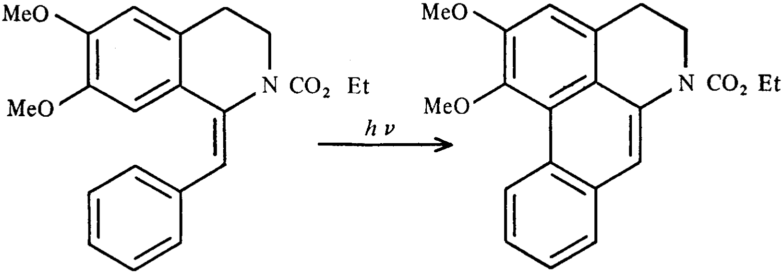
[53] H. H. Perkampus and G. Kassebeer, *Ann.*, 1966, **696**, 1.

[54] R. E. Doolittle and C. K. Bradsher, *J. Org. Chem.*, 1966, **31**, 2616.



(XXXIX) (XL)

The photocyclisation reaction has been applied to the synthesis of aporphine alkaloids.[55] The aporphine alkaloid derivative *N*-carbethoxy-6*a*,7-dihydronornuciferine (XLII) has been prepared by the photocyclisation of the stilbene analogue, benzylidene-2-carbethoxy-6,7-dimethoxy-1,2,3,4-tetrahydroiso quinoline (XLI).



(XLI) (XLII)

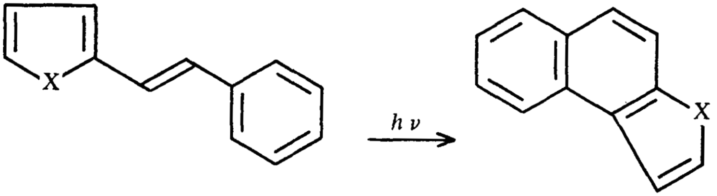
Either one of both of the heterocyclic rings may be five membered. Carruthers and Stewart reported the cyclisation of 2-styrylthiophen (XLIII; X=S) and 3-styrylbenzothiophen to the corresponding cyclised product in good yield on irradiation in hexane.[56] 2-Styrylfuran (XLIII; X=O) has also been photocyclised but the yield of cyclised product was poor.[57] 1,2-Di(2-furyl)ethylene and 1,2-di(2-thienyl)ethylene (XLV) photocyclised as expected. The compounds containing thiophen rings rather than furan rings appeared to be less liable to photochemical decomposition. Light filtered through Pyrex improved the yields.

[55] M. P. Cava and S. C. Havlicek, *Tetrahedron Letters*, 1967, 2625; N. C. Yang, A. Shani, and G. R. Lenz, *J. Amer. Chem. Soc.*, 1966, **88**, 5369; G. R Lenz and N. C. Yang, *Chem. Comm.*, 1967 1136.

[56] W. Carruthers and H. N. M. Stewart, *J. Chem. Soc.*, 1965, 6221.

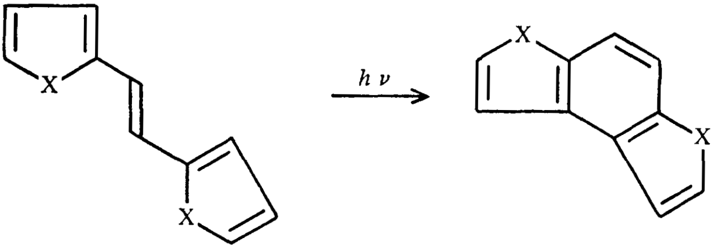
[57] C. E. Loader and C. J. Timmons, *J. Chem. Soc.* (*C*), 1967, 1677.

1-(2-Furyl)-2-(2-thienyl)ethylene gave thieno[3,2-*e*]benzofuran on irradiation. Photocyclisation of 1,2-di(2,3′-dithienyl)ethylene gave benzo[1,2-*b*:3,4-*b*′]-dithiophen but 1,2-di(3-thienyl)ethylene failed to undergo photocyclodehydrogenation even though the formation of a yellow colour developed which was attributed to the dihydro-intermediate in the reaction.[58]



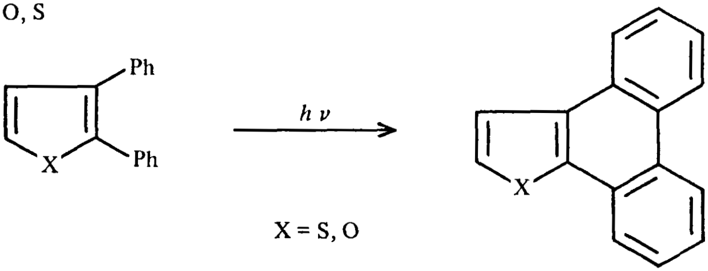
(XLIII) (XLIV)

2,3-Diphenylthiophen[59] and 2,3-diphenylfuran[60] (XLVII) have been photocyclised to the phenanthro[9,10-*b*]thiophen and phenanthro[9,10-*b*]furan (XLVIII) repectively.



(XLV) (XLVI)

X = O, S



(XLVII) (XLVIII)

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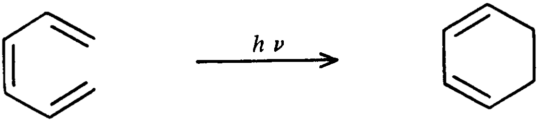
[58] R. M. Kellogg, M. B. Groen, and H. Wynberg, *J. Org. Chem.*, 1967, **32**, 3093.

[59] H. Wynberg, H. van Driel, R. M. Kellogg, and J. Buter, *J. Amer. Chem. Soc.*, 1967, **89**, 3487.

[60] A. Padwa and R. Hartman, *J. Amer. Chem. Soc.*, 1966, **88**, 3759.

4 Photocyclisation of 1,3,5-Hexatrienes

The photocyclisation of stilbenes can be considered as a special case of a general reaction of which the photocyclisation of *cis*-1,3,5-hexatriene (XLIX) to 1,3-cyclohexadiene (L) is the simplest example. Stilbene possesses the hexatriene system in which two of the double bonds are derived from aromatic rings. Srinivasan has observed the formation of (L) in the vapour phase[61] but reaction in solution is confined to derivatives of 1,3,5-hexatriene.[62] Thus irradiation of 1,6-dimethyl-1,3,5-hexatriene, in ether, gave some 1,2-dimethyl-$\Delta^{3,5}$-cyclohexadiene in which the methyl groups had *trans* stereochemistry.[62] No aromatisation was observed.



(XLIX) (L)

Examples are also known in which only one of the terminal unsaturated linkages is incorporated into an aromatic ring. These reactions parallel the stilbene reactions as photocyclodehydrogenation occurs. Irradiation of a chloroform solution of dibenzalsuccinic anhydride gave 1-phenylnaphthalene-2,3-dicarboxylic anhydride.[63] Heller and co-workers have also observed this reaction in the 1,2-bisbenzylideneindane series.[64]

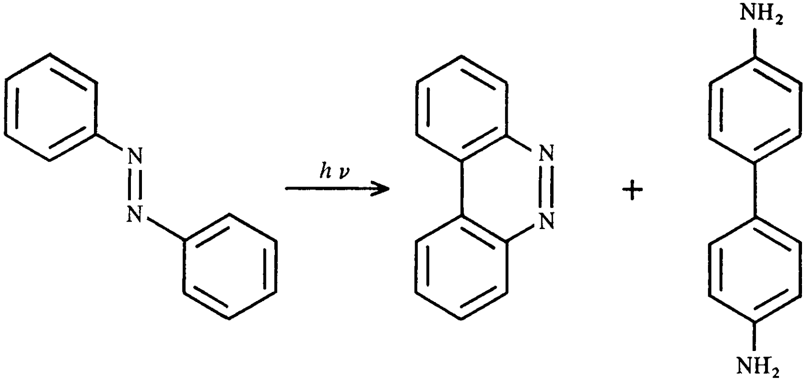
The photocyclisation reaction is of some importance in the vitamin D field.[65]

5 Related Photocyclisation Reactions

Azobenzene (LI) and benzalaniline do not photocyclise under the same conditions as stilbene. Thus azobenzene undergoes only *cis-trans* isomerisation on irradiation in neutral solvents, but irradiation in 11M sulphuric acid gave benzo[*c*]cinnoline (LII) and benzidine (LIII) in approximately equal amounts. It seems certain that the reaction involves photochemical disproportionation. Thus for every molecule of azobenzene that undergoes cyclodehydrogenation, one more is reduced to hydrazobenzene which, under the acid conditions, rearranges to benzidine.[66] Many substituted benzo[*c*]cinnolines have been prepared.[67]

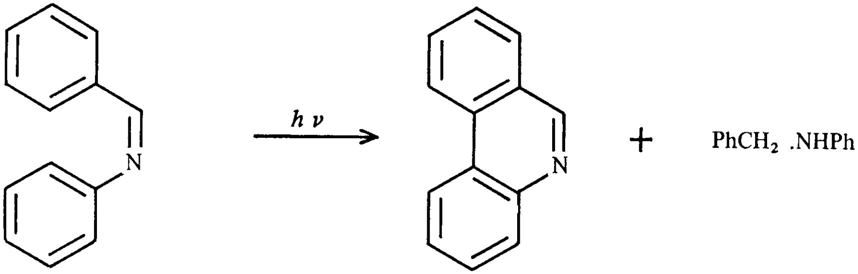
The lowest energy singlet state of azobenzene is an n, π^* state which lies below the lowest π,π^* state. In acid media, the protonation of the nitrogen atoms raises the energy of the n,π^* state above that of the π,π^* state and therefore it seems likely that it is the conjugate acid of *cis*-azobenzene which is excited to a π,π^* state and then cyclises.[68]

[61] R. Srinivasan, *J. Amer. Chem. Soc.*, 1961, **83**, 2806.
[62] G. J. Fonken, *Tetrahedron Letters*, 1962, **549**.
[63] B. Weinstein and D. N. Brattesani, *Chem. and Ind.*, 1967, 1292.
[64] H G. Heller, D. Ault, and K. Salisbury, *J. Chem. Soc.* (*C*), 1967, 682.
[65] E. Havinga and J. L. M. A. Schlatmann, *Tetrahedron*, 1961, **16**, 146.
[66] G. M. Badger, R. J. Drewer, and G. E. Lewis, *Austral. J. Chem.*, 1963, **16**, 1042.
[67] N. C. Jamieson and G. E. Lewis, *Austral. J. Chem.*, 1967, **20**, 2777 and refs therein.
[68] G. M. Badger, R. J. Drewer, and G. E. Lewis, *Austral. J. Chem.*, 1966, **19**, 643.

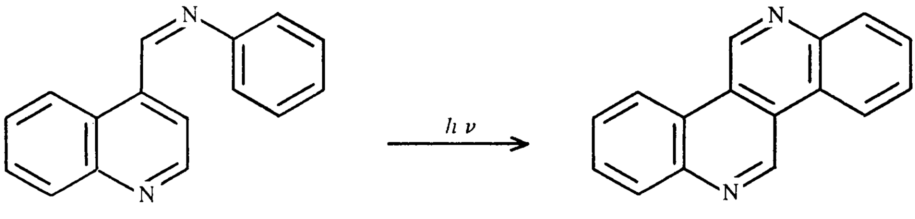


(LI) (LII) (LIII)

Badger, Joshua, and Lewis have isolated phenanthridine (LV) and benzylaniline (LVI) on irradiation of benzalaniline (LIV) in concentrated sulphuric acid.[69] Clark and Cox have used this reaction in the synthesis of calycanine (LVIII) by irradiation of (LVII) in concentrated sulphuric acid for 24 hr.[70]



(LIV) (LV) (LVI)



(LVII) (LVIII)

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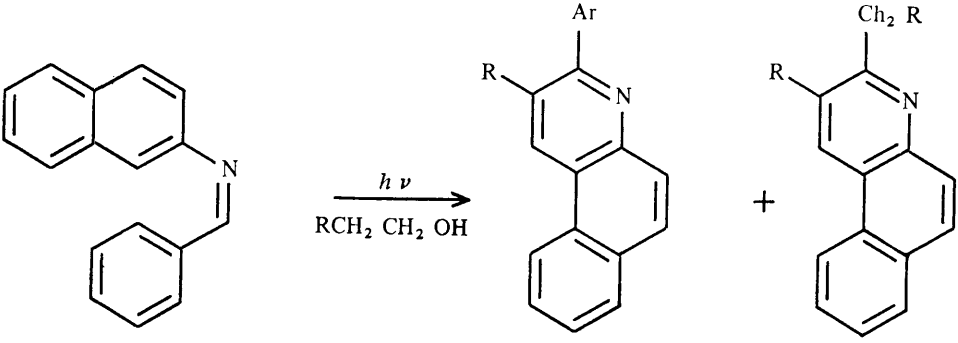
[69] G. M. Badger, C. P. Joshua, and G. E. Lewis, *Tetrahedron Letters*, 1964, 3711.

[70] V. M. Clark and A. Cox, *Tetrahedron*, 1966, **22**, 3421.

Some Schiff's bases can be photocyclised in the absence of concentrated sulphuric acid. Thus irradiation of 1-naphthal-1′-naphthylamine in ethanol gave dibenzo[*c*,*i*]phenanthridine in 40% yield and no reduced product was reported.[71] A re-examination of the photochemistry of benzalaniline indicated no photocyclisation in cyclohexane, benzene, or ethanolic solutions.[72] The failure of the cyclisation of benzalaniline was attributed to the internal conversion of the π,π^* states to the n,π^* states, and to the very short lifetime of the *cis* isomer. This was borne out by the fact that 2% of the cyclised product was detected in the early stages of the reaction when the solution was cooled. Irradiation of *N*-diphenylmethyleneaniline gave 6-phenylphenanthridine. The isomerisation for 1-naphthal-1′-naphthylamine will be slower than for (LIV) and *N*-diphenylmethyleneaniline must always have a *cis*-benzalaniline chromophore and it is suggested that these facts account for the cyclisation of these two compounds in ethanolic solution.[72]

The formation of benzo[*f*]quinolines (LX) by the incorporation of one or more solvent fragments on irradiation of benzal-2-naphthylamines (LIX) has been reported.[73] It was suggested that in some cases these compounds are formed by replacing the aldehyde part of the original Schiff's base by the aldehyde formed from the alcohol used as solvent.



(LIX) (LX)

Ar = C_6H_5 – , 4-MeO.C_6H_4 – , 4-NO_2.C_6H_4 – , or 2-Cl.C_6H_4 –
R = H , $CH(CH_3)_2$ – , n-C_4H_9 –

Grellmann and Tauer have reported briefly an interesting photocyclisation reaction of some Schiff's bases substituted in the *ortho* position (LXI) to some novel heterocyclic systems (LXII).[74]

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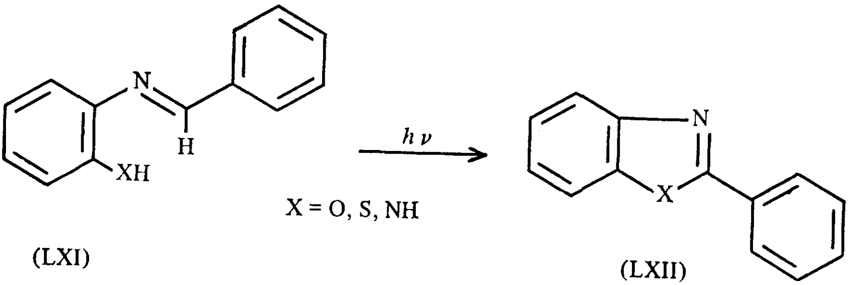
[71] M. P. Cava and R. H. Schlessinger, *Tetrahedron Letters*, 1964, 2109.

[72] F. B. Mallory and C. S. Wood, *Tetrahedron Letters*, 1965, 2643.

[73] P. J. Collin, H. Silberman, S. Sternhell, and G. Sugowdz, *Tetrahedron Letters*, 1965, 2063.

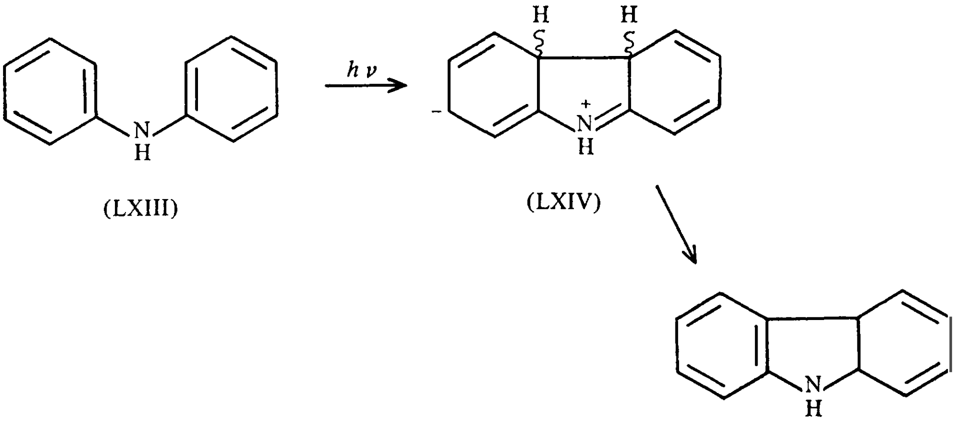
[74] K. H. Grellmann and E. Tauer, *Tetrahedron Letters*, 1967, 1909.



(LXI)

(LXII)

The photocyclisation of diphenylamine (LXIII) to carbazole (LXV) was once thought to proceed *via* a similar mechanism to the photocyclisation of stilbenes. A transient species has been observed, on flash-excitation of *N*-substituted diphenylamines in solution, with $\lambda_{max.}$ 610 nm.[75] Structure (LXIV) was assigned to this transient which was suggested as an intermediate in the photocyclisation reaction.



(LXIII)

(LXIV)

(LXV)

The reaction has been shown to proceed *via* a triplet mechanism as opposed to the singlet mechanism invoked for the photocyclisation of stilbene from the results of flash experiments and from the quenching effects of oxygen.[76] Carruthers has synthesised several substituted carbazoles by this route.[77] He prepared the alkaloid glycozoline (LXVII) by the irradiation of 4-methoxy-4′-methyldiphenylamine (LXVI) in petroleum (b.p. 40—60°). Similarly anilino-pyridines and dipyridylamines gave carbolines and pyrrolodipyridines on

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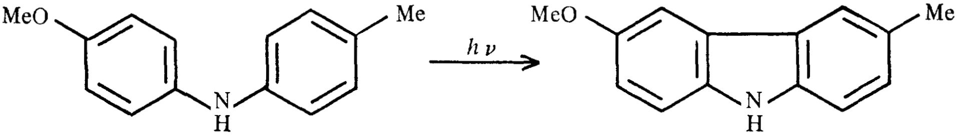
[75] K.-H. Grellmann, G. M. Sherman, and H. Linschitz, *J. Amer. Chem. Soc.*, 1963, **85**, 1881.

[76] H. Linschitz and K.-H. Grellmann, *J. Amer. Chem. Soc.*, 1964, **86**, 303.

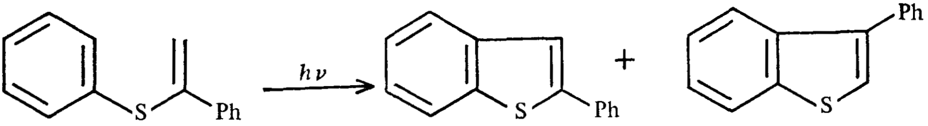
[77] W. Carruthers, *Chem. Comm.*, 1966, 272; W. Carruthers, *J. Chem. Soc.* (*C*), 1968, 2244.



(LXVI) (LXVII)

irradiation in cyclohexane or tetrahydrofuran. No cyclisation was observed on irradiation of 2-α-, 2-β-naphthylaminopyridines, or *N*-phenyl-β-naphthylamine.[78]

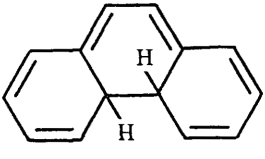
Several phenylthioethenes undergo a low yield photocyclisation. Irradiation of 1-phenyl-1-phenylthioethene (LXVIII) gave (LXIX) and (LXX). Compounds similar to (LXX) were only obtained when the α-position was substituted by a phenyl group. Yields of up to 11·5% were obtained.[79]



(LXVIII) (LXIX) (LXX)

6 Mechanism

The mechanism of the photocyclisation reaction is still the subject of much controversy. The initial rate of phenanthrene formation was finite on irradiation of *cis*-stilbene and zero on irradiation of *trans*-stilbene and an intermediate available only from *cis*-stilbene was suggested.[80] It was further shown that 0·915 mole of oxygen was consumed per mole of phenanthrene formed.[20] The intermediate was postulated as (LXXI).



(LXXI)

Moore, Morgan, and Stermitz have provided direct evidence for the existence of intermediate (LXXI).[81] Irradiation of a dilute cyclohexane solution of *trans*-stilbene using light of wavelength less than 310 nm produced a yellow colour which disappeared rapidly on removal of the light source. The irradiated

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[78] V. M. Clark, A. Cox, and E. J. Herbert, *J. Chem. Soc.* (*C*), 1968, 831.

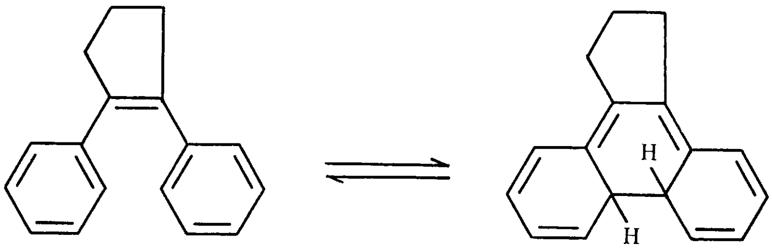
[79] S. H. Groen, R. M. Kellog, J. Buter, and H. Wynberg, *J. Org. Chem.*, 1968, **33**, 2218.

[80] H. Stegemeyer, *Z. Naturforsch*, 1962, **17B**, 153.

[81] W. M. Moore, D. D. Morgan, and F. R. Stermitz, *J. Amer. Chem. Soc.*, 1963, **85**, 829.

solution gave a positive test for hydrogen peroxide and phenanthrene formation was also observed. Irradiation of a degassed solution of *trans*-stilbene again produced a yellow solution ($\lambda_{max.}$ 447 nm). G.l.c. analysis of the product obtained when the colour had faded and the cell opened, showed the presence of *cis*-stilbene and a small amount of *trans*-stilbene. If the cell was opened to the air immediately after the yellow colour had formed, then the yellow colour faded at about the same rate as phenanthrene was produced. Irradiation of a *trans*-stilbene solution with filtered light of 290—310 nm produced only traces of phenanthrene and the product was predominantly *cis*-stilbene. Irradiation with light of wavelength greater than 310 nm destroyed the yellow colour. Mallory has calculated that the over-all conversion of *cis*-stilbene in its ground state (S^0) to the dihydro-intermediate (S^0) to be endothermic by 33·3 kcal/mole. Thus ring opening in the absence of oxygen to regenerate *cis*-stilbene is not surprising.[24]

Evidence exists which indicates that the photocyclisation to the dihydrophenanthrene (LXXI) does not proceed *via* triplet-state stilbene molecules. The reaction is not inhibited by oxygen and the formation of (LXXI) is not observed in experiments in which stilbene (T^1) is produced by way of triplet photosensitisation. Hence the photocyclisation of *cis*-stilbene proceeds by a singlet mechanism.[24]



(LXXII) (LXXIII)

Muszkat and Fischer studied the temperature dependence of the quantum yields of fluorescence and of photocyclisation in diphenylcyclopentene (LXXII).[82] The quantum yield of fluorescence of (LXXII) at different temperatures showed an increase and the quantum yield of cyclisation to (LXXIII) a decrease on cooling. These results were explained by assuming that the only temperature-dependent reaction of the first excited singlet state of (LXXII) is the photocyclisation, with an activation energy of about 3 kcal/mole. This would appear to be adequate evidence for the cyclisation proceeding *via* *cis*-stilbene in its first excited singlet state. However, Güsten and Klasinc have recently suggested that photochemical ring closure proceeds *via* a high vibrational level of the ground singlet state of stilbene.[83] This conclusion was based on H.M.O. calculations which correctly predict the isomeric distribution of 2-

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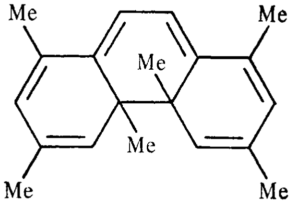
[82] K. A. Muszkat and E. Fischer, *J. Chem. Soc.* (*B*), 1967, 662.

[83] H. Güsten and L. Klasinc, *Tetrahedron*, 1968, **24**, 5499.

and 4-substituted phenanthrenes obtained on irradiation of *m*-substituted stilbenes and the linear dependence of calculated charge densities of the reacting *o*,*o*′ positions of substituted stilbenes with quantum yields if a ground state mechanism pertains.

Comprehensive studies of the dihydrophenanthrene intermediates have been made.[36, 82] These compounds were obtained as a mixture with the parent stilbene by irradiation of degassed solutions of the corresponding stilbene with filtered light. About 15% conversion was obtained. The electronic spectra of the intermediates and the first order kinetics of the thermal ring opening have been reported.

^{1}H N.m.r. studies and cryoscopic measurements on photostationary mixtures of (LXXIV) and *cis*- and *trans*-2,2′,4,4′,6,6′-hexamethylstilbene were in accord with the intermediate having the structure shown.[82]



(LXXIV)

The kinetics of the thermal oxidation of (LXXIII) have been examined in detail.[82, 84] A considerable deuterium isotope effect is shown by this thermal oxidation and the reaction is inhibited by aniline and 2,6-di-t-butyl-*p*-cresol.[84]

It was not possible to distinguish between direct photochemical oxidation of stilbenes and the photochemical oxidation of the dihydrophenanthrenes, however, photochemical oxidation could be distinguished from thermal oxidation. The photochemical oxidation was found to be seventy times faster than the thermal oxidation of (LXXIII). The mechanisms may well differ and it is suggested that photo-oxidation proceeds *via* the formation of a complex between the excited molecule and an oxygen molecule followed by decomposition to the final products.[82]

The stereochemistry of the allylic 4a,4b-hydrogens in the dihydrophenanthrene intermediates is unknown. Mallory and his co-workers tentatively proposed that the intermediates had the *trans* configuration based on the analogy between the cyclisation of stilbenes and the cyclisation of various substituted 1,3,5-hexatrienes which give the corresponding 1,3-cyclohexadienes with the *trans* configuration at the point of ring closure.[26] The advent of the Woodward–Hoffmann orbital symmetry rules allows a prediction to be made of the steric consequences of thermal and photochemical cyclisations.[85]

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[84] A. Bromberg, K. A. Muszkat, and E. Fischer, *Chem. Comm.*, 1968, 1352; A. Bromberg and K. A. Muszkat, *J. Amer. Chem. Soc.*, 1969, **91**, 2860

[85] R. B. Woodward and R. Hoffmann, *J. Amer. Chem. Soc.*, 1965, **87**, 395.

In the photochemical cyclisation of *cis*-stilbene conrotatory cyclisation must result and hence *trans* configuration at the point of ring closure. Similarly, thermal cyclisation must proceed in a disrotatory manner. Evidence does exist that the dihydro-intermediates prepared by the photochemical cyclisation of stilbene analogues have the *trans* configuration for the 4a,4b protons as no elimination of hydrogen takes place on irradiation of degassed solutions of stilbene analogues to give the dihydrointermediates.[82] Unfortunately, no ^{1}H n.m.r. evidence has been presented to confirm the stereochemistry of the 4a,4b groups.

It has been shown that stilbene analogues which have low values for the free valence indices at the atoms between which the new bond would form on cyclisation fail to photocyclise.[86, 87] Similarly, substituents present which promote a high degree of inter-system crossing also prevent photocyclisation. Failure of compounds to cyclise on electron impact has also been correlated with the failure of such compounds to photocyclise.[87]

7 The Effect of Electron Impact on Stilbene Analogues

Useful empirical correlations have been shown to exist between the unimolecular reactions induced by electron impact and by non-ionising ultraviolet irradiation.[88]

Woodward–Hoffmann rules predict the *cis* stereochemistry for the 4a,4b-protons in the dihydro-intermediates formed in the cyclisation of stilbene analogues by a ground state reaction and the *trans* stereochemistry if an excited state reaction takes place.[85] Similarly, cyclisation of stilbene in the mass spectrometer would be expected to proceed by such stereochemical pathways depending on the electronic state of the *cis*-stilbene ion involved. It is possible to detect the loss of hydrogen atoms or molecules during a fragmentation process in the mass spectrometer by the position of the metastable ion formed for this process. Thus, if elimination of the hydrogens takes place from the intermediates to form phenanthrene analogues, then molecular hydrogen will be lost in one step from the *cis*-dihydro-intermediate or hydrogen will be lost in two steps as atoms from the *trans*-dihydro-intermediate. It is therefore possible to determine whether a ground state mechanism governs the cyclohydrogenation of stilbenes in the mass spectrometer or whether an excited state mechanism is involved.[89,90] This conclusion is however suspect as the systems studied which showed the loss of hydrogen atoms in two steps, were radical cations, whereas the systems which lost a hydrogen molecule were even-electron species. These results are in accord with the fact that radical cations tend to lose radicals and even-electron ions tend to lose molecules on electron impact.[91]

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[86] W. H. Laarhoven, Th. J. R. M. Cuppen, and R. J. F. Nivard, *Rec. Trav. chim.*, 1968, **87**, 687.

[87] E. V. Blackburn and C. J. Timmons, *J. Chem. Soc.* (*C*), 1969, in the press.

[88] R. C. Dougherty, *J. Amer. Chem. Soc.*, 1968, **90**, 5780.

[89] R. A. W. Johnstone and S. D. Ward, *J Chem. Soc.* (*C*), 1968, 1805.

[90] R. A. W. Johnstone and S. D. Ward, *J. Chem. Soc.* (*C*), 1968, 2540.

[91] M. J. Bishop and I. Fleming, *J. Chem. Soc.* (*C*), 1969, 1712.

Johnstone and Ward have observed the successive elimination of two hydrogen atoms from the *ortho* positions of stilbene to give the phenanthrene radical cation in the mass spectrometer,[89] which led them to suggest that the cyclisation of stilbene to give 4*a*,4*b*-dihydrophenanthrene in the mass spectrometer proceeds through the first excited state. Correlations between photocyclisation reactions of other stilbene analogues and electron impact reactions have also been reported.[36,90]