Studies in Photochemistry. Part VIII.[1] The Ultraviolet, Proton Magnetic Resonance, and Mass Spectra, and Photocyclisation of Some Styrylnaphthalenes to Some Benzo[*c*]phenanthrenes and Chrysenes

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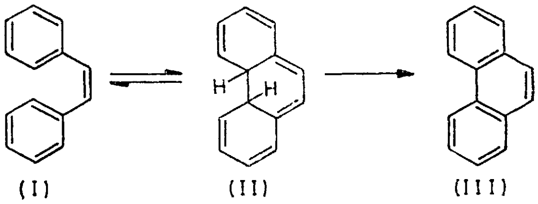
Kinetic data for the first-order ring opening of the dihydro-intermediates, formed on the photocyclisation of several styrylnaphthalene analogues, are presented and some aspects of their electronic spectra are discussed. The photocyclodehydrogenation of 1,2-di-(2-naphthyl)ethylene to benzo[*g,h,i*]perylene proceeded *via* dibenzo[*c,g*]-phenanthrene. Photocyclodehydrogenation of 2-methyl-1-(2,4,6-trimethylstyryl)naphthalene, 2-methyl-1-styrylnaphthalene, 1-(2,4,6-trimethylstyryl)naphthalene, and 1-(2,6-dichlorostyryl)naphthalene yielded the expected chrysene derivatives. 1-Bromo-2-styrylnaphthalene and 2-(2,4,6-trimethylstyryl)naphthalene photocyclised to benzo[*c*]phenanthrene and 2,4-dimethylbenzo[*c*]phenanthrene respectively. No migration of substituents was observed. The effect of electron impact on these styrylnaphthalenes correlates with their photochemical behaviour. The u.v. and ^{1}H n.m.r. spectra of the styrylnaphthalenes are discussed.

Intermediates in Some Photocyclodehydrogenation Reactions.—In 1950, Parker and Spoerri isolated phenanthrene (III) on irradiation of stilbene (I).[2] Since then this basic reaction has been exploited as a very useful synthetic route to polycyclic aromatic and heterocyclic ring systems.[3] Unfortunately the mechanism of the photocyclodehydrogenation of *cis*-stilbene analogues has not received as much attention.

It has been known for a long time that irradiation of a degassed solution of stilbene gives a yellow colour and that this colour disappears slowly when the irradiating source is removed or when the solution is heated.[4] Only



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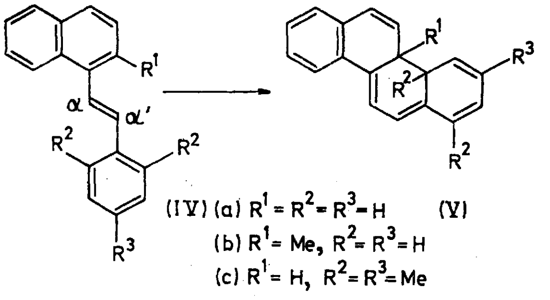
[1] Part VII, E. V. Blackburn, C. E. Loader, and C. J. Timmons, *J. Chem. Soc.* (*C*), 1968, 1576.

[2] C. O. Parker and P. E. Spoerri, *Nature*, 1950, **166**, 603.

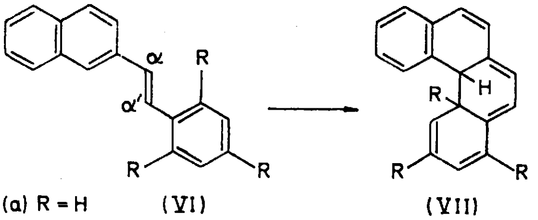
[3] E. V. Blackburn and C. J. Timmons, *Quart. Rev.*, 1969, **23**, 482.

[4] P. Hugelshofer, J. Kalvoda, and K. Shaffner, *Helv. Chim. Acta*, 1960, **43**, 1322.

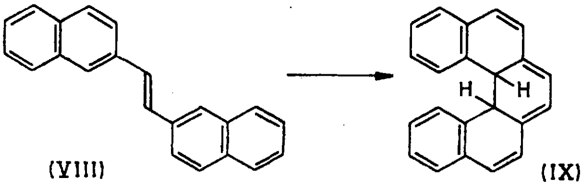
cis- and *trans*-stilbene are present in the resulting solution after the decay of the colour. The yellow colour also disappeared on exposure to air, and phenanthrene was formed at the same rate as that at which the colour faded.[5] This yellow colour has been ascribed to the presence of a dihydro-intermediate (II). Muszkat and Fischer have made a study of solutions of the dihydro-intermediates prepared from substituted stilbenes.[6]



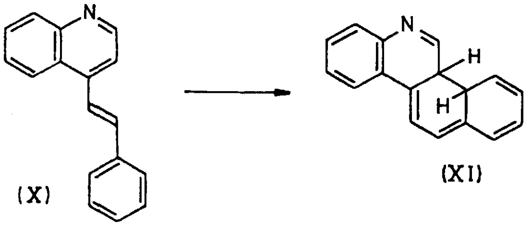
(IV) (a) $R^1 = R^2 = R^3 = H$ (V)
(b) $R^1 = Me$, $R^2 = R^3 = H$
(c) $R^1 = H$, $R^2 = R^3 = Me$



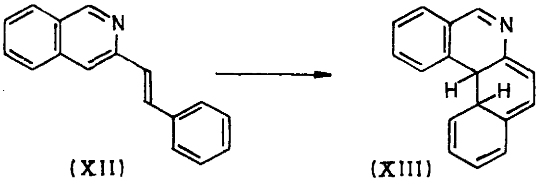
(a) R = H (VI) (VII)
(b) R = Me



(VIII) (IX)



(X) (XI)



(XII) (XIII)

We have examined the photochemistry of some sterically hindered styrylnaphthalene analogues [(IV), (VI), (VIII), (X), and (XII)] as these compounds were expected to form dihydro-intermediates [(V), (VII), (IX), (XI), and (XIII)] with more stability than the unhindered compounds, as aromatisation might be less favoured in these cases even though ring-opening might be expected to be smoother the more sterically hindered the molecule. In fact, the last possibility was found to be not wholly the case.

Hexane solutions of the styrylnaphthalenes were degassed in a 100-mm. optical silica cell and irradiated with u.v. light filtered by a cobalt sulphate–nickel sulphate solution until the photostationary state was established. The cell was then placed in a thermostatted jacket in a Unicam SP 800 spectrophotometer and the kinetics of the thermal ring-opening reaction of the resulting yellow coloured dihydro-intermediates were followed by repeated scanning of the spectrum.

The possibility that photochemical reaction occurred during the scanning of the spectrum was investigated by irradiation of the yellow solution of (VIIa) at constant wavenumber in the spectrophotometer and observing the decrease in the maximum absorbance with time for 20 min. with a constant wavenumber scanner. The wavenumber chosen for this experiment was that at which the compound had a maximum absorbance in the visible spectrum. No alteration in rate was observed using this method. As (VIIa) was at least as readily decomposed by white light as the other intermediates, no photochemical reaction had occurred in the spectrometer.

Some photocyclodehydrogenation was observed when the solutions were first irradiated. Further irradiation was without effect. This result was ascribed to the initial formation of the aromatic product through oxidation of the intermediate by oxygen left in the cell after outgassing, and ruled out the possibility of photochemical splitting off of molecular hydrogen either from the dihydro-intermediate or from the *cis*-stilbene analogues. Thus, the intermediates probably have the *trans*-stereochemistry about the 4a,4b-bonds and if the cyclisation of the *cis*-stilbene analogues is concerted, then an excited-state mechanism would be involved according to the Woodward–Hoffmann rules.[7]

The thermal ring-opening of the dihydro-intermediates obeyed first-order kinetics and the kinetic data obtained for these reactions are summarised in Table 1. The activation energies (E_a) were obtained from plots of the logarithm of the rate constant (k) against the reciprocal of the absolute temperature ($1/T$). The correlation coefficients show that there exists a good correlation between the values obtained for ln k and $1/T$.

The activation entropies ($\Delta S^\ddagger$) are linearly related to the activation energies as shown in the Figure as expected for similar reactions. Values of E_a and $\Delta S^\ddagger$ obtained by Muszkat and Fischer for the thermal ring-opening of several substituted 4a,4b-dihydrophenanthrenes are also plotted in the Figure.[6] These values also lie on the straight line within experimental error and this indicates the close similarity between the ring-opening reactions of the dihydro-intermediates prepared from stilbene analogues. It is evident from the Figure that more activation energy is generally required

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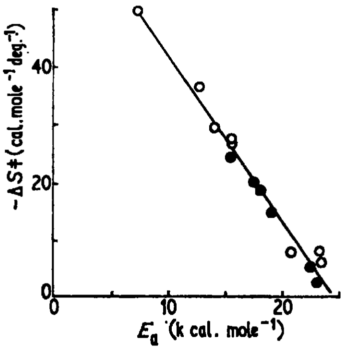
[5] W. M. Moore, D. D. Morgan, and F. R. Stermitz, *J. Amer. Chem. Soc.*, 1963, **85**, 829.

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

[7] R. B. Woodward and R. Hoffmann, *J. Amer. Chem. Soc.*, 1965, **87**, 395; G. B. Gill, *Quart. Rev.*, 1968, **22**, 338.

for the ring-opening of the sterically hindered dihydro-intermediates; thus it requires more energy for these compounds to attain the geometry of the transition state. The unhindered molecules are more flexible than the hindered ones and so the conformation of the hindered molecules will not be capable of as much vibrational and rotational motion as the unhindered molecules. Thus the hindered molecules are more ordered and less entropy change is involved in imposing the constraints required to reach the transition state. Models show that the most favoured conformation of the sterically hindered compounds is one in which the central ring is puckered and the potentially aromatic rings are planar.



The relation between activation energies and activation entropies; filled in circles from K. A. Muszkat and E. Fischer, *J. Chem. Soc.* (*B*), 1967, 662

TABLE 1

Kinetic data for the thermal ring-opening of some dihydro-intermediates in hexane

Compound	Computed k at 25° (s^{-1})	Temp. range investigated	E_a (kcal./mole)	$\Delta S\ddagger$ (cal./mole -degree)	Correlation coefficient for log k vs. $1/T$	Frequency factor at 25° (s^{-1})
(Va)	$5{\cdot}39 \times 10^{-5}$	20—50°	12·8	−36·4	−0·977	$1{\cdot}1 \times 10^{5}$
(Vb)	$9{\cdot}46 \times 10^{-5}$	20—40	15·6	−27·0	−0·987	$2{\cdot}0 \times 10^{7}$
(Vc)	$3{\cdot}50 \times 10^{-6}$	20—45	23·5	−5·9	−0·996	$8{\cdot}0 \times 10^{11}$
(VIIa)	$2{\cdot}18 \times 10^{-4}$	25—45	14·2	−29·2	−1·000	$6{\cdot}6 \times 10^{6}$
(VIIb)	$2{\cdot}90 \times 10^{-4}$	20—40	20·7	−7·8	−0·994	$3{\cdot}3 \times 10^{11}$
(IX)	$2{\cdot}18 \times 10^{-7}$	25—50	23·3	−8·0	−0·993	$2{\cdot}95 \times 10^{11}$
(XI)	$1{\cdot}33 \times 10^{-3}$	20—40	7·3	−49·7	−0·979	$2{\cdot}25 \times 10^{2}$
(XIII)	$1{\cdot}13 \times 10^{-4}$	20—45	15·7	−26·5	−0·997	$2{\cdot}5 \times 10^{7}$

Thus, the transition state probably has a similar conformation. The high activation energy required for the ring-opening of the sterically hindered compounds can be explained simply by the need for more energy to twist these molecules into the conformation of the transition states than to form these states from the flexible unhindered molecules, as might be expected. The high activation energy required for the decomposition might also be due to the mass effect of the methyl groups as more energy is necessary for stretching or twisting the 4a,4b-carbon–carbon bond than in the unsubstituted cases.

1,2-Di-(2-naphthyl)ethylene (VIII) was found to produce the most stable intermediate. The intermediate could be prepared by irradiation of a solution in ether, without degassing the solution (solutions of other substituted ethylenes were rapidly oxidised to the aromatic products under these conditions even though a yellow solution, which was extremely unstable, could be observed in some cases). This is not surprising as dibenzo[*c*,*g*]phenanthrene (XIV), the expected product of the photocyclodehydrogenation reaction, shows considerable steric overcrowding and the loss in delocalisation energy due to distortion of the ring system from planarity has been calculated to be 18 kcal./mole.[8] A very little cyclised material was detected by ^{1}H n.m.r. spectroscopy using a C.A.T. after the decay of a concentrated solution of (IX). Peaks were observed at τ 1·51, 1·59, 2·23, and 2·27 which had the same relative intensities as peaks at the same τ value in the ^{1}H n.m.r. spectrum of dibenzo[*c*,*g*]phenanthrene. No cyclised material was detected after the decay of dilute solutions of (IX) indicating that the ring-opening reaction, rather than oxidation, is the primary dark reaction of this molecule. However, irradiation of 1,2-di-(2-naphthyl)ethylene in ether for a week with a Pyrex cooling jacket gave benzo-[*g*,*h*,*i*]perylene (XV) and no dibenzophenanthrene (XIV) was detected. It was necessary, therefore, to determine whether (IX) was the intermediate producing the yellow colour or whether either (XVI) or (XVII) was the intermediate observed. MO calculations predict initial cyclisation to occur between the 1- and 1′-positions of the naphthalene nuclei rather than the 8 and 8′-positions. This eliminates (XVII) as a possible structure for the intermediate. Intermediate (XVI) would arise if cyclisation first proceeded to give dibenzo[*c*,*g*]phenanthrene (XIV) followed by further cyclisation to (XVI). If this was the case then irradiation of a degassed solution of dibenzo[*c*,*g*]phenanthrene (XIV) under similar conditions to those used for the production of the intermediate from (VIII) should give a yellow colour with an identical visible spectrum to that of this intermediate. In fact, no colour could be obtained under these conditions; hence (XIV) cannot be the *precursor* of the coloured intermediate, which must therefore have structure (IX). The dibenzophenanthrene (XIV) could be postulated, however, as an intermediate in the photocyclodehydrogenation of (VIII) to (XV). This possibility was tested by irradiating a cyclohexane solution of dibenzo[*c*,*g*]-phenanthrene. Very rapid photocyclisation was observed to give the benzoperylene (XV). It seems that dibenzo[*c*,*g*]phenanthrene is formed slowly by oxidation

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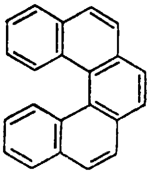
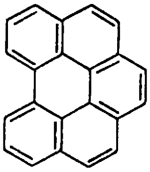
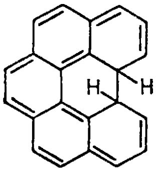
[8] M. A. Ali and C. A. Coulson, *J. Chem. Soc.*, 1959, 1558.

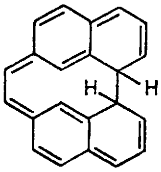
of the observed intermediate (IX), as would be expected from steric considerations, and then rapidly undergoes further cyclisation and dehydrogenation to give the benzoperylene.


(XIV)


(XV)



(XVI)



(XVII)

The compounds investigated showed two types of spectra, those with, and those without fine structure in their low-energy bands (Table 2). The spectra reported by Muszkat and Fischer for their dihydrophenanthrene showed no fine structure in their low-energy bands.[6] However, at −180°, the visible band of the intermediate prepared from 2,2′,4,4′,6,6′-hexamethylstilbene was resolved into four vibrational components. No fine structure in the low-energy bands was observed for the compounds formed from the 1-styrylnaphthalenes and 4-styrylquinoline at room temperature. Compounds formed from the cyclisation of 2-naphthylethylenes all showed fine structure in their low-energy bands.

TABLE 2

The positions of the low-energy bands in the electronic spectra of the coloured intermediates (in hexane)

Compound	$\nu_{max.}$ (cm.$^{-1}$)	Compound	$\nu_{max.}$ (cm.$^{-1}$)
(Va)	23,600	(VIIb)	*20,500*
(Vb)	22,900		21,700
(Vc)	23,000		*22,600*
(XI)	22,900		*24,200*
(VIIa)	22,400	(XIII)	*22,000*
	23,700		22,800
	24,900		23,700
			24,800
		(IX)	22,300
			23,700
			25,200

Generally, polyenes with the *trans*-configuration about each double bond and *s*-*trans*-configuration about each single bond show vibrational fine structure in their low-energy bands. *Cis*-compounds are generally characterised by little or no fine structure in the main band and very low molar absorptivities. Zechmeister and his co-workers[9] demonstrated this effect for a series of 1,4-diphenylbutadienes and 1,8-diphenyloctatetraenes.[10] In the spectra of these compounds the low-energy band loses its fine structure and decreases in intensity as *cis*-double bonds are introduced. A new band appears at a higher wavenumber (*cis*-band) which is due to a symmetry-forbidden transition which becomes increasingly 'allowed' as *cis*-double bonds are introduced and the molecule becomes more sterically hindered. The spectra of the dihydrophenanthrenes obtained by Muszkat and Fischer[6] showed a moderately intense *cis*-band and a weak structureless low-energy band, as would be expected in view of the number of *cis*-double bonds and *s*-*cis*-bonds in these compounds. The intermediates prepared from the styrylnaphthalenes have some degree of planarity enforced on them due to the ring systems; hence more *cis*-bonds may be introduced, before the fine structure is lost, than in the 1,8-diphenyloctatetraenes. The intermediates formed from the 1-styrylnaphthalene analogues [*e.g.* (Va)] have a greater ratio of *s*-*cis*- to *s*-*trans*-single bonds than does the intermediate (IX) formed from the 2-naphthylethylene analogue (VIII) which shows fine structure in its low-energy bands. However, the fine structure is less pronounced in the spectrum of the intermediate (VIIb) prepared from 2-(2,4,6-trimethylstyryl)naphthalene (VIb) which might be expected in view of the increase in steric hindrance caused by the methyl group in the 4b-position. Apart from a large bathochromic shift in the low-energy band which probably arises because of the planarity enforced on the rigid system the visible spectrum of compound (IX) closely resembles the spectra of the 1,8-diphenyloctatetraenes which possess more *trans*- than *cis*-double bonds.

The Photocyclisation of the Styrylnaphthalenes.—Several workers have reported the elimination of *ortho*-groups in the photocyclisation of stilbene analogues.[1,11] However, the photocyclisation of 2,4,6-trimethylazobenzene to give some 1,2,4-trimethylbenzo[*c*]cinnoline is the only example of the migration of an *ortho*-substituent in such a cyclisation.[11a]

1-Styryl-2-methylnaphthalene (XVIIIa), 1-(2,4,6-trimethylstyryl)naphthalene (XVIIIb), and 1-(2,6-dichlorostyryl)naphthalene (XVIIIc) photocyclised to the expected chrysene derivatives. The absence of any product formed by migration of a methyl group was shown by t.l.c. and spectroscopic techniques.

The photocyclisation of 2-methyl-1-(2,4,6-trimethylstyryl)naphthalene (XVIIId) was attempted. The styrylnaphthalene was extensively photolysed but only a very small quantity of 1,3-dimethylchrysene (XIXb) was detected by u.v. spectroscopy and t.l.c. No cyclisation of a compound has been reported in which all possible positions of cyclisation are substituted. 1,3-Dimethyl-

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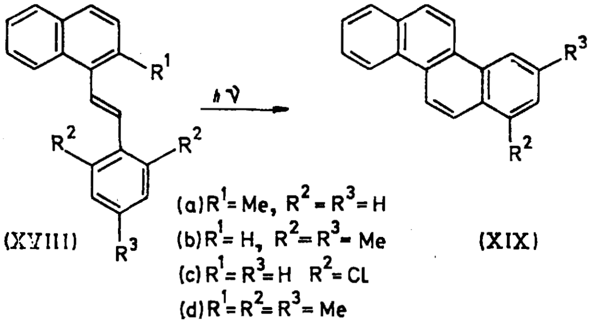
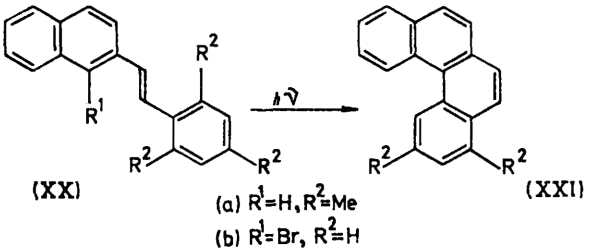
[9] J. H. Pinckard, B. Wille, and L. Zechmeister, *J. Amer. Chem. Soc.*, 1948, **70**, 1938.

[10] L. Zechmeister and J. H. Pinckard, *J. Amer. Chem. Soc.*, 1954, **76**, 4144.

[11] (*a*) G. M. Badger, R. J. Drewer, and G. E. Lewis, *Austral. J. Chem.*, 1964, **17**, 1037; (*b*) P. Bortolus, G. Cauzzo, and G. Galiazzo, *Tetrahedron Letters*, 1966, 239; (*c*) W. Carruthers and H. N. M. Stewart, *J. Chem. Soc.* (*C*), 1967, 556; (*d*) C. S. Wood and F. B. Mallory, *J. Org. Chem.*, 1964, **29**, 3373.

chrysene (XIXb) itself decomposed fairly rapidly under the irradiation conditions used for the photocyclisation, and this may, in part, account for the very poor yield of cyclised material isolated.





2,4-Dimethylbenzo[*c*]phenanthrene (XXIa) and benzo[*c*]phenanthrene (XXIb) were formed by the photocyclisation of 2-(2,4,6-trimethylstyryl)naphthalene (XXa) and 1-bromo-2-styrylnaphthalene (XXb) respectively. G.l.c. and t.l.c. of the tars isolated from the above irradiations showed the absence of any other benzo[*c*]phenanthrenes caused by substituent migration.

The photocyclisation of 2,4,6-trisubstituted styrylnaphthalenes provides a useful synthesis for the unknown 1,3-disubstituted chrysenes and 2,4-disubstituted benzo[*c*]phenanthrenes as reasonable yields were obtained.

The Effect of Electron Impact on some Styrylnaphthalene Analogues.—Useful empirical correlations have been shown to exist between the unimolecular reactions induced by electron impact and by nonionising u.v. irradiation.[12] Woodward–Hoffmann rules [7] predict the *cis*-stereochemistry for the 4a,4b-protons in the dihydro-intermediates formed in a concerted cyclisation of stilbene analogues by a ground-state mechanism and the *trans*-stereochemistry if an excited state reaction takes place. 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 should be possible therefore to determine whether a ground-state mechanism governs the cyclodehydrogenation of stilbenes in the mass spectrometer or whether an excited-state mechanism is involved.

Johnstone and Ward [13] 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 which indicates that the initial cyclisation to the 4a,4b-dihydrophenanthrene proceeded through the first excited state of stilbene. Johnstone and Millard have also shown that one *ortho*-hydrogen atom from each ring in stilbene is transferred to the central double-bond to form 9,10-dihydrophenanthrene in the mass spectrometer. 9,10-dihydrophenanthrene then loses one of the central carbon atoms as a methyl radical.[14] The effect of electron impact on the stilbazoles and 2-styrylthiophen has also been reported.[15]

No report has been made of cyclisation of stilbene analogues, substituted at the points of cyclisation, on electron impact. The effect of electron impact on some styrylnaphthalene analogues was investigated in order to see if the behaviour of these compounds under such conditions paralleled their photochemical behaviour and to observe any substituted methyl radicals which might be formed from any 9,10-disubstituted-9,10-dihydrophenanthrene analogues produced. The mass spectra of some styrylnaphthalene analogues are summarised in Table 3.

The mass spectra of 1-styrylnaphthalene (IVa) and 2-styrylnaphthalene (VIa) are very similar. Two hydrogen atoms are lost successively from the parent ion in each case to give chrysene (m/e 228) and benzo[*c*]phenanthrene (m/e 228) radical-cations respectively. The peak at m/e 215 in the spectra corresponds to the loss of a methyl group from an ion of M 230 as shown by the presence of metastable ions for this process. Thus, electron impact has a similar effect on these compounds to the effect it has on stilbene itself. Cyclisation may well take place, if concerted, *via* an excited state mechanism because hydrogen atoms, as opposed to molecular hydrogen, are lost and this is similar to the mechanism considered for the photochemical cyclisation. The peak at m/e 202 is formed by the loss of a molecule of acetylene from the polycyclic aromatic hydrocarbons (m/e 228).

The mass spectrum of 2-methyl-1-styrylnaphthalene shows a very strong peak at m/e 229 corresponding to the loss of a methyl radical. A hydrogen atom is eliminated from the parent ion and from the $(M - 15)^+$ ion. The

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[12] N. J. Turro, D. C. Neckers, P. A. Leermakers, D. Seldner, and P. D'Angelo, *J. Amer. Chem. Soc.*, 1965, **87**, 4097; R. C. Dougherty, *J. Amer. Chem. Soc.*, 1968, **90**, 5780.

[13] R. A. W. Johnstone and S. D. Ward, *J. Chem. Soc.* (*C*), 1968, 1805; see also M. J. Bishop and I. Fleming, *J. Chem. Soc* (*C*), 1969, 1712.

[14] R. A. W. Johnstone and B. J. Millard, *Z. Natursforsch.*, 1966, **21a**, 604.

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

TABLE 3

Mass spectra *

1-Styrylnaphthalene (IVa)

231 (20), *230 (100)*, 229 (84), 228 (28), 227 (10), 226 (13), 216 (3), 215 (13), 203 (3), 208 (8) 153 (9·5), 152 (17), 151 (5), 128 (3), 115 (10), 114 (13), 113 (9), 101 (11), 51 (3).

2-Styrylnaphthalene (VIa)

231 (20), 230 (100), 229 (70), 228 (39), 227 (11·5), 226 (13·5), 216 (3·5), 215 (19), 203 (4), 202 (8), 152 (5), 128 (5), 115 (10), 114 (12·5), 113 (7), 101 (9).

2-Methyl-1-styrylnaphthalene (IVb)

245 (21), 244 (100), 243 (38), 242 (4), 241 (5), 240 (3), 239 (7), 230 (18), 229 (90), 228 (29), 227 (9), 226 (10), 215 (6), 202 (6), 167 (9), 166 (10·5), 165 (16), 163 (3), 153 (6), 152 (9), 151 (4), 141 (6), 139 (5), 122 (10), 121 (7), 120 (3), 115 (11), 114·5 (9), 114 (16), 113 (10), 108 (4), 101 (8), 91 (8), 77 (4), 63 (3·5), 51 (4).

1-(2,4,6-Trimethylstyryl)naphthalene (IVc)

274 (4), 273 (27), 272 (100), 271 (6), 258 (11), 257 (45), 256 (9), 255 (5), 253 (3), 243 (12), 242 (40), 241 (10), 240 (5), 239 (9), 229 (3), 228 (5), 225 (3), 215 (5), 202 (3), 165 (8), 153 (7), 152 (9), 145 (3), 144 (12), 143 (4), 141 (6), 136 (11), 130 (4), 129 (19), 128 (17), 127 (8), 126 (7), 111 (13), 110 (9), 109 (9)

2-(2,4,6-Trimethylstyryl)naphthalene (VIb)

274 (3), 273 (24), 272 (100), 271 (5), 258 (10), 257 (43·5), 256 (7), 255 (4), 243 (9), 242 (32), 241 (11), 240 (5), 239 (8), 229 (4), 228 (6), 227 (3), 226 (4), 215 (6), 202 (4), 189 (3), 165 (6), 156 (6), 154 (4), 153 (3), 152 (6), 151 (3·5), 145 (5), 144 (24), 143 (6), 142 (3·5), 141 (6), 140 (3·5), 139 (3), 137 (4), 136 (6), 135 (5·5), 130 (5), 129 (24), 128 (17), 127 (7·5), 126 (4), 125 (5), 124 (5), 123 (4·5), 122 (3), 121 (5·5), 120 (4), 119 (6), 116 (5), 115 (12), 114 (3)

2-Methyl-1-(2,4,6-trimethylstyryl)naphthalene (XVIIId)

288 (4), 287 (26), 286 (100), 285 (4), 272 (17), 271 (34), 270 (3), 258 (3), 257 (16), 256 (34), 255 (8), 254 (4), 253 (5), 252 (5), 243 (5), 242 (9), 241 (10), 240 (7), 239 (11), 229 (5), 228 (5), 227 (3), 226 (4), 215 (5), 202 (5), 189 (4), 179 (5), 178 (4), 167 (10), 166 (23), 165 (27), 164 (3), 153 (5), 152 (10), 144 (7), 143 (10), 142 (9·5), 141 (13), 139 (5), 135 (3), 133 (3), 130 (3), 129 (15), 128 (18), 127 (7), 120 (4), 119 (15), 117 (4), 116 (4), 115 (18), 114 (4), 105 (7), 103 (3)

1-(2,6-Dichlorostyryl)naphthalene (XVIIIc)

302 (9), 301 (14), 300 (64·5), 299 (31), 298 (100), 297 (14), 266 (4), 265 (17), 264 (16), 263 (57), 262 (17), 229 (16), 228 (78), 227 (22), 226 (55), 225 (8), 224 (10), 200 (5), 153 (19), 152 (11), 151 (5), 150 (4), 149 (4), 132 (5), 131 (15), 128 (8), 126 (3), 118 (5), 114 (9), 113 (60), 112 (14), 101 (6)

1,2-Di(2-naphthyl)ethylene (VIII)

282 (5), 281 (26), 280 (100), 279 (60), 278 (41), 277 (16), 276 (17), 275 (4), 274 (3), 266 (3), 265 (13), 264 (3), 263 (5), 253 (6), 152 (8·5), 151 (3), 140·5 (4), 140 (16·5), 139·5 (7), 139 (16·5), 138·5 (5), 138 (12), 132·5 (9), 128 (6), 127 (3), 126 (9), 125 (3·5)

4-Styrylquinoline (X)

233 (3·5), 232 (21), 231 (100), 230 (87), 229 (15), 228 (8), 227 (4), 216 (5), 204 (5), 203 (8), 202 (20), 201 (5·5), 200 (3·5), 176 (3), 154 (13), 153 (9), 152 (3), 127 (5), 126 (4), 115·5 (7), 115 (7), 114·5 (3·5), 114 (5), 102 (7), 101 (17), 100 (4), 95 (3), 91 (4), 89 (9), 88 (5), 81 (3), 77 (6), 76 (6), 75 (6), 69 (4), 63 (5), 55 (5), 51 (7), 50 (3·5)

3-Styrylisoquinoline (XII)

232 (14), 231 (89), 230 (100), 229 (11), 228 (8), 227 (3), 203 (4), 202 (16), 201 (3·5), 129 (6), 128 (7·5), 127 (3·5), 116 (3), 115·5 (15), 115 (26), 114·5 (6), 114 (9), 113·5 (3), 102 (12), 101 (7·5), 89 (3), 76 (6·5), 75 (4), 63 (4), 51 (6)

* Peaks with relative abundance greater than 3% are recorded.

peak at m/e 228 could also be due to the loss of a methyl radical from the $(M - 1^+$ ion. The rest of the spectrum below m/e 228 resembled that of (IVa) as would be expected as both are expected to give chrysene radical-cations on electron impact.

1-(2,4,6-Trimethylstyryl)naphthalene (IVc) and 2-(2,4,6-trimethylstyryl)naphthalene (VIb) have similar mass spectra. Both have peaks corresponding to the loss of methyl and hydrogen radicals. There are peaks at m/e 243 in the mass spectra of these two compounds corresponding to the loss of ethyl radicals from methyl-dihydro-compounds, analogous to 9,10-dihydrophenanthrene, but no metastable peaks were present to confirm this interpretation.

2-Methyl-1-(2,4,6-trimethylstyryl)naphthalene (XVIIId) ejects two methyl radicals on electron impact to give 1,3-dimethylchrysene. The subsequent fragmentation pattern follows that of the cyclised product from 1-(2,4,6-trimethylstyryl)naphthalene (IVc), presumably also the 1,3-dimethylchrysene radical-cation, in most respects. However, the peaks at m/e 166 (23%) and m/e 165 (27%) in the mass spectrum of (XVIIId) do not appear in the spectrum of (IVc) but do appear in the spectrum of 2-methyl-1-styrylnaphthalene and in no other styrylnaphthalene investigated. These peaks must be due to some ion formed from the methylnaphthalene part of the molecules but no metastable peaks are present to indicate any mechanism for the formation of ions of these masses. As in the spectra of all these styrylnaphthalenes, doubly charged ions occur and also peaks corresponding to the loss of molecules of acetylene. There is no significant peak corresponding to $(M - 2)$ in the mass spectra of the methyl substituted styrylnaphthalenes which indicates the absence of any methyl migration following cyclisation and preceding aromatisation in these compounds upon electron bombardment.

Since a chlorine atom and hydrogen atom are lost successively, on electron bombardment of 1-(2,6-dichlorostyryl)naphthalene (XVIIIc), as indicated by the presence of metastable peaks for these fragmentations, cyclisation on electron impact is an excited-state process and parallels the photochemical cyclisation. No $(M - 2)$ peak is present, which indicates the absence of chlorine migration following cyclisation of (XVIIIc). There is no peak corresponding to the loss of a methyl group; hence it seems that aromatisation in this case occurs faster than the formation of the 9-chloro-9,10-dihydrophenanthrene analogue.

The effect of electron impact on 1,2-di-(2-naphthyl)-ethylene (VIII) closely resembles the effect of u.v. irradiation on this compound. Thus four atoms of hydrogen are lost consecutively from the parent ion as would be expected for the cyclisation to dibenzo[*c*,*g*]-phenanthrene followed by further cyclisation to benzo-[*g*,*h*,*i*]perylene. This indicates that both cyclisations may be excited-state reactions and provides some evidence for a similar mechanism occurring in the photochemical reaction. The $(M - 15)^+$ ion arises from fragmentation of the parent ion as shown by the presence of a metastable peak.

4-Styrylquinoline (X) loses two atoms of hydrogen consecutively on electron impact. A methyl radical is also lost on electron impact; hence the effect of electron impact on this compound resembles the effect on stilbene. The peak at m/e 202 is due to the loss of HCN from the cyclo-dehydrogenated styrylquinoline. Doubly charged ions are also present.

The base peak in the mass spectrum of 3-styrylisoquinoline (XII) is the (M–1) peak which is probably formed following cyclisation onto the nitrogen with formation of a stable pyridinium-type cation. Cyclisation to the 4-position also takes place followed by loss of two hydrogen atoms to give the expected benzo[α]-phenanthridine radical-cation as occurs on irradiation with u.v. light. No loss of methyl occurs in the spectrometer and a similar result has been reported for electron impact on 2-stilbazole.[15] The rest of the spectrum resembles that of 4-styrylquinoline.

TABLE 4

The u.v. spectra of some styrylnaphthalenes (in ethanol)

Compound		^1B_b Band [a]				^1L_a Band [a]				K Band				
(IVa)	$\nu_{max.}$ cm.$^{-1}$	49,100		42,900			37,800					30,800		
	ε	53,900		34,500			12,500					21,900		
(XVIIId)	$\nu_{max.}$ cm.$^{-1}$	47,500		43,800			*38,700*					33,700		
	ε	56,400		67,800			*9800*					12,600		
(IVb)	$\nu_{max.}$ cm.$^{-1}$	48,200		43,900			*39,400*					33,000		
	ε	42,200		48,100			*12,500*					12,500		
(IVc)	$\nu_{max.}$ cm.$^{-1}$	48,900		43,700			38,100	*36,900*				32,100		
	ε	51,000		41,900			7900	*7300*				14,900		
(XVIIIc)	$\nu_{max.}$ cm.$^{-1}$	49,200		43,900			39,400					31,800		
	ε	49,200		42,700			9100					14,900		
(VIa)	$\nu_{max.}$ cm.$^{-1}$	49,000	44,300	*43,500*	*42,100*	39,700	*38,000*	36,800	35,500	*32,600*	31,600	30,100	*28,800*	*28,300*
	ε	26,500	27,500	*24,700*	*17,500*	15,600	*18,900*	29,700	32,000	*30,800*	40,000	30,400	*6700*	*4200*
(VIb)	$\nu_{max.}$ cm.$^{-1}$			42,900			36,900					33,000		
	ε			31,300			26,400					26,100		
(XXb)	$\nu_{max.}$ cm.$^{-1}$	48,500	43,900	*43,200*	*41,800*	39,200	*37,100*	36,000	34,100		*31,900*	30,800	*29,600*	*28,900*
	ε	23,100	26,400	*24,300*	*16,500*	15,500	*24,400*	33,200	32,200		*31,400*	36,800	*25,600*	*15,700*

[a] These band assignments, though not strictly correct, show their relation to the spectrum of naphthalenes.

The elimination of a methyl group together with *ortho*-atoms on electron bombardment of the styrylnaphthalene analogues can be rationalised by a mechanism involving cyclisation through an electronically excited state. No migration of substituents to give other than the expected polycyclic aromatic compounds was observed. Thus, no methylchrysene is observed in the mass spectrum of 2-methyl-1-styrylnaphthalene. It seems, therefore, that there is a good correlation between the effect of u.v. irradiation and of electron bombardment on the styrylnaphthalenes, since no substituent migration was observed on irradiation of these compounds, photocyclodehydrogenation took place, and no molecular hydrogen was eliminated from the degassed solutions of the dihydro-intermediates. The elimination of a carbon from the olefinic linkage, however, has no parallel in the photochemistry of these compounds.

The U.v. Spectra of some Styrylnaphthalenes.—Substitution at the *ortho*-positions in the *trans*-stilbene molecule, causing an increased hindrance to planarity, resulted in the expected hypsochromic and hypochromic shifts; these effects have been explained theoretically.[16]

The u.v. spectra of the styrylnaphthalenes prepared in this work are summarised in Table 4. The hypsochromic and hypochromic shifts of the bands increased with the size and the number of *ortho*-substituents as expected.

The absence of fine structure in the u.v. spectrum of 1-styrylnaphthalene (IVa) indicates that steric hindrance in the 1-styrylnaphthalenes is greater than in the 2-styrylnaphthalenes as 2-styrylnaphthalene (VIa) shows considerable fine structure in its u.v. spectrum. This is due to the additional steric effect between the α-ethylenic proton and the 8-proton of the naphthalene nucleus. Any substituent in the 2-position or 2- or 6-position of the styryl substituent will increase the steric interaction in the molecule and cause further deformation.

The ^{1}H *N.m.r. Spectra of the Styrylnaphthalenes.*—These are summarised in Table 5. Δ_α and Δ_α' are the differences between the τ values for the α- and α'-protons for the substituted styrylnaphthalene and for the unsubstituted styrylnaphthalene.

TABLE 5

The ^{1}H n.m.r. spectra of some styrylnaphthalenes *

Compd.	H_α (τ)	Δ_α	$H_{\alpha'}$ (τ)	$\Delta_{\alpha'}$	J_{AB} (Hz)	2-Naphthyl (τ)	2,6-Styryl (τ)	4-Styryl (τ)
(IVa)	2·16	0	2·90	0	16·0			
(XVIIId)	2·40	+0·24	3·38	+0·48	16·7	7·46	7·60	7·75
(IVb)	2·42	+0·26	3·36	+0·46	16·5	7·56		
(IVc)	2·31	+0·15	3·01	+0·11	16·8		7·65	7·76
(XVIIIc)	2·17	+0·01	3·06	+0·16	16·0			
(VIa)	2·79	0	2·79	0				
(VIb)	3·34	+0·55	2·86	+0·07	16·6		7·66	7·73
(XXb)	2·95	+0·16	2·29	−0·50	16·8			

* Determined using a Varian HA 100 spectrometer at 100 MHz in carbon tetrachloride solution.

H_α experiences a greater deshielding effect than H_α' in the planar 1-styrylnaphthalenes as it lies in the magnetic field caused by the ring current of all three rings whereas H_α' only experiences the field due to two of the aromatic rings. 1-Styrylnaphthalene (IVa) has H_α at τ 2·16 and H_α' at τ 2·90. The coupling constant

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[16] H. H. Jaffé and M. Orchin, *J. Chem. Soc.*, 1960, 1078.

between these two protons is 16 Hz, hence the compound has the *trans*-stereochemistry. Substitution in the 2-position of the naphthalene nucleus, *e.g.* 2-methyl-1-styrylnaphthalene (IVb), causes a twist of the 1,α-bond and so reduces the amount of conjugation between the naphthalene nucleus and the benzene nucleus as compared with the conjugation in 1-styrylnaphthalene. The upfield shifts (Δ_α and $\Delta_{\alpha'}$) in the hindered compounds arise mainly from a reduction in the deshielding effects of the aromatic rings brought about by twisting. $\Delta_{\alpha'}$ is greater than Δ_α in (IVb) due to the additional shielding effect of the methyl substituent. A similar upfield shift occurs in the spectrum of 1-(2,4,6-trimethylstyryl)naphthalene (IVc) in which the 1,α'-bond is twisted. In this case the signal from H_α is shifted further than that from H_{α}' due to the shielding effect of the 2-methyl group on H_α which is greater than the effect of the 6-methyl group on H_{α}' as H_α is closer to a methyl group than H_{α}'. In the dichloro-compound (XVIIIc), twisting about the 1',α'-bond again occurs and an upfield shift is consequently expected. However, the chlorine groups deshield the olefinic protons and hence the upfield shift is very small. The shift is less for H_α as this proton is closer to a chlorine atom than is H_{α}'. H_{α}' is moved upfield in 2-methyl-1-(2,4,6-trimethystyryl)naphthalene (XVIIId) more than H_α as it is shielded by two methyl groups (2-naphthyl and 6-styryl) whereas the H_α-proton is only shielded by the 2-methyl group of the styryl component. Each styrylnaphthalene studied had the *trans*-stereochemistry as is seen from the values obtained for J_{AB}.

The greatest shift in the position of H_α and H_{α}', as compared with the position of these protons in the ^1H n.m.r. spectrum of 1-styrylnaphthalene, was in (XVIIId) and (IVb). These compounds also appeared to be the most twisted of the styrylnaphthalenes by their large hypochromic and hypsochromic shifts in their u.v. spectra.

The ^1H n.m.r. spectrum of 2-styrylnaphthalene (VIa) exhibited a singlet for the olefinic protons. H_α is no longer deshielded by a third ring and so H_α and H_{α}' have equivalent chemical shifts. The ^1H n.m.r. spectrum of 2-(2,4,6-trimethylstyryl)naphthalene (VIb) showed an AB system for H_α and H_{α}'. Twisting occurs about the 1,α'-bond and so, whilst signals due to both protons are moved to higher field due to shielding by the methyl groups, the signals due to H_α are moved to higher field than those due to H_{α}' as a result of the closer proximity of a methyl group to the H_α proton. This twisting also results in a loss of fine structure, and hypochromic and hypsochromic shifts in the u.v. spectrum of this compound. The bromine atom in 1-bromo-2-styrylnaphthalene (XXb) causes considerable deshielding of the α'-proton and also results in some twisting of the 1,α'-bond as the signal due to H_α is moved upfield by 0·16 p.p.m. However the twisting is not very great in this compound as $\Delta_{\alpha'}$ is −0·50 as compared to Δ_α in (XVIIIc) being +0·01. The chlorine atom is closer to the α-proton in (XVIIIc), if this compound were planar, than the bromine atom is to the α'-proton in (XXb), but has less effect due to deshielding on the position of the signal due to H_α. The u.v. spectra of 1-bromo-2-styrylnaphthalene and 1-(2,6-dichlorostyryl)naphthalene also indicated that steric hindrance was far greater in the latter compound. Thus the u.v. spectrum of 1-bromo-2-styrylnaphthalene closely resembles that of 2-styrylnaphthalene whereas a hypsochromic and a hypochromic shift are observed in the u.v. spectrum of 1-(2,6-dichlorostyryl)naphthalene compared with that of 1-styrylnaphthalene.

EXPERIMENTAL

The reaction conditions and apparatus have been described previously.[17] The mass spectra of all the 1-styrylnaphthalenes, 2-styrylnaphthalene, and 2-(2,4,6-trimethylstyryl)naphthalene were determined on an A.E.I. MS 9 instrument. The mass spectra of 1-bromo-2-styrylnaphthalene, 1,2-di-(2-naphthyl)ethylene, 4-styrylquinoline, and 3-styrylisoquinoline were determined on an A.E.I. MS 12 instrument.

trans-1-*Styryl-2-methylnaphthalene* (IVb).—This was prepared from a Wittig reaction [1] involving the phosphonium salt (45 g.), prepared from 1-chloromethyl-2-methylnaphthalene [18] in the usual manner,[19] and benzaldehyde (6·6 g.). The resulting oil was converted into the picrate, m.p. 138—140°. The picrate in acetone was decomposed on a short, alumina column. The *styrylnaphthalene* recrystallised from light petroleum (9 g., 60%), had m.p. 77—78° (Found: C, 93·3; H, 6·5. $C_{19}H_{16}$ requires C, 93·5; H, 6·5%); $\nu_{max.}$ (KBr) *inter alia*, 969s cm.$^{-1}$ (*trans*-ethylenic C–H bending).

trans-1-(2,4,6-*Trimethylstyryl*)*naphthalene* (IVc).—This was prepared from a Wittig reaction involving the phosphonium salt (35 g.), prepared from 1-chloromethylnaphthalene [20] in the usual manner,[19] and mesitaldehyde [21] (11·1 g.). The reaction proceeded overnight after which the triphenylphosphine oxide was filtered off. Some of the ether was removed and the *styrylnaphthalene* precipitated from the cool solution. Recrystallisation from ethanol yielded needles (12·3 g., 60%), m.p. 91—92° (Found: C, 92·6; H, 7·25. $C_{21}H_{20}$ requires C, 92·65; H, 7·35%); $\nu_{max.}$ (KBr) *inter alia*, 966 cm.$^{-1}$ *trans*-ethylenic C–H bending).

2-*Methyl*-1-(2,4,6-*trimethylstyryl*)*naphthalene* (XVIIId).—A Wittig reaction was performed as described above involving the phosphonium salt (22·5 g.), prepared from 1-chloromethyl-2-methylnaphthalene,[18] and mesitaldehyde [21] (7·4 g.). Recrystallisation of the *styrylnaphthalene* from ethanol yielded needles (8 g., 57%), m.p. 84—85° (Found: C, 92·3; H, 7·9. $C_{22}H_{22}$ requires C, 92·3; H, 7·7%); $\nu_{max.}$ (KBr) 700w, 720m, 739s, 775s, 806s, 820s, 853s, 884w, 943w, 953w, 991s, 1013w, 1031m, 1179w, 1224w, 1373m, 1423m, 1439m, 1478m, 1507m, 1566w, 1609m, 2725w, 2857m, 2913m, 2937m, 3009m, and 3047m cm.$^{-1}$; τ (CCl_4) 7·67

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[17] C. E. Loader and C. J. Timmons, *J. Chem. Soc.* (*C*), 1966, 1078.

[18] G. Darzens and A. Levy, *Compt. rend.*, 1936, **202**, 73.

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

[20] O. Grummitt and A. Buck, *Org. Synth.*, 1944, **24**, 30.

[21] R. C. Fuson, E. C. Horning, S. P. Rowland, and H. L. Ward, *Org. Synth.*, 1943, **23**, 57.

(3H, s, 4-methylstyryl H), 7·52 (6H, s, 2- and 6-methylstyryl H), 7·40 (3H, s, 2-methylnaphthyl H).

trans-1-(2,6-*Dichlorostyryl*)*naphthalene* (XVIIIc).—2,6-Dichlorobenzaldehyde (17·5 g.) reacted with the ylide from the triphenylphosphonium salt (44 g.), prepared from 1-chloromethylnaphthalene,[20] in a Wittig reaction as for (IVc). Recrystallisation of the *styrylnaphthalene* from ethanol yielded needles (18 g., 60%), m.p. 85—86°, (Found: C, 72·2; H, 4·05; Cl, 23·6. $C_{18}H_{12}Cl_2$ requires C, 72·25; H, 4·0; Cl, 23·75%); $\nu_{max.}$ (KBr) 713m, 783s, 800s, 842m, 857w, 886w, 900w, 911w, 958s, 972s, 1014m, 1036w, 1088s, 1143m, 1159m, 1182s, 1217w, 1250m, 1293w, 1347m, 1393m, 1428s, 1439s, 1507m, 1555s, 1581m, 1590m, 3066m, and 3079m cm.$^{-1}$.

trans-2-(2,4,6-*Trimethylstyryl*)*naphthalene* (VIb).—This was prepared from a Wittig reaction involving mesitaldehyde[21] (11·1 g.) and the triphenylphosphonium salt (35 g.) prepared from 2-chloromethylnaphthalene,[22] as for (IVc). The *styrylnaphthalene* recrystallised from ethanol as needles (10 g., 50%), m.p. 93—94° (Found: C, 92·5; H, 7·2. $C_{21}H_{20}$ requires C, 92·65; H, 7·35%); $\nu_{max.}$ (KBr) *inter alia*, 965s cm.$^{-1}$ (*trans* ethylenic C–H bending).

trans-1-*Bromo*-2-*styrylnaphthalene* (XXb).—Benzaldehyde (7 g.) reacted with the ylide from the triphenyl phosphonium salt (45 g.), prepared from 1-bromo-2-bromomethyl naphthalene,[23] in a Wittig reaction as for (IVc). Recrystallisation of the *styrylnaphthalene* from ethanol yielded needles (12 g., 52%), m.p. 121—122° (Found: C, 69·6; H, 4·4. $C_{18}H_{13}Br$ requires C, 69·9; H, 4·2%); $\nu_{max.}$ (KBr) 689s, 744s, 768m, 809s, 865m, 910m, 961s, 971m, 1027m, 1069w, 1152w, 1200w, 1235m, 1265m, 1293w, 1330m, 1372w, 1424w, 1446m, 1493s, 1548m, 1593w, 1626w, and 3063w cm.$^{-1}$.

Irradiation of 2-*Methyl*-1-*styrylnaphthalene* (IVb).—The styrylnaphthalene (0·5 g.) was irradiated in cyclohexane (2 l.) containing iodine (150 mg.) for 4·5 hr. with a Pyrex filter. The solvent was removed and the residue was chromatographed on an alumina column which was eluted with 10% ether in light petroleum. Only one fraction was obtained which had a chrysene-type u.v. spectrum. The product was recrystallised from light petroleum (0·17 g., 34%), m.p. 249—250° (lit.,[24] 248—250°); $\nu_{max.}$ (KBr) 681m, 759vs, 818vs, 863m, 869m, 877w, 943w, 1025m, 1033m, 1146w, 1193w, 1234w, 1265s, 1298m, 1359w, 1434s, 1485m, 1514m, 1549m, 1615w, 3057m, and 3085w cm.$^{-1}$; $\nu_{max.}$ (ethanol) 45,200, 41,400, 38,800, 37,400, 35,400, 34,000, 32,600, 31,200, 29,000, 28,500, 28,200, and 27,700 cm.$^{-1}$ (ε 34,400, 21,100, 85,000, 156,000, 12,900, 12,700, 13,900, 13,900, 680, 338, 374, and 690); $\nu_{infl.}$ 45,900, 40,000, and 29,800 cm.$^{-1}$ (ε 33,400, 35,300, and 540).

1,3-*Dimethylchrysene* (XIXb).—1-(2,4,6-Trimethylstyryl)-naphthalene (IVc) (1 g.) was irradiated for 5 hr. and the 1,3-*dimethylchrysene* was isolated in the same manner as (IXa). Recrystallisation from petroleum gave needles (0·4 g., 40%), m.p. 178·5—179° (Found: C, 93·8; H, 5·9. $C_{20}H_{16}$ requires C, 93·8; H, 6·2%); $\nu_{max.}$ (KBr) 673w, 749vs, 788w, 824vs, 853s, 863m, 942m, 960w, 1032m, 1144w, 1174w, 1202w, 1233w, 1246w, 1273m, 1286m, 1378w, 1438m, 1462m, 1484m, 1509w, 1593m, 1616m, 2861w, 2918m, 2949m, 2961m, 3014m, and 3053m cm.$^{-1}$; $\nu_{max.}$ (ethanol) 43,500, 41,000, 38,100, 36,800, 33,400, 32,000, 30,600, 28,700, and 27,300 cm.$^{-1}$ (ε 36,600, 19,300, 75,000, 123,000, 11,100, 13,400, 14,000, 920, and 870); $\nu_{infl.}$ 44,300, 39,400, 34,900, and 28,200 cm.$^{-1}$ (ε 33,600, 38,900, 12,400, and 410); τ ($CDCl_3$) 7·45 (3H, s, methyl H), 7·31 (3H, s, methyl H), 1·8—2·5 (6H, m, ArH), and 1·18—1·53 (4H, m, 4-, 5-, 10-, and 11-H).

Irradiation of 2-*Methyl*-1-(2,4,6-*trimethylstyryl*)*naphthalene* (XVIIId).—The styrylnaphthalene (0·3 g.) was irradiated for 48 hr. as for (Vc). The solvent was removed and the residue was chromatographed on an alumina column which was eluted with 10% ether in light petroleum. The first fraction contained unchanged styrylnaphthalene. The second fraction had a u.v. spectrum and R_F values (on alumina t.l.c. plates) identical with those of authentic 1,3-dimethylchrysene. The yield of the chrysene was obtained by spectroscopic measurements on this fraction and was 1·5 mg. (0·5%). No other chrysenes were obtained.

1-*Chlorochrysene* (XIXc).—Irradiation of 1-(2,6-dichlorostyryl)naphthalene (XVIIIc) (1 g.) for 17·5 hr. and isolation of the photolysis product as for (Vc) gave a product which sublimed (200°/0·5 mm.) to yield 1-*chlorochrysene* as pale yellow needles (0·53 g., 53%), m.p. 243—245° (Found: C, 82·3; H, 4·4; Cl, 13·6. $C_{18}H_{11}Cl$ requires C, 82·3; H, 4·2; Cl, 13·5%), $\nu_{max.}$ (KBr) 679w, 752s, 768s, 795s, 823m, 862m, 890w, 956w, 1028m, 1047m, 1097m, 1142m, 1189w, 1207m, 1234w, 1259s, 1288s, 1408m, 1424m, 1448w, 1482w, 1518w, 1589m, 1614w, and 3062w cm.$^{-1}$; $\nu_{max.}$ (ethanol) 43,700, 41,100, 38,400, 37,000, 34,900, 33,520, 32,200, 30,800, 28,800, 28,300, 28,100, and 27,500 cm.$^{-1}$ (ε 34,600, 19,200, 72,000, 126,200, 11,000, 11,300, 14,000, 14,200, 1000, 506, 487, and 1000); $\nu_{infl.}$ 46,500, 44,800, and 39,500 cm.$^{-1}$ (ε 19,000, 30,800, and 36,800).

2,4-*Dimethylbenzo*[c]*phenanthrene* (XXIa).—Irradiation of 2-(2,4,6-trimethylstyryl)naphththalene (XXa) (0·5 g.) for 4 hr. and chromatography of the product gave 2,4-*dimethylbenzo*[c]*phenanthrene* which recrystallised from light petroleum as needles (0·2 g.; 40%), m.p. 89—90° (Found: C, 94·1; H, 6·1. $C_{20}H_{16}$ requires C, 93·8; H, 6·2%); $\nu_{max.}$ (KBr) 670w, 718w, 741s, 753s, 763m, 790s, 806m, 831vs, 860m, 871m, 902m, 949w, 958w, 1019w, 1038m, 1132w, 1185m, 1213w, 1361w, 1407w, 1432m, 1455w, 1488m, 1602m, 1610m, 2868w, 2917w, 2972w, and 3053m cm.$^{-1}$; $\nu_{max.}$ (ethanol) 45,100, 43,000, 36,000, 34,800, 31,300, 27,800, and 26,400 cm.$^{-1}$ (ε 46,400, 27,400, 53,700, 67,000, 10,300, 496, and 317); $\nu_{infl.}$ 44,600, 40,400, 38,800, 37,100, 33,400, 32,700, and 30,300 cm.$^{-1}$ (ε 42,100, 12,400, 17,500, 31,900, 16,900, 13,100, and 5100); τ (CCl_4) 7·40 (3H, s, methyl H), 7·22 (3H, s, methyl H), 2·70 (1H, s, 3-H), 1·20br (2H, s, 1- and 12-H), and 1·8—2·6 (7H, m, ArH).

Irradiation of 1-*Bromo*-2-*styrylnaphthalene* (XXb).—The styrylnaphthalene (0·5 g.) was irradiated for 9·5 hr., the solvent removed, and the oily residue was chromatographed as for (IXa). The resulting oil was converted into the picrate which crystallised from ethanol as red needles, m.p. 127—128° (lit.,[25] 126—127°). Regeneration on an alumina column and recrystallisation from ethanol yielded the benzo[*c*]phenanthrene (0·09 g., 18%), m.p. 66—68° (lit.,[25] 67—68°).

Irradiation of Degassed Solutions.—Solutions of the ethylenes (0·5 mg./10 ml.) in a 10-cm. silica cell were degassed with eight freeze–thawing cycles with a vacuum of 10^{-5}—10^{-6} mm. and were irradiated with a filter solution of

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$NiSO_4,6H_2O$ (46 g.) and $CoSO_4,7H_2O$ (14 g.) in deionised water (100 ml.) until the photostationary state was established. The cell was then placed in a thermostatted jacket and this was placed in a Unicam SP 800 spectrophotometer. The rate of ring-opening was observed at various temperatures by the repeated scanning of the spectrum with a SP 825 programme controller and an SP 820 constant wavenumber scanner.

Irradiation of 1,2-*Di*-(2-*naphthyl*)*ethylene*.—1,2-Di-(2-naphthyl)ethylene (100 mg.) in ether (2 l.) was irradiated for 96 hr. The ether was removed and the residual tar was chromatographed on an alumina column which was eluted with 10% ether in light petroleum. Removal of the solvent gave benzo[*g*,*h*,*i*]perylene which gave leaflets (16 mg., 16%), m.p. 273—274° (lit.,[26] 272—273°) (from benzene).

Irradiation of Dibenzo[c,g]*phenanthrene*.—The dibenzophenanthrene (51 mg.) was dissolved in cyclohexane (2 l.) containing iodine (100 mg.). This solution was irradiated for 2 hr. with a Pyrex filter. The benzo[*g*,*h*,*i*]perylene was isolated as described above and gave leaflets (30 mg., 59%), m.p. 272—273° (lit.,[26] 272—273°) (from benzene).

We thank Dr. L. A. Cort (University of Surrey) and Professor L. Crombie (University College, Cardiff) for mass spectra, and the Imperial Tobacco Company Limited for a research grant (to E. V. B.).

[9/1217 *Received, July 17th*, 1969]

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