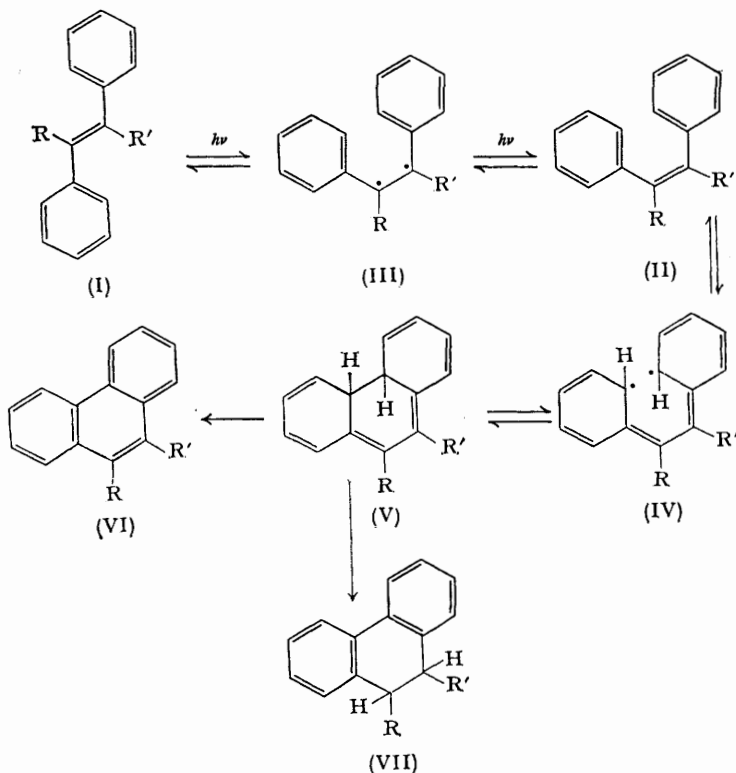


1063. *Studies in Photochemistry. Part I. The Stilbenes.*

By M. V. SARGENT and C. J. TIMMONS.

Some α -substituted and $\alpha\alpha'$ -disubstituted stilbenes have been cyclo-dehydrogenated photochemically to the corresponding 9-mono- and 9,10-di-substituted phenanthrenes (VI). In certain cases, in the absence of oxygen, 9,10-dihydrophenanthrenes (VII) were isolated. 9-Cyanophenanthrene underwent photodimerisation to a cyclobuta[1,2-*l*:3,4-*l'*]diphenanthrene (X; R = CN).

STILBENES are known¹⁻⁶ to undergo photochemical cyclo-dehydrogenation to phenanthrenes. Stegemeyer⁴ showed that the initial rate of phenanthrene formation on ultraviolet irradiation of *trans*-stilbene (I; R = R' = H) was zero, but in the case of *cis*-stilbene (II; R = R' = H)



the initial rate was finite. Mallory and his co-workers⁵ showed that, in the complete absence of oxygen, on ultraviolet irradiation of *cis*- or *trans*-stilbene only *cis*-*trans*-isomerisation took place. They proposed that the dihydrophenanthrene (V; R = R' = H) was an intermediate in the reaction. The function of oxygen was to remove the tertiary allylic hydrogen atoms.

¹ R. E. Buckles, *J. Amer. Chem. Soc.*, 1955, **77**, 1040.

² D. G. Coe, E. W. Garnish, M. M. Gale, and C. J. Timmons, *Chem. and Ind.*, 1957, 665.

³ P. Hugelshofer, J. Kalvoda, and K. Schaffner, *Helv. Chim. Acta*, 1960, **43**, 1322.

⁴ H. Stegemeyer, *Z. Naturforsch.*, 1962, **17b**, 153.

⁵ F. B. Mallory, C. S. Wood, J. T. Gordon, L. C. Lindquist, and M. L. Savitz, *J. Amer. Chem. Soc.*, 1962, **84**, 4361.

⁶ W. M. Moore, D. D. Morgan, and F. R. Stermitz, *J. Amer. Chem. Soc.*, 1963, **85**, 830.

In the absence of oxygen the dihydrophenanthrene (V; $R = R' = H$) would undergo ring-opening and revert to *cis*-stilbene. Moore *et al.*⁶ identified the dihydrophenanthrene intermediate (V) spectrophotometrically.

We have studied the photochemistry of a number of α -substituted stilbene systems: $\alpha\alpha'$ -dicyano-*trans*-stilbene (I; $R = R' = CN$), α -cyano-*trans*-stilbene (I; $R = H$; $R' = CN$), α -carbamoyl-*trans*-stilbene (I; $R = H$; $R' = CONH_2$), α -methyl-*trans*-stilbene (I; $R = H$; $R' = Me$), $\alpha\alpha'$ -dimethyl-*trans*-stilbene (I; $R = R' = Me$), triphenylethylene (I; $R = H$; $R' = Ph$), tetraphenylethylene (I; $R = R' = Ph$), diphenylmaleic anhydride (II; $RR' = CO \cdot O \cdot CO$), and diphenylmaleimide (II; $RR' = CO \cdot NH \cdot CO$). When these reactions were conducted in the presence of oxygen or iodine, the expected 9-substituted or 9,10-disubstituted phenanthrenes were obtained. In the cases of $\alpha\alpha'$ -dicyano-*trans*-stilbene (I; $R = R' = CN$) and diphenylmaleimide (II; $RR' = CO \cdot O \cdot CO$) on irradiation in vessels open to the air, small quantities of 9,10-dihydrophenanthrenes were isolated from the reactions, as reported in a preliminary communication.⁷

When $\alpha\alpha'$ -dicyano-*trans*-stilbene (I; $R = R' = CN$) was irradiated in the complete absence of oxygen an almost quantitative yield of *trans*-9,10-dicyano-9,10-dihydrophenanthrene (VII; $R = R' = CN$) was obtained. This was demonstrated by carrying out the reaction in a sealed absorption cell which had been degassed under high vacuum and following the course of the reaction by ultraviolet spectrophotometry. The reaction was also carried out on a larger scale in an apparatus attached to a high-vacuum frame. Diphenylmaleimide (II; $RR' = CO \cdot NH \cdot CO$), even in the presence of oxygen, gave a small yield of *cis*-9,10-dihydrophenanthrene-9,10-dicarboxyimide (VII; $RR' = CO \cdot NH \cdot CO$), an unstable compound which decomposed on melting or on attempted recrystallisation from acetone to phenanthrene-9,10-dicarboxyimide (VI; $RR' = CO \cdot NH \cdot CO$).

Irradiation of diphenylmaleic anhydride (II; $RR' = CO \cdot O \cdot CO$) in the absence of oxygen gave *cis*-9,10-dihydrophenanthrene-9,10-dicarboxylic anhydride (VII; $RR' = CO \cdot O \cdot CO$).

The dicyanodihydrophenanthrene (VII; $R = R' = CN$) on alkaline hydrolysis gave 9-carbamoylphenanthrene (VI; $R = H$, $R' = CONH_2$). This reaction presumably occurs by *cis*-elimination of CN^- in the presence of base to give 9-cyanophenanthrene (VI; $R = H$, $R' = CN$), followed by hydrolysis of the nitrile to the amide. Acidic hydrolysis of the compound, however, gave the known⁸ *trans*-9,10-dihydrophenanthrene-9,10-dicarboxylic acid (VII; $R = R' = CO_2H$). The *cis*-isomer of this acid is unknown since it spontaneously forms the *cis*-anhydride.⁸ By analogy, the dihydro-imide (VII; $RR' = CO \cdot NH \cdot CO$) is assigned *cis*-stereochemistry.

Ultraviolet irradiation of *trans*-stilbene (I; $R = R' = H$) in the complete absence of oxygen led only to *cis*-*trans*-isomerisation, as shown by gas-liquid chromatography. No 9,10-dihydrophenanthrene (VII; $R = R' = H$) was detected although conditions were used which were known to separate 9,10-dihydrophenanthrene. Similar experiments were carried out with α -methyl-*trans*-stilbene (I; $R = H$, $R' = Me$) and α -cyano-*trans*-stilbene (I; $R = H$, $R' = CN$), but in neither case was a 9,10-dihydrophenanthrene detected by gas-liquid chromatography.

Support for the 9,10-dihydrophenanthrene structures is given by their electronic spectra which are typical of *o,o'*-linked biphenyls and by the positions of the 9,10-proton resonances of the dihydrophenanthrenes in their nuclear magnetic resonance (n.m.r.) spectra (Table I). These all occur as sharp two-proton singlets and the chemical shifts reflect the effective shieldings of the various 9,10-substituents. The magnetic equivalence of the 9,10-protons is indicative of the rapid interconversion of the conformers about the 9,10-bond.

9,10-Dicyanophenanthrene (VI; $R = R' = CN$) on alkaline hydrolysis gave phenanthrene-9,10-dicarboxylic anhydride (VI; $RR' = CO \cdot O \cdot CO$), which on treatment with alcoholic ammonia gave phenanthrene-9,10-dicarboxyimide (VI; $RR' = CO \cdot NH \cdot CO$).

Ultraviolet irradiation of α -cyano-*trans*-stilbene (I; $R = H$, $R' = CN$) in ethanol gave rise

⁷ M. V. Sargent and C. J. Timmons, *J. Amer. Chem. Soc.*, 1963, **85**, 2186.

⁸ A. Jeanes and R. Adams, *J. Amer. Chem. Soc.*, 1937, **59**, 2608.

TABLE I.

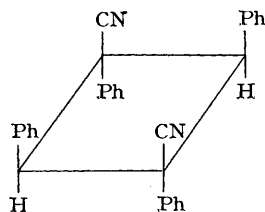
Electronic spectra (in ethanol) and 9,10-proton resonances (in dimethyl sulfoxide) of 9,10-disubstitued 9,10-dihydrophenanthrenes.

9,10-Substituents	$\lambda_{\max.}(\text{m}\mu)$	ϵ	$\lambda_{\max.}(\text{m}\mu)$	ϵ	$\lambda_{\max.}(\text{m}\mu)$	ϵ	τ
None	209	43,500	265	17,500	290	4400	7.20
	220	10,200			298	4300	
<i>cis</i> -(CO.O.CO)	208	36,500	262	17,000			4.75
			269	19,000			
			280	13,500			
<i>cis</i> -(CO.NH.CO)	208	35,500	265	14,000	303	1200	5.18
	230	10,000	275	16,000			
	240	5,800	284	11,500			
<i>trans</i> -(CN) ₂	206	39,000	268	17,500			4.68
	211	41,000					
<i>trans</i> -(CO ₂ H) ₂	208	36,000	266	16,000	298	1600	5.50
	211	36,500					
<i>trans</i> -(OH) ₂	211	40,000	269	15,000	298	2600	5.22
	225	10,000					
<i>cis</i> -(OH) ₂	208	39,500	270	16,500			5.25*
	225	10,000	282	11,000			
<i>trans</i> -(OAc) ₂	211	51,500	270	18,000	301	1200	4.14
	225	12,000					
	232	6,700					
<i>cis</i> -(OAc) ₂	211	45,000	268	18,000			3.84
	222	10,500	281	11,000			
	230	5,800					

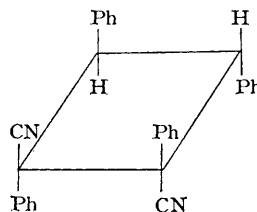
Figures in italics denote inflections.

* Determined in D₂O-dimethyl sulphoxide.

to a mixture of products which were separated by chromatography on alumina. 9-Cyano-phenanthrene (VI; R = H, R' = CN) was obtained, as expected, but accompanied by other products, one in small yield. The latter showed only low-intensity benzenoid absorption in its ultraviolet spectrum and on pyrolysis reverted to α -cyano-*trans*-stilbene. A molecular-weight determination indicated a dimeric structure. The n.m.r. spectrum, in deuteriochloroform solution, was extremely simple, exhibiting a singlet at τ 2.70 due to the aromatic protons, and a singlet at τ 4.68 assigned to two protons on a cyclobutane ring, shifted to low field by the deshielding effect of the nitrile groups.



(VIII)



(IX)

Schechter, Link, and Tiers⁹ examined the n.m.r. spectra of the two isomeric photodimers of stilbene, and their chlorination products. On the grounds of their measurements it is possible to reject structures for the photodimer of α -cyano-*trans*-stilbene which contain three phenyl groups in a *cis*-vicinal arrangement, since these structures would be expected to give aromatic proton resonances at $\tau > 3$, because of the double shielding of the central one of three adjacent phenyl groups, on the same side of a cyclobutane ring. On similar grounds structures containing *cis*-1,2-diphenyl groups may be rejected.

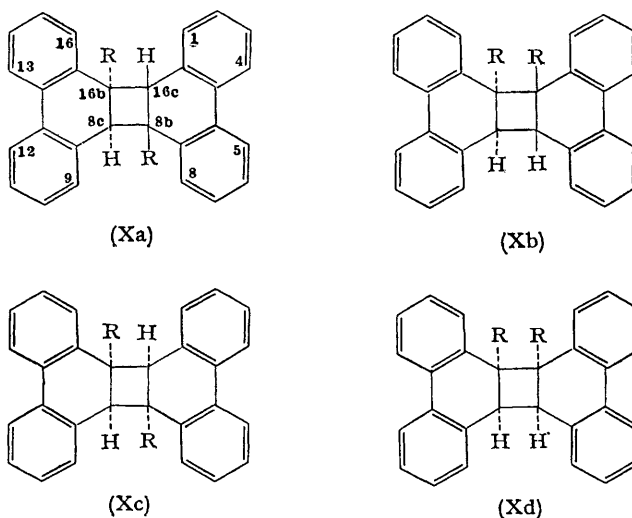
Thus, either structure (VIII) or (IX), which both contain two equivalent protons on the cyclobutane ring, is proposed for the photodimer of α -cyano-*trans*-stilbene.

⁹ H. Schechter, W. J. Link, and G. V. D. Tiers, *J. Amer. Chem. Soc.*, 1963, **85**, 1601.

The other product of the ultraviolet irradiation of α -cyano-*trans*-stilbene was also a dimer and showed a high-intensity absorption band, λ_{\max} , 275 m μ (ϵ 22,500), indicating that the compound was more conjugated than the cyclobutane photodimer of α -cyano-*trans*-stilbene described above. The n.m.r. spectrum, in deuteriochloroform, showed a singlet at τ 4.84 equivalent to two protons, and a complex aromatic resonance equivalent to sixteen protons.

Pyrolysis of this photodimer gave a high yield of 9-cyanophenanthrene (VI; R = H, R' = CN). Photolysis of the photodimer gave an equilibrium mixture of the photodimer and 9-cyanophenanthrene. The same equilibrium mixture was obtained on ultraviolet irradiation of a solution of 9-cyanophenanthrene. Hydrolysis of the photodimer gave a dicarboxylic acid, which underwent pyrolysis to phenanthrene-9-carboxylic acid (VI; R = H, R' = CO₂H).

The evidence presented above indicates that the compound is one of the isomeric dicyanotetrahydrocyclobutadiphenanthrenes (Xa—d; R = CN), and results from photodimerisation of 9-cyanophenanthrene across the 9,10-double bond. This is the first reported case of the photodimerisation of a phenanthrene.



Attempted formation of an anhydride from the dicarboxylic acid (X; R = CO₂H) failed. This means that structures (Xc; R = CN) and (Xd; R = CN) are unlikely. Wittig and his co-workers¹⁰ prepared the parent compound (X; R = H). The electronic spectra of these compounds (Table 2) show a striking resemblance to the spectra of 9,10-dihydrophenanthrenes, although the extinction coefficients are higher. This is to be expected since the molecules contain two 9,10-dihydrophenanthrene systems.

TABLE 2.
Electronic spectra (in ethanol) and n.m.r. spectra of
cyclobutadiphenanthrenes.

Compound	λ_{\max} (m μ)	ϵ	τ^*
(X; R = H)†	268	30,000	†
(X; R = CN)	275	22,500	4.84
(X; R = CO ₂ H)	277	22,500	4.96
(X; R = CO ₂ Me)	270	19,500	5.06

* Cyclobutane proton resonances only. The full spectra and solvents used are given in the Experimental Section. † Ref. 10. ‡ A sample kindly provided by Professor G. Wittig was insufficiently soluble.

¹⁰ G. Wittig, G. Koenig, and K. Claus, *Annalen*, 1955, 593, 127.

It appears that the mechanism of photochemical cyclodehydrogenation of stilbenes to phenanthrenes proceeds through an excited state of the *cis*-stilbene which is not available to the *trans*-stilbene, and the intermediate (V) is formed. In the presence of oxygen or iodine this intermediate is dehydrogenated in a dark reaction to the phenanthrene (VI). In the absence of oxygen, if the groups R and R' are both strongly electron-withdrawing (V; R = R' = CN; RR' = CO·O·CO; RR' = CO·NH·CO) the intermediate is thought to undergo a 1,3-prototropic shift to the 9,10-dihydrophenanthrene (VII; R = R' = CN; RR' = CO·O·CO; RR' = CO·NH·CO). As a result of this the systems become stabilised by the difference in resonance energies of the biphenyl (VII) and the tricyclic hexaene (V). If, however, both groups R and R' are not strongly electron-withdrawing, the intermediate (V) in the absence of oxygen, undergoes thermal ring-opening and reverts to the *cis*-stilbene (II).

EXPERIMENTAL

Melting points were determined on a Kofler hot-stage apparatus and are corrected. Light petroleum refers to the fraction, b. p. 40—60°. Alumina was Spence grade H. Ultraviolet spectra were determined on a Unicam SP700 spectrophotometer and refer to ethanolic solutions. Infrared spectra were determined on a Unicam SP100 spectrophotometer with a prism-grating double monochromator. Nuclear magnetic resonance spectra were determined on an A.E.I. RS2 spectrometer at 60 Mc./sec., with tetramethylsilane as internal standard, and were calibrated by the side-band technique. Except where stated otherwise, irradiations were carried out using a Hanovia 400w medium-pressure mercury lamp, surrounded by a water-cooled jacket constructed either in quartz or in Pyrex. The jacketed lamp was placed in the solutions, which were stirred with a magnetic stirrer. Molecular weights, except where stated otherwise, were determined with a Mechrolab vapour-pressure osmometer in chloroform solution. Gas chromatography was carried out on a Perkin-Elmer model 800 apparatus, except where otherwise stated.

9,10-Dicyanophenanthrene (VI; R = R' = CN).— $\alpha\alpha'$ -Dicyano-*trans*-stilbene (1.69 g.) in chloroform (300 ml.) containing a trace of iodine was irradiated (Pyrex jacket) for 3.5 hr. Removal of the solvent and crystallisation of the residue from acetone gave the phenanthrene (1.02 g; 60%), as pale yellow needles, m. p. 295° (lit.,² 286°), λ_{\max} . 213.5, 235.5, 250, 259, 320, 334, 362, and 382 m μ . (ϵ 26,000, 37,000, 34,500, 39,500, 12,500, 16,000, 2000, and 1900), and λ_{inf} . 278 m μ (ϵ 13,000), ν_{\max} . (KBr) *inter alia* 2231 cm.⁻¹ (C=N).

Phenanthrene-9,10-dicarboxylic Anhydride (VI; RR' = OC·O·CO).—(a) A solution of 9,10-dicyanophenanthrene (0.42 g.) and potassium hydroxide (0.40 g.) in ethanol (60 ml.) was heated under reflux for 48 hr. The solution was poured into water, acidified with concentrated hydrochloric acid, and the yellow product was filtered off, washed with water, and dried. Crystallisation from acetic anhydride gave the anhydride as yellow needles (0.32 g.; 70%), m. p. 321—322° (lit.,⁸ 322°) (Found: C, 77.3; H, 3.4. Calc. for C₁₆H₈O₃: C, 77.4; H, 3.2%), λ_{\max} . 213, 229, 258, 303, 338, and 355 m μ (ϵ 25,500, 23,500, 43,000, 9800, 7800, and 5900), and λ_{inf} . 249 and 270 m μ (ϵ 38,000 and 16,500), ν_{\max} . (KBr) *inter alia* 1848 (C=O), 1814 (C=O), and 1777 cm.⁻¹ (C=O).

(b) A suspension of diphenylmaleic anhydride (2.0 g.) in a solution of anhydrous sodium carbonate (5.0 g.) in water (1800 ml.) was irradiated (Pyrex jacket) for 42 hr. The solution was concentrated to 300 ml. and then acidified with concentrated hydrochloric acid. The yellow precipitate obtained was filtered off, washed with water, and dried. Crystallisation from acetic anhydride gave the product as yellow needles (0.85 g.; 43%) identical with that obtained in (a).

Phenanthrene-9,10-dicarboxyimide (VI; RR' = CO·NH·CO).—To a solution of phenanthrene-9,10-dicarboxylic anhydride (0.31 g.) in ethanol (80 ml.) was added aqueous ammonia (50 ml.; *d* 0.88), and the mixture heated under reflux for 24 hr. The solution was allowed to cool, the product was filtered off, washed with water, and dried. Recrystallisation from acetone gave the imide as long yellow needles (0.14 g.; 57%), m. p. 334—335° (lit.,⁷ 334—335°), λ_{\max} . 212, 238, 279, and 370 m μ (ϵ 32,500, 45,500, 18,000, and 6900), and λ_{inf} . 251, 266, and 286 m μ (ϵ 29,500, 20,500, and 11,000), ν_{\max} . (KBr) *inter alia* 3199 (NH), 1769 (C=O), and 1719 cm.⁻¹ (C=O).

Ultraviolet Irradiation of Degassed $\alpha\alpha'$ -Dicyano-*trans*-stilbene (I; R = R' = CN).—(a) A solution of the stilbene (1.2 \times 10⁻⁴M) in *n*-butanol, or in ethanol contained in a 5 mm. silica absorption cell, was degassed under high vacuum at -195°, sealed, and placed 1 cm. away from the lamp (Pyrex jacket). After 15 min. the stilbene spectrum had disappeared completely and a band at 268 m μ , characteristic of *trans*-9,10-dicyano-9,10-dihydrophenanthrene was observed.

(b) Ultraviolet irradiation of a similar ethanol solution but exposed to the air, gave after 15 min. a solution with bands at 320, 333, 360, and 380 μ characteristic of 9,10-dicyanophenanthrene.

(c) A solution of the stilbene (5.22 g.) in purified benzene (275 ml.) was degassed at -70° under high vacuum. The solution was then irradiated (Pyrex jacket) for 15.75 hr., under vacuum. Prisms of *trans*-9,10-dihydro-9,10-dicyanophenanthrene crystallised from the solution during the reaction. After filtration, removal of the solvent, and crystallisation of the residue from acetone, prisms of the dihydrophenanthrene (3.23 g.; 85%), m. p. 199—204° (lit.,⁷ 199—204°),* were obtained (Found: C, 83.1; H, 4.4; N, 12.5%; *M*, 230. Calc. for $C_{16}H_{10}N_2$: C, 83.1, H, 4.4; N, 12.2%; *M*, 230), ν_{\max} . (KBr) *inter alia* 3080 (aromatic CH), 3022 (aromatic CH), 2948 (aliphatic CH), 2886 (aliphatic CH), and 2245 cm^{-1} (aliphatic C=N), τ ($CHCl_3$) 5.58 (singlet, 9,10-protons). τ (dimethyl sulphoxide) 1.36—2.34 (multiplet, aromatic protons), and 4.68 (singlet, 9,10-protons).

(d) The stilbene (15.6 g.) in chloroform (1800 ml.) was irradiated (Pyrex jacket) for 15 hr. Removal of the solvent and fractional crystallisation of a portion of the residue from benzene gave small amounts of 9,10-dicyanophenanthrene and 9,10-dicyano-9,10-dihydrophenanthrene.

trans-9,10-Dihydrophenanthrene-9,10-dicarboxylic Acid (VII; R = R' = CO_2H).—A solution of *trans*-9,10-dicyano-9,10-dihydrophenanthrene (1.03 g.) in glacial acetic acid (125 ml.), concentrated sulphuric acid (50 ml.), and water (50 ml.) was heated under reflux for 17 hr. After cooling, the solution was poured into water (500 ml.) and the product filtered off, washed with water, and dried. Crystallisation from glacial acetic acid gave prisms, m. p. 231—234° (decomp.) [lit.,⁸ 235—242° (decomp.)] undepressed on admixture with a sample prepared by the method of Jeanes and Adams,⁸ ν_{\max} . (KBr) *inter alia* 3426 (free OH), 3075 (aromatic CH), 3030 (aromatic CH), 2918 (aliphatic CH), 2592 (bonded OH), and 1711 cm^{-1} (C=O).

cis-9,10-Dihydrophenanthrene-9,10-dicarboxylic Anhydride (VII; RR' = OC.O.CO) and Phenanthrene-9,10-dicarboxylic Anhydride (VI; RR' = OC.O.CO).—Diphenylmaleic anhydride (3.95 g.) in purified benzene (275 ml.) was heated under reflux in an atmosphere of dry nitrogen. The solution was then degassed ten times at -70° under high vacuum and irradiated (Pyrex jacket) for 14 hr. The solution was then concentrated to 50 ml. and the crude phenanthrene filtered off. Crystallisation from acetic anhydride gave the phenanthrene as yellow needles (0.76 g.; 20%), m. p. 321—322° (lit.,⁸ 322°). Complete removal of the solvent and trituration of the resulting gum with ethanol gave the crude dihydrophenanthrene, which crystallised from ethanol-chloroform as pale yellow needles (0.59 g.; 15%), m. p. 189—191° (lit.,⁸ 193.5°) (Found: C, 76.8; H, 4.1. Calc. for $C_{16}H_{10}O_3$: C, 76.8; H, 4.0%), ν_{\max} . (KBr) *inter alia* 3064 (aromatic CH), 3025 (aromatic CH), 2937 (aliphatic CH), 2898 (aliphatic CH), 1866 (C=O), 1825 (C=O), and 1780 cm^{-1} (C=O), τ (dimethyl sulphoxide), 1.58—2.40 (multiplet, aromatic protons) and 4.75 (singlet, 9,10-protons).

cis-9,10-Dihydrophenanthrene-9,10-dicarboxyimide (VII; RR' = CO.NH.CO) and Phenanthrene-9,10-dicarboxyimide (VI; RR' = CO.NH.CO).—Diphenylmaleimide (3.44 g.) in ethanol (1800 ml.) was irradiated (Pyrex jacket) for 2.5 hr. After 1 hr. yellow needles (0.37 g.) began to be deposited from the solution. After 2.5 hr. these were filtered off and recrystallised from acetone to give the phenanthrene, m. p. 334—335° (lit.,⁷ 334—335°) (Found: C, 77.7; H, 3.8; N, 5.7. Calc. for $C_{16}H_9NO_2$: C, 77.7; H, 3.7; N, 5.7%). The filtered solution showed a band in the ultraviolet spectrum at 275 μ . Removal of the solvent and crystallisation of the yellow residue from ethanol gave needles of the dihydrophenanthrene (1.35 g.; 40%), m. p. 245—246° (decomp.) [lit.,⁷ 245—246° (decomp.)]. Recrystallisation from chloroform gave prisms, but recrystallisation from acetone brought about dehydrogenation to the phenanthrene. Similarly, melting produced the phenanthrene, the m. p. rising to 334—335° (Found: C, 76.9; H, 4.6; N, 5.7. Calc. for $C_{16}H_{11}NO_2$: C, 77.1; H, 4.45; N, 5.6%), ν_{\max} . (KBr) *inter alia* 3195 (NH), 3077 (aromatic CH), 2934 (aliphatic CH), 2898 (aliphatic CH), 1796 (C=O), 1785 (C=O), and 1699 cm^{-1} (C=O), τ (dimethyl sulphoxide) —1.84 (broad singlet, NH proton), 1.48—2.33 (multiplet, aromatic protons), and 5.18 (singlet, 9,10-protons). Concentration of the mother liquors gave a further crop of the phenanthrene (1.05 g.).

Ultraviolet Irradiation of Degassed trans-Stilbene (I; R = R' = H).—A solution of *trans*-stilbene ($1.2 \times 10^{-1}M$) in benzene was degassed at -195° under high vacuum and then exposed to ultraviolet light for 3 hr. in a silica vessel 1 cm. away from the lamp (silica jacket). The solution was examined by gas-liquid chromatography using a 6 ft. \times $\frac{1}{8}$ in. column (G-22 support, 80—100 mesh, coated with 15% silicone oil DC710) at a column temperature of 165°, and an injector

* Varies with rate of heating.

temperature of 240°, N₂ flow-rate of 41 ml./min. Under these conditions the mixture was shown to contain *cis*-stilbene (80%) retention time 18.9 min. and *trans*-stilbene (20%) retention time 40.4 min. The mixture contained no phenanthrene, retention time 53.5 min., or 9,10-dihydrophenanthrene, retention time 37.8 min., under these conditions. Ultraviolet irradiation of a similar solution, but exposed to the air, produced some phenanthrene.

Ultraviolet Irradiation of Degassed α -Methyl-*trans*-stilbene (I; R = H, R' = Me).—A solution of the stilbene (5.4×10^{-2} M) in ethanol contained in a silica vessel was degassed at -195° under high vacuum, and exposed for 16.5 hr., 2 cm. away from the lamp (silica jacket). The solvent was removed under reduced pressure and the residue was dissolved in ether. The solution was examined by gas-liquid chromatography using a 3 ft. \times $\frac{1}{8}$ in. column (G-22 support, 60–80 mesh, coated with 2.5% silicone gum rubber SE 30) at a column temperature of 115°, and an injector temperature of 200°, N₂ flow-rate of 140 ml./min. Under these conditions α -methyl-*trans*-stilbene had a retention time of 12.9 min. and α -methyl-*cis*-stilbene a retention time of 5.3 min. The solution consisted of the *trans*-isomer (20%) and the *cis*-isomer (80%). No phenanthrene or dihydrophenanthrene was detected. A similar solution irradiated under identical conditions, but exposed to the air, was shown (column temperature of 145°, injector temperature of 200°) to contain a high proportion of 9-methylphenanthrene, retention time 10.8 min., under these conditions.

Ultraviolet Irradiation of Degassed α -Cyano-*trans*-stilbene (I; R = H; R' = CN).—The stilbene (1.07 g.) in ethanol (100 ml.) was degassed in a silica vessel under high vacuum at -195° . The solution was exposed 5 cm. away from the lamp (silica jacket) for 17 hr. The solvent was removed and the residue dissolved in a small volume of ether. The solution was examined by gas-liquid chromatography using a 6 ft. \times $\frac{1}{8}$ in. column (G-22 support, 80–100 mesh, coated with 15% silicone oil DC710) at a column temperature of 145°, and an injector temperature of 200°, N₂ flow rate of 41 ml./min. Under these conditions the retention times of the *cis*- and the *trans*-isomers were 7.3 and 9.2 min., respectively. The solution contained chiefly the *cis*-isomer and no peaks were resolved other than the *trans*-isomer.

9-Carbamoylphenanthrene (VI; R = H; R' = CONH₂).—(a) A solution of *trans*-9,10-dicyano-9,10-dihydrophenanthrene (2.0 g.) in ethanol (90 ml.) was heated under reflux for 200 hr. The solution was allowed to cool, poured into water (150 ml.), acidified with concentrated hydrochloric acid, and the amide (0.85 g.; 89%) filtered off, washed with water, and dried. Crystallisation of the product from ethanol gave needles m. p. 226°† (lit.¹¹ 226°) (Found: N, 6.3. Calc. for C₁₅H₁₁NO: N, 6.3%), λ_{\max} 212, 221, 248, 254, 285, 296, 332, 342, and 348 m μ (ϵ 28,500, 21,500, 44,500, 51,500, 18,500, 22,000, 310, 270, and 50), and λ_{inf} 275 m μ (ϵ 22,500), ν_{\max} (KBr) *inter alia* 3379 (bonded NH), 3200 (bonded NH), 3088, 1650 (C=O), and 1629 cm.⁻¹ (primary amide).

(b) A solution of *trans*- α -carbamoylstilbene (2.18 g.) in ethanol was placed in a silica vessel for 75 hr., 5 cm. away from a Hanovia 220w type 501/1 medium-pressure mercury lamp. After being stood in the dark for 48 hr. the solution deposited needles of the phenanthrene. Concentration of the solution to small volume gave a further crop of the phenanthrene. Crystallisation of the crude product from aqueous ethanol gave needles (0.88 g.; 41%) identical in every respect with that under (a). Complete removal of the solvent left an intractable yellow gum.

9-Methylphenanthrene (VI; R = H; R' = Me) and **α -Methyl-*cis*-stilbene** (II; R = H; R' = Me).—A solution of α -methyl-*trans*-stilbene (3.01 g.) in ethanol (125 ml.) was exposed for 125 hr. in a silica vessel 5 cm. away from a Hanovia 220w type 501/1 medium-pressure mercury lamp. Concentration of the solution to small volume gave the phenanthrene (1.18 g.; 39%) which crystallised from ethanol as needles, m. p. 91–92° (lit.¹² 91–92°), λ_{\max} 212.5, 252, 269, 275, 283, 295, 316, 323, 332, 340, and 348 m μ (ϵ 28,500, 57,000, 14,000, 12,500, 9600, 11,500, 300, 290, 430, 270, and 440), and λ_{inf} 220, 246, and 310 m μ (ϵ 19,000, 46,500, and 230). Complete removal of the solvent left an oil which on distillation under reduced pressure gave the *cis*-stilbene, b. p. 90–98°/0.4 mm. Crystallisation from methanol gave plates (0.69 g.; 23%), m. p. 35–44°. The crude *cis*-isomer was purified in benzene solution by gas-liquid chromatography using a 20 ft. \times $\frac{3}{8}$ in. column (Chromosorb P support, 60–80 mesh, coated with 30% silicone gum rubber SE30), at a column temperature of 230°, an injector temperature of 328°, a cooling cycle of 0.5 min., a pre-collection cycle of 8 min., and a post-collection cycle of 5 min., in an Aerograph Autoprep model A-700 gas chromatography apparatus, He flow-rate of 150 ml./min. Under

† Determined in sealed capillary in an electrical coil apparatus; uncorrected.

¹¹ A. Werner, *Annalen*, 1902, **321**, 248.

¹² R. D. Haworth and C. R. Mavin, *J.*, 1932, 2720.

these conditions the *cis*- and *trans*-isomers had retention times of 12.3 and 18.3 min., respectively. The *cis*-isomer was crystallised from methanol as needles m. p. 47.5—48.5° (lit.,¹³ 48°), λ_{\max} . 223.5 and 264 m μ (ϵ 13,000 and 12,000).

9,10-Dimethylphenanthrene (VI; R = R' = Me).— $\alpha\alpha'$ -Dimethyl-*trans*-stilbene (1.82 g.) in ethanol (300 ml.) was irradiated (silica jacket) for 25 hr. The ultraviolet spectrum of the solution showed development of bands at 254 and 299 m μ . Removal of the solvent left a brown oil which was chromatographed in benzene on acid-washed alumina. Elution with benzene gave the phenanthrene (0.96 g.) which sublimed at 100°/1 mm. as laths, m. p. 145—146° (lit.,¹⁴ 142—142.6°) (Found: C, 93.6; H, 6.8. Calc. for C₁₆H₁₄: C, 93.2; H, 6.8%), λ_{\max} . 214, 223, 248, 254, 271, 278, 296, 298, 320, 328, 336, and 353 m μ (ϵ 30,000, 21,500, 46,000, 57,000, 18,000, 13,500, 9800, 10,000, 290, 260, 420, and 390).

9-Phenylphenanthrene (VI; R = H; R' = Ph).—Triphenylethylene (5.65 g.) in ethanol (300 ml.) was irradiated (silica jacket) for 19.5 hr. The ultraviolet spectrum of the solution showed the development of an intense band at 255 m μ . The solvent was removed and the residual oil was dissolved in light petroleum and chromatographed on alumina. The phenanthrene was eluted by benzene—light petroleum (1:1, v/v) as an oil which crystallised on trituration with light petroleum. Recrystallisation from methanol gave lustrous plates of the product (3.24 g.; 57%), m. p. 104.5—106° (lit.,¹⁵ 105—106°) (Found: C, 94.0; H, 5.3. Calc. for C₂₀H₁₄: C, 94.4; H, 5.5%), λ_{\max} . 209, 212, 255, 296, 333, 341, and 350 m μ (ϵ 34,000, 34,000, 57,500, 13,500, 390, 280, and 320), and λ_{\min} . 248, 285, and 325 m μ (ϵ 48,500, 11,000, and 400).

9,10-Diphenylphenanthrene (VI; R = R' = Ph).—Tetraphenylethylene (1.04 g.) with iodine (25 mg.) in ethanol (300 ml.) was irradiated (silica jacket) for 3 hr. The solvent was removed and the residue chromatographed in benzene on B.D.H. alumina. Benzene eluted the phenanthrene (0.67 g.) which recrystallised from ethanol as colourless needles, m. p. 239—240° (lit.,¹⁶ 235°) (Found: C, 94.3; H, 5.6. Calc. for C₂₆H₁₈: C, 94.5; H, 5.5%), λ_{\max} . 210, 257, 288, 300, 334, 342, and 351 m μ (ϵ 43,500, 60,000, 11,500, 12,500, 550, 360, and 500), λ_{\min} . 250, 271, and 328 m μ (ϵ 49,500, 23,500, and 460).

Ultraviolet Irradiation of α -Cyano-*trans*-stilbene (V; R = H; R = CN).— α -Cyanostilbene (6.12 g.) in ethanol (320 ml.) was irradiated (Pyrex jacket) for 11.25 hr. During irradiation, material (0.40 g.) was deposited. This was collected and crystallised from ethanol as needles of the *dicyano*-8b,8c,16b,16c-*tetrahydrocyclobuta*[1,2-1:3,4-1']*diphenanthrene* (X; R = CN), m. p. 214—216° (Found: C, 88.3; H, 4.3; N, 6.8%; M, 391. C₃₀H₁₈N₂ requires C, 88.6; H, 4.5; N, 6.9%; M, 406.5), λ_{\max} . 207.5 and 275 m μ (ϵ 48,500 and 22,500), and λ_{\min} . 216 and 267 m μ (ϵ 47,500 and 19,500), ν_{\max} . (CHCl₃) *inter alia* 2235 cm.⁻¹ (C=N), τ (CDCl₃) *inter alia* 4.84 (singlet, cyclobutane protons). Removal of the solvent left an oil which was chromatographed on alumina. Elution with benzene gave α -cyano-*cis*-stilbene (1.90 g.) as an oil, b. p. 124—128°/0.1 mm. (lit.,¹⁷ 90—100°/0.05 mm.), α -cyano-*trans*-stilbene (35 mg.), 9-cyanophenanthrene (1.04 g.), and *dicyano*-1,2,3,4-*tetraphenylcyclobutane* (70 mg.). Crystallisation of the phenanthrene from ethanol gave needles, m. p. 111—113° (lit.,¹⁸ 109°) (Found: C, 88.9; H, 4.3; N, 7.0%; M, 190. Calc. for C₁₅H₉N: C, 88.6; H, 4.5; N, 6.9%; M, 203), λ_{\max} . 210.5, 229, 258, 267, 272, 298, 310, 339, and 356 m μ (ϵ 32,500, 37,500, 46,500, 15,500, 10,500, 12,500, 13,500, 7600, and 8900) and λ_{\min} . 251 and 288 m μ (ϵ 43,000 and 7600). Crystallisation of the tetraphenylcyclobutane from acetone gave needles, m. p. 247—248° [Found: C, 87.5; H, 5.3; N, 6.8%; M (Rast), 396. C₃₀H₂₂N₂ requires: C, 87.7; H, 5.4; N, 6.8%; M, 410.5], λ_{\max} . 255, 261, 267, and 271 m μ (ϵ 820, 1400, 9100, and 6100) and λ_{\min} . 220 m μ (ϵ 29,000), ν_{\max} . (KBr) *inter alia* 3062 (aromatic CH), 3040 (aromatic CH), 2955 (aliphatic CH), 2238 (C=N) and 2229 cm.⁻¹ (C=N), τ (CDCl₃) 2.70 (singlet, aromatic protons), and 4.68 (singlet, cyclobutane protons). Elution with methanol gave a further crop of the cyclobutadiphenanthrene (1.11 g.).

8b,8c,16b,16c-Tetrahydrocyclobuta[1,2-1:3,4-1']*diphenanthrenedicarboxylic Acid* (X; R = CO₂H).—A solution of the foregoing dicyano-compound (2.0 g.) in glacial acetic acid (275 ml.), concentrated sulphuric acid (90 ml.), and water (90 ml.) was heated under reflux for 12 hr. The solution was allowed to cool, then poured into water (500 ml.), and the product (1.52 g.) collected, washed with water, and dried. Crystallisation from glacial acetic acid gave the *acid* as prisms,

¹³ E. E. Ellingboe and R. C. Fuson, *J. Amer. Chem. Soc.*, 1933, **55**, 2960.

¹⁴ B. M. Mikhailov and N. G. Chernova, *Zhur. obshchei Khim.*, 1951, **21**, 1517.

¹⁵ C. F. Koelsch, *J. Amer. Chem. Soc.*, 1934, **56**, 480.

¹⁶ C. S. Schoepfle and J. D. Ryan, *J. Amer. Chem. Soc.*, 1932, **54**, 3687.

¹⁷ J. F. Coddington and E. Mosettig, *J. Org. Chem.*, 1952, **17**, 1027.

¹⁸ C. W. Shoppee, *J.*, 1933, 37.

m. p. 291—292° [Found: C, 80·9; H, 5·5%; Equiv. (by titration as a dibasic acid), 222. $C_{30}H_{10}O_4$ requires C, 81·1; H, 4·5%; Equiv., 224], λ_{max} 209 and 277 m μ (ϵ 58,000 and 22,500) and λ_{inf} 218, 245, 269, and 300 m μ (ϵ 55,500, 19,500, 21,000, and 6500). Recrystallisation from chloroform gave a *solvate*, m. p. 291—292°, containing chloroform of crystallisation [Found: C, 65·9; H, 4·1; Cl, 18·3%; Equiv. (by titration as a dibasic acid), 264. $C_{30}H_{20}O_4 \cdot CHCl_3$ requires C, 66·0; H, 3·8; Cl, 18·9%; Equiv. 282], τ (acetone) *inter alia* 1·96 (singlet, H-bonded chloroform), 4·81 (broad singlet, CO_2H proton, disappeared on deuteration), and 4·96 (singlet, cyclobutane protons). Treatment of a methanolic solution of the acid with diazomethane gave the *dimethyl ester*, which crystallised from acetone-methanol as needles, m. p. 237—239° (Found: C, 81·0; H, 5·1%; *M*, 458. $C_{32}H_{24}O_4$ requires C, 81·3; H, 5·1%; *M*, 472), λ_{max} 206 and 270 m μ (ϵ 48,000 and 19,500), and λ_{inf} 214, 262, and 289 m μ (ϵ 45,500, 15,500, and 6400), ν_{max} ($CHCl_3$) *inter alia* 1729 cm^{-1} (C=O), τ (CH_2Cl_2) *inter alia* 5·06 (singlet, cyclobutane protons), and 6·38 (singlet, methyl protons).

Ultraviolet Irradiation of the Dicyano-compound (X; R=CN).—The cyclobutane (0·81 g.), in ethanol (220 ml.) and chloroform (100 ml.), was irradiated (Pyrex jacket) for 6·25 hr. The ultraviolet spectrum of the solution showed the appearance of bands characteristic of 9-cyanophenanthrene. Concentration of the solution to 25 ml. gave the starting material (0·45 g.), m. p. and mixed m. p. 214—217°. Complete removal of the solvent and crystallisation of the residue from ethanol gave 9-cyanophenanthrene (0·22 g.), m. p. and mixed m. p. 111—113°.

Ultraviolet Irradiation of 9-Cyanophenanthrene (VI; R=H; R'=CN).—9-Cyanophenanthrene (0·39 g.), in ethanol (300 ml.), was irradiated (Pyrex jacket) for 2·25 hr. The ultraviolet spectrum of the solution showed the gradual diminution in intensity of the phenanthrene bands. The solution was reduced in volume, when needles of the dicyanocyclobutadiphenanthrene (0·11 g.) crystallised from the solution, m. p. and mixed m. p. 214—216°. On complete removal of the solvent and crystallisation of the residue from ethanol starting material (0·15 g.) was obtained.

Pyrolysis of the Dicyanocyclobutadiphenanthrene (X; R=CN).—The nitrile (0·29 g.) was fractionally sublimed at 200°/0·2 mm. for 1 hr. The sublimate (0·26 g.) was recrystallised from ethanol as needles of 9-cyanophenanthrene, m. p. and mixed m. p. 111—113°.

Pyrolysis of the Cyclobutadiphenanthrenedicarboxylic Acid (X; R=CO₂H).—The acid (0·54 g.) was fractionally sublimed at 210°/0·2 mm. for 1 hr. The sublimate (0·26 g.) was recrystallised from methanol-chloroform as needles of phenanthrene-9-carboxylic acid, m. p. 260—260·5° (lit.,¹⁸ 251—252°) [Found: C, 80·6; H, 4·6%; *M* (Rast), 219; Equiv. (by titration as a monobasic acid), 222. $C_{15}H_{10}O_2$ requires: C, 81·0; H, 4·5%; *M*, 222; Equiv. 222], λ_{max} 211, 231, 254, 300, 339, and 356 m μ (ϵ 27,500, 23,000, 42,000, 10,000, 620, and 390) and λ_{inf} 227 m μ (ϵ 21,500).

Attempted Formation of a Cyclic Anhydride from the Diacid (X; R=CO₂H).—The acid (0·39 g.) in acetic anhydride (20 ml.) was heated under reflux for 9 hr. The solution was reduced in volume under reduced pressure and water (20 ml.) was added. The product (0·26 g.) was collected and crystallised from glacial acetic acid. Its infrared spectrum was superposable with that of the starting material.

Pyrolysis of Dicyano-1,2,3,4-tetraphenylcyclobutane.—The cyclobutane (31 mg.) was mixed with copper bronze (100 mg.) and sublimed at 310°/0·2 mm. for 5 min. The sublimate (25 mg.) was recrystallised from ethanol as plates of α -cyano-*trans*-stilbene, m. p. 85—86° (lit.,¹⁷ 85—86°), undepressed on admixture with an authentic sample.

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