Studies in Photochemistry. Part VII.[1] The Photocyclisation of Some Nuclear-substituted Stilbenes to Substituted Phenanthrenes

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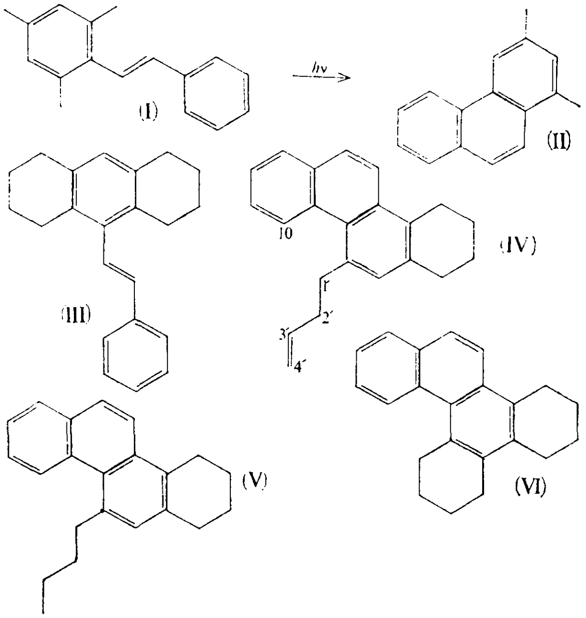
Photocyclodehydrogenation of *trans*-9-styryl-1,2,3,4,5,6,7,8-octahydroanthracene in cyclohexane solution formed a mixture of 11-butyl- and 11-but-3-enyl-1,2,3,4-tetrahydrochrysene in very small yield, identified by their i.r., u.v., ^1H n.m.r., and mass spectra. 2,4,6-Trimethylstilbene photocyclised to 1,3-dimethylphenanthrene with the elimination of a methyl group. 3,3′,5,5′-Tetramethylstilbene formed 2,4,5,7-tetramethylphenanthrene when irradiated in cyclohexane solution. Similarly, 4,4′-dibromo- and 4,4′-dicyano-stilbene formed the corresponding 3,6-disubstituted phenanthrenes.

Badger, Drewer, and Lewis have reported the elimination of several *ortho*-groups in the photocyclisation of azobenzenes to benzo[*c*]cinnolines.[2] They reported the migration of the *ortho*-methyl group in the cyclisation of 2,4,6-trimethylazobenzene to give some 1,2,4-trimethylbenzo[*c*]cinnoline.[2a] Similarly, 3-methyl- and 3,6-dimethyl-2-styrylpyridine underwent photocyclisation, to benzo[*f*]quinoline and 3-methylbenzo[*f*]quinoline respectively, with elimination of a methyl group.[3] There is only one reported case of the elimination of a methyl group in the stilbene series,[4] though Wood and Mallory have reported the elimination of *ortho*-methoxy-groups in the photocyclisation of stilbenes to phenanthrenes.[5]

Further investigations of the photochemistry of stilbenes with only one benzene ring blocked in the *ortho*-positions have been undertaken in this laboratory.



Preliminary investigations showed that 2,4,6-trimethylstilbene (I) photocyclised to give a small yield of 1,3-dimethylphenanthrene (II) with elimination of one methyl group. Methyl migration was not observed.

In the case of irradiation of *trans*-9-styryl-1,2,3,4,5,6,7,8-octahydroanthracene (III) the ejected substituent is held to the ring system by a second bond, and hence its fate can be followed more readily. Irradiation in the absence of iodine gave very little cyclised material; however photocyclisation was detectable when iodine was used. The product was purified by chromatography and regeneration from its picrate to yield a pale yellow oil with a phenanthrene-like u.v. spectrum.

Structures (IV), (V), and (VI) were considered for the photoproduct. The ^1H n.m.r. spectrum (Table 1) of the oil was very complex but appeared to support structure (IV); the resonances in the region τ 4—5 were similar to the ABX system found in the spectrum of eugenol,[6] although the peak areas could not be explained adequately. Tentative assignments of the resonances based on (IV) are shown in Table 1.

Table 1

^1H N.m.r. resonances (carbon tetrachloride solution) of the irradiation product from 9-styryl-1,2,3,4,5,6,7,8-octahydroanthracene (III)

Resonances (τ)	Multiplicity	Number of protons	Assignment (IV)
1·3	Multiplet	2	C(10)-H
2·0—3·4	Multiplets	12	Aromatic protons
4	Broad multiplet	1	C(3′)-H
4·6—5·0	AB Part of ABX spectrum	2	C(4′)-H_2
6—9	Multiplets	32	Aliphatic methylenes

The i.r. spectrum included bands at 1385 cm.$^{-1}$ and 920 cm.$^{-1}$. The former must be due to a methyl group and the band at 920 cm.$^{-1}$ is due to a terminal methylene group. Structure (VI) was eliminated on the basis of these results. However the ^1H n.m.r. and the i.r. spectra can be explained if the product was a mixture of 11-but-3-enyl- (IV) and 11-butyl-1,2,3,4-tetrahydrochrysene (V). The sample with the integrated spectrum given in Table 1 would be a 1 : 1 mixture in this case.

The mass spectra of the hydrocarbon oil and its picrate are recorded in Table 2. In the case of the oil, pumping on the inlet system of the mass spectrometer followed

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[1] Part VI, C. E. Loader and C. J. Timmons, *J. Chem. Soc.* (*C*), 1968, 330.

[2] (*a*) G. M. Badger, R. J. Drewer, and G. E. Lewis, *Austral. J. Chem.*, 1964, **17**, 1036; (*b*) G. M. Badger, R. J. Drewer, and G. E. Lewis, *Austral. J. Chem.*, 1963, **16**, 1042; (*c*) G. M. Badger, R. J. Drewer, and G. E. Lewis, *Austral J. Chem.*, 1966, **19**, 643.

[3] P. Bartolus, G. Cauzzo, and G. Galiazzo, *Tetrahedron Letters*, 1966, 239.

[4] W. Carruthers and H. N. M. Stewart, *J. Chem. Soc.* (*C*), 1967, 556.

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

[6] J. N. Shoolery, 'Varian N.m.r. Spectra Catalog,' Varian Associates, vols. 1 and 2.

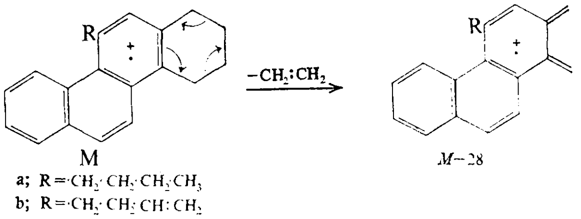
by recharging of the sample into the spectrometer disclosed a continuous increase in the relative intensity of the peak at *m/e* 286. This strongly suggests that this peak was not caused by fragmentation of the compound with M^+ 288. Therefore the spectrum of the oil is that of two different compounds, one with M^+ 288 and the other M^+ 286. The absence in the mass spectrum of the picrate of peaks at *m/e* 515 and *m/e* 517, which would be expected for the picrates of (IV) and (V), indicates the decomposition of the picrate in the mass spectrometer into the hydrocarbon and picric acid (*m/e* 229).

TABLE 2

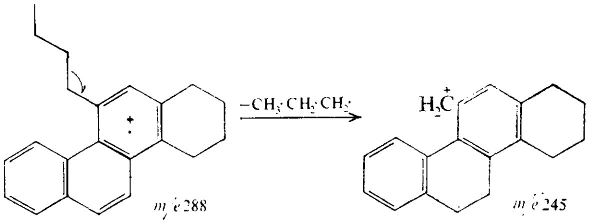
Mass spectra of the irradiation product from 9-styryl-1,2,3,4,5,6,7,8-octahydroanthracene and of the derived picrate

	Relative abundances			Relative abundances	
m/e	Hydrocarbon	Picrate	*m/e*	Hydrocarbon	Picrate
289	25		183	14	
288	100	5	182	14	
287	26	24	181	15	
286	16	100	178	16	
285		6·3	169	27	
274	23		167	24	
273	78		166	12	
261	16		165	24	
260	70		155	18	
259	36	7·1	154	11	
258		27·1	153	17	
257		17·1	152	15	
246	15	6·1	143	12	
245	41	27·2	141	26	
244		13·3	126		5
243		19·8	122		8·3
242		6	120		6·4
241		9·1	119·5		7
240		5·6	115	23	
239		10·9	114		8·6
232	11		113		5·8
231	20	6·3	108	11	9·2
230		12·5	105	15	
229	10	23·2	101		7·6
228		17·4	91	36	
227		11·3	85	17	
226		9·3	83	15	
217	24	7·9	82	11	
216	10	13·4	77	16	
215	17	25	71	27	7·5
210	14		69	14	
209	12		67	14	
203	16	16·8	66	17	
202	17	16	65·5	13	
199	20		64·5	17	
197	14		57	50	9·0
195	18		55	26	7·1
189		6·4	43	39	
184	10				

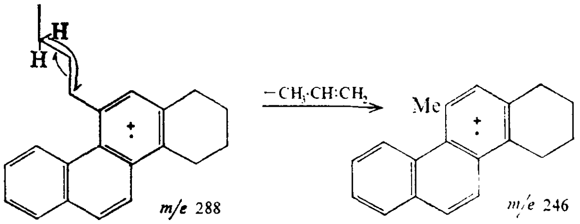
The fact that the mass spectrum of the oil shows the presence of two compounds helps to confirm that both (V) and (IV) are formed in the irradiation. The fragmentation patterns bear this out. The mass spectrum of the picrate has a base and parent peak at *m/e* 286 and no peak at *m/e* 288, which indicates that the picrate is that of (IV) alone. There is no peak at *m/e* 273 in the spectrum of the picrate. The relative abundance of the peak at *m/e* 273 in that of the oil falls when the mass spectrometer is recharged after the oil has been pumped under high vacuum. This indicates that this peak is caused by the fragmentation of (V). The loss of 15 mass units must be due to the loss of a methyl group from the n-butyl side-chain of (V). This indicates the presence of a methyl group in (V); however the relative abundance of *m/e* 273 is surprisingly high, as the corresponding peak is only 0·87% in the mass spectrum of butylbenzene.[7a] The presence of a branched chain could explain this, but branching is unlikely to have occurred during the irradiation. The parent ions of (V) and (IV) both fragment with loss of ethylene. Tetralin fragments in the same way, therefore Scheme 1 is probably the mechanism of this fragmentation.[7b] Scheme 2 accounts for the peak at *m/e* 245 and Scheme 3 for the peak at *m/e* 246 in the mass spectrum of the oil. This follows the fragmentation pattern of butylbenzene.[7b] Metastable peaks in the spectrum confirmed these Schemes. Similarly, the fragmentation of (IV) could lead to the peak *m/e* 245 (Scheme 4).



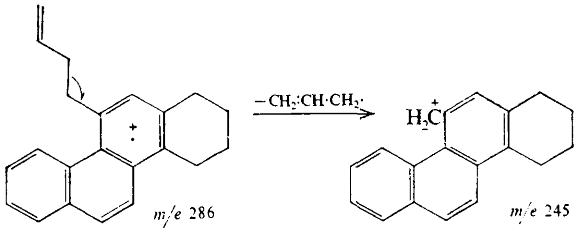
SCHEME 1



SCHEME 2



SCHEME 3



SCHEME 4

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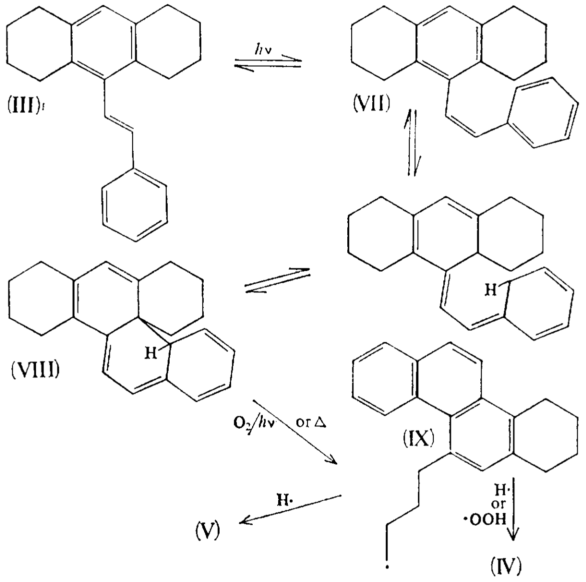
[7] (*a*) 'Catalogue of Mass Spectral Data,' American Petroleum Institute of Research Project 44, Carnegie Institue of Technology, Pittsburg, serial no. 494; (*b*) H. C. Hill, 'Introduction to Mass Spectrometry,' Heyden and Son Ltd., London, 1966.

Attempts to separate and isolate the two compounds failed. The picrate of (IV) was obtained in very small yield.

Scheme 5 is suggested to account for the formation of (IV) and (V). The first step involves the reversible isomerisation of *trans*-9-styryl-1,2,3,4,5,6,7,8-octahydroanthracene (III) to the *cis*-compound (VII), which then cyclises to the dihydro-compound (VIII). This is then oxidised to the phenanthrene (IV). This sequence has been well authenticated for stilbene-like systems.[8]

The intermediate radical (IX) is suggested as being formed during the oxidation of (VIII). It can combine with a hydrogen radical to form (V) or a hydrogen radical may be abstracted from the 3′-position on the butyl side-chain of (IX) by a peroxy-radical or a hydrogen atom to form (IV).

Levi and Orchin have reported the cyclisation of 3,3′,5,5′-tetramethylstilbene (X) to 2,4,5,7-tetramethylphenanthrene (XI) in the presence of selenium radicals.[9] Their yield of the stilbene was very low and they isolated the phenanthrene only as the 1,3,5-trinitrobenzene derivative. We have prepared the stilbene in good yield from a Wittig reaction and have isolated the pure phenanthrene from the photocyclisation of the stilbene by regeneration from its picrate. The ^{1}H n.m.r. spectrum of this compound was very simple. The resonance due to the 2- and 7-methyl groups occurred at τ 7·55 and that due to the 4- and 5-methyl groups at τ 7·50. The latter resonance occurred at lower field because the methyl groups experience the deshielding effects of two benzenoid rings. The aromatic region consisted of two broad singlets. The one at τ 2·92 (2H) is due to the protons in the 3- and 6-positions, which are shielded by the two methyl groups and must differ from those in positions 8 and 1, as the latter are shielded only by the methyl groups in positons 2 and 7. This shielding effect makes the chemical shifts of protons 1, 8, 9, and 10 virtually equivalent; the singlet at τ 2·75 integrates for four protons.



SCHEME 5

TABLE 3

The mass spectrum of 3,6-dicyanophenanthrene

m/e		Relative abundance	Fragmentation scheme *
230	$(M + 2)^+$	1·7	
229	$(M + 1)^+$	19·8	
228	M^+	100	
227	$(M - 1)^+$	8·4	$M \xrightarrow{-H} M - 1$
226	$(M - 2)^+$	7·7	$M - 1 \xrightarrow{-H} M - 2$
202	$(M - 26)^+$	4·9	$M \xrightarrow{-C_2H_2} M - 26$
201	$(M - 27)^+$	11·9	$M \xrightarrow{-HCN} M - 27$
			$M - 1 \xrightarrow{-C_2H_2} M - 27$
			$M - 26 \xrightarrow{-H} M - 27$
200	$(M - 28)^+$	8·6	$M - 1 \xrightarrow{-HCN} M - 28$
			$M - 27 \xrightarrow{-H} M - 28$
199	$(M - 29)^+$	3·7	$M - 2 \xrightarrow{-HCN} M - 29$
			$M - 28 \xrightarrow{-H} M - 29$
177	$(M - 51)^+$	2·6	
176	$(M - 52)^+$	3·0	
175	$(M - 53)^+$	4·5	$M - 27 \xrightarrow{-C_2H_2} M - 53$
			$M - 26 \xrightarrow{-HCN} M - 53$
174	$(M - 54)^+$	3·7	$M - 28 \xrightarrow{-C_2H_2} M - 54$
			$M - 27 \xrightarrow{-HCN} M - 54$
151	$(M - 77)^+$	1·8	
150	$(M - 78)^+$	1·7	
149	$(M - 79)^+$	1·8	$M - 53 \xrightarrow{-C_2H_2} M - 79$
114·5	$(M + 1)^{2+}$	1·7	
114	M^{2+}	10·5	
113·5	$(M - 1)^{2+}$	2·1	
101	$(M - 26)^{2+}$	2·5	
100·5	$(M - 27)^{2+}$	7·5	
100	$(M - 28)^{2+}$	4·1	
99·5	$(M - 29)^{2+}$	1·5	
99	$(M - 129)^+$	2·4	
98	$(M - 130)^+$	1·9	
88		1·8	
87·5	$(M - 53)^{2+}$	2·6	
87		9·2	
86·5		2·3	
85		2·3	
76	M^{3+}	1·7	
75·7	$(M - 1)^{3+}$	<1·5	
75		3·7	
74·5	$(M - 79)^{2+}$	<1·5	
71		3·3	
69		1·7	
63		2·0	
62		1·8	
57		5·1	
56		1·7	
55		2·7	
51		1·5	
50		1·8	

* Metastable ions are present to support this fragmentation pattern.

4,4′-Dibromostilbene (XIIa) was irradiated in cyclohexane with unfiltered light to yield 3,6-dibromo-

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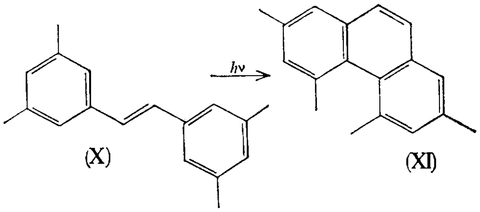
[8] K. A. Muszkat and E. Fischer, *J. Chem. Soc.* (*B*), 1967, 662.

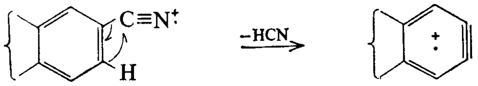
[9] E. J. Levi and M. Orchin, *J. Org. Chem.*, 1966, **31**, 4302.

phenanthrene (XIIIa). The ^{1}H n.m.r. spectrum of the stilbene showed an AB system for the aromatic protons (τ 2·4—2·8, J_{AB} 9 c./sec., appropriate for *ortho*-coupled protons). The olefinic protons gave a singlet at τ 2·98.



(X) (XI)

4,4′-Dicyanostilbene (XIIb) was photocyclised to 3,6-dicyanophenanthrene (XIIIb) when irradiated in benzene. The mass spectrum and proposed fragmentation scheme of the product are given in Table 3. The parent ion is the most abundant. The fragment ions corresponding to the abstraction of hydrogen atoms and the presence of doubly and triply charged ions are general features of the mass spectra of aromatic hydrocarbons.[10] The loss of HCN is accounted for by Scheme 6 and results in the formation of a benzyne-type ion.



Scheme 6

The u.v. spectra of *trans*-9-styryl-1,2,3,4,5,6,7,8-octahydroanthracene (III) and of *trans*-2,4,6-trimethylstilbene (I) suggest a large steric effect due to the *ortho*-substituents. Jaffé and Orchin [11] have attempted to relate observed changes in the u.v. spectra of substituted stilbenes to steric effects. They showed that steric strain was more easily relieved by twisting the benzene rings out of the plane than by twisting the double bond. As the steric effect increased, the low energy band decreased in intensity and showed a hypsochromic shift. Thus the spectra of the *trans*-isomers became similar to those of the *cis*-isomers. The u.v. spectra of *trans*-stilbene and these hindered stilbenes are compared with that of *cis*-stilbene in Table 4.

Table 4

U.v. spectra of some hindered stilbenes (in ethanol) *

trans-Stilbene		*trans*-2,4,6-Trimethylstilbene	
$\nu_{max.}$ (cm.$^{-1}$)	ε	$\nu_{max.}$ (cm.$^{-1}$)	ε
49,490	25,000	*48,300*	*29,500*
44,680	*16,300*	35,860	14,550
43,750	17,400		
42,360	*11,450*		
33,920	30,200		
32,540	29,100		
31,370	*18,300*		

trans-9-Styryl-1,2,3,4,5,6,7,8-octahydroanthracene		*cis*-Stilbene †	
$\nu_{max.}$ (cm.$^{-1}$)	ε	$\nu_{max.}$ (cm.$^{-1}$)	ε
48,400	31,500	49,500	25,100
36,300	17,260	44,720	22,100
		36,140	10,400

* Figures in italics indicate inflections. † Ref. 12.

EXPERIMENTAL

The reaction conditions and the apparatus have been described previously.[13,14] Full curves for the u.v. spectra of some of the compounds have been published.[12]

1,2,3,4,5,6,7,8-*Octahydroanthracene*-9-*carbaldehyde*.[15]—Aluminium chloride (105 g.) was added to a vigorously stirred solution of 1,2,3,4,5,6,7,8-octahydroanthracene (100 g.) dissolved in dichloromethane at 0°, contained in a three-necked flask fitted with stirrer, condenser, dropping funnel, and drying tubes. Butyl dichloromethyl ether (120 g.) was added dropwise, as rapidly as possible, and stirring was continued for a further 2 hr. without cooling. The mixture was then poured on crushed ice and the organic layer was separated, washed successively with water, sodium hydrogen carbonate solution, and water, and dried ($MgSO_4$). The dichloromethane was distilled off and the oily residue fractionally distilled. After removal of a low-boiling fraction containing mostly unchanged hydrocarbon, the aldehyde fraction, b.p. 147—157°/1·5 mm., was collected (37·5 g., 33%). The product was contaminated with a little unchanged hydrocarbon (as shown by spectra) and the purity was not improved by redistillation. The *semicarbazone* crystallised from ethanol as needles, m.p. 185—186° (Found: C, 70·9; H, 7·9; N, 15·5. $C_{16}H_{21}N_3O$ requires C, 70·9; H, 7·8; N, 15·5%). Regeneration from the semicarbazone yielded the pure *aldehyde* (Found: C, 83·9; H, 8·7. $C_{15}H_{18}O$ requires C, 84·1; H, 8·4%), $\nu_{max.}$ (CCl_4) 1032, 1265, 1438, 1451, 1460, 1691, 2838, 2859, and 2934 cm.$^{-1}$ (ε^a 66, 81, 75, 79, 76, 308, 108, 168, and 355), τ (CCl_4) −0·48 (s, CHO), 3·13 (10H), and 6·8—7·6 and 8·0—8·4 (multiplets, aliphatic protons). The 2,4-*dinitrophenylhydrazone* (red needles from benzene) had m.p. 207—208° (Found: C, 64·0; H, 5·6; N, 14·1. $C_{21}H_{22}N_4O_4$ requires C, 64·0; H, 5·6; N, 14·2%).

The aldehyde, as obtained from the distillation of the hydrocarbon–aldehyde mixture, was used in the preparation of *trans*-9-styryl-1,2,3,4,5,6,7,8-octahydroanthracene (see later).

3,5-*Dimethylbenzaldehyde*.— α-Bromo-3,5-dimethyltoluene [16] (25 g.), hexamethylenetetrammine (35 g.), glacial acetic acid (65 ml.), and water (65 ml.) were heated under reflux for 2 hr. Concentrated hydrochloric acid (50 ml.) was added and the mixture was heated under reflux for a further 15 min., cooled and extracted with ether. The extract was washed with water (3 × 100 ml.), 10% sodium carbonate solution (100 ml.), and water (100 ml.) again, and dried (Na_2SO_4). The ether was distilled off and fractional distillation of the residue gave the aldehyde (9·7 g., 62%), b.p. 221—223° (lit.,[17] 220—222°).

trans-9-*Styryl*-1,2,3,4,5,6,7,8-*octahydroanthracene* (III).—Benzyltriphenylphosphonium chloride (38·8 g.) was added

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[10] P. Natalis and J. L. Franklin, *J. Phys. Chem.*, 1965, **69**, 2935.

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

[12] 'D.M.S.—U.v. Atlas of Organic Compounds,' Butterworths and Verlag Chemie, London and Weinheim.

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

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

[15] Cf. A. Rieche, H. Gross, and E. Höft, *Chem. Ber.*, 1960, **93**, 88.

[16] R. G. Kadesch, *J. Amer. Chem. Soc.*, 1944, **66**, 1207.

[17] 'Dictionary of Organic Compounds,' ed. J. R. A. Pollock and R. Stevens, Eyre and Spottiswoode, London, 1965, vol. 2.

to a stirred cooled solution of potassium t-butoxide [from potassium (3·9 g.) in t-butyl alcohol (50 ml.)] and ether (100 ml.) under nitrogen. After 10 min., a solution of 1,2,3,4,5,6,7,8-octahydroanthracene-9-carbaldehyde (10·5 g.) in ether (50 ml.) was added during *ca.* 10 min. The mixture was stirred for a further 8 hr. at room temperature and then water (200 ml.) was added. The organic layer was separated, washed several times with water, and dried ($MgSO_4$). The solution was evaporated and the residue chromatographed on a short silica gel column. Elution with benzene gave the *styryloctahydroanthracene*, which gave needles (8·5 g., 63%), m.p. 127—127·5° (from n-hexane) (Found: C, 91·4; H, 8·5. $C_{22}H_{24}$ requires C, 91·7; H, 8·3%), τ (CCl_4) 3·13 (1H, 10-proton), 7·24 (8H, methylenes), 8·26 (8H, methylenes), 2·3—2·8 (benzenoid resonances), and 3·41 and 2·89 (q, ethylenic AB system, B part at higher field). The coupling constant (J_{AB} 17·5 c./sec.) and broadness of the benzenoid resonances indicated that the material was the *trans*-isomer.

trans-3,3′,5,5′-*Tetramethylstilbene* (X).—This was prepared from a Wittig reaction involving 3,5-dimethylbenzylmethyltriphenylphosphonium bromide (40 g.) (prepared from α-bromo-3,5-dimethyltoluene[16] and triphenylphosphine in benzene as for 2-furylmethyltriphenylphosphonium chloride,[18] and 3,5-dimethylbenzaldehyde (10 g.). The product was chromatographed on a silica gel column with benzene as eluent. The product (10·8 g., 61%) gave needles, m.p. 140° (from petroleum) (lit.,[9] 140—141°), $\nu_{max.}$ (KBr) 970 cm.$^{-1}$ (*trans* ethylenic C–H bending mode), τ (CCl_4) 3·16 (2H, s, olefinic), 3·27br (2H, s, 4- and 4′-protons), 3·03 (4H), and 7·77 (12H). The slightly broadened aromatic resonances indicated coupling with the ring protons and hence a *trans*-configuration.

1,3-*Dimethylphenanthrene* (II).—*trans*-2,4,6-Trimethylstilbene (1 g.) in cyclohexane (1 l.) was irradiated with use of a silica cooling jacket until the reaction appeared to have ceased. The only product isolated was 1,3-dimethylphenanthrene (0·03 g., 3%), m.p. 75·5—77° (lit.,[19] 76—77°) [picrate m.p. 154—156° (lit.,[19] 154—155°)].

11-*But*-3-enyl- (IV) *and* 11-*Butyl*-1,2,3,4-*tetrahydrochrysene* (V).—9-Styryl-1,2,3,4,5,6,7,8-octahydroanthracene (1·5 g.) was dissolved in cyclohexane (2 l.) and iodine (150 mg.) was added. The solution was irradiated for 8 hr. The solvent was then evaporated off and the residue was chromatographed on an alumina column. Elution with ether–petroleum (10%) gave several fluorescent fractions, but only the first contained phenanthrene-like material (blue-white fluorescence). The first fraction was collected and the solvent evaporated off. The oily residue was treated with a solution of picric acid in acetone, and set aside. After several days a red crystalline precipitate had formed which gave needles (12 mg.), m.p. 172—174° (from acetone) (Found: N, 8·0. $C_{28}H_{25}N_3O_7$ and $C_{28}H_{27}N_3O_7$ require N, 8·1%). The picrate was dissolved in acetone and decomposed on an alumina column. Removal of the solvent left a pale yellow oil which was used for spectral analysis.

The picrate used for the mass spectrum was obtained by rapidly cooling the acetone solution of the picrate with ice and recrystallising the precipitated needles from acetone three times.

2,4,5,7-*Tetramethylphenanthrene* (XI).—*trans*-3,3′,5,5′-Tetramethylstilbene (0·65 g.) was irradiated in cyclohexane (2 l.) in the presence of iodine (140 mg.) for 2·5 hr. The product was chromatographed on an alumina column with ether–petroleum (10%) as eluent. The oil obtained was added to a hot saturated solution of picric acid in ethanol and the picrate formed gave blood-red needles, m.p. 130—131° (from ethanol) (Found: N, 9·15. $C_{24}H_{21}N_3O_7$ requires N, 9·07%). The picrate was dissolved in acetone and decomposed on an alumina column. The phenanthrene formed (0·4 g., 60%) had m.p. 112—114° (from n-hexane) (lit.,[20] 111—113°) [1,3,5-trinitrobenzene derivative m.p. 146—147° (lit.,[20] 146·5—148°)]. The rate of photocyclisation was double in the presence of iodine.

3,6-*Dibromophenanthrene* (XIIIa).—4,4′-Dibromostilbene[21] (0·6 g.) in cyclohexane (2 l.) was irradiated for 6 hr. with use of a silica filter. The solvent was removed and the phenanthrene (0·24 g.; 40%) had m.p. 194° (from chloroform) (lit.,[22] 188–191°), $\nu_{max.}$ (ethanol) 45,300, 43,260, 39,130, 36,290, 35,510, 34,450, 33,060, 30,950, 30,200, 29,470, 28,780, and 28,080 cm.$^{-1}$ (ε 25,800, 31,600, 56,100, 18,100, 17,200, 12,900, 19,000, 407, 328, 581, 314, and 638), $\nu_{infl.}$ 46,710, 44,490, 41,470, 40,130, 36,600, and 33,400 cm.$^{-1}$ (ε 20,300, 26,100, 32,000, 48,600, 16,700, and 11,600), τ ($CDCl_3$) 1·25 (s; 4- and 5-protons), 2·29 (s, 9- and 10-protons), and 2·24 and 2·26 (1-, 2-, 7-, and 8-protons).

3,6-*Dicyanophenanthrene* (XIIIb).—4,4′-Dicyanostilbene[21] (0·15 g.) in benzene (2 l.) was irradiated for 9 hr. with use of a Pyrex filter. The product was chromatographed on an alumina column which was eluted with benzene. The pale yellow solid obtained was sublimed (230—240°/5 mm.) and recrystallised from glacial acetic acid to yield the phenanthrene (0·06 g., 40%), m.p. 260—261° (lit.,[22] 257—259°), $\nu_{max.}$ (ethanol) 45,810, 42,000, 38,940, 37,450, 35,580, 34,410, 33,040, 31,570, 29,360, 28,410, and 27,960 cm.$^{-1}$ (ε 23,800, 52,500, 60,200, 20,600, 11,730, 10,610, 21,200, 23,200, 1053, 236, and 377), $\nu_{infl.}$ 46,590, 43,120, 39,860, 30,190, and 29,810 cm.$^{-1}$ (ε 21,600, 33,200, 52,200, 823, and 560), τ ($CDCl_3$) 0·98 (s, 4- and 5-protons), 1·8—2·2 (6H, multiplets), $\nu_{max.}$ (KBr) 2233 cm.$^{-1}$ ($C\vdots N$ stretching mode).

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