

Cyclisation with Hydrazine and its Derivatives. Part V.¹ Condensation Products of Arylhydrazines with Biphenyl-2,2'-dicarbaldehyde and Related Carbonyl Compounds

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Biphenyl-2,2'-dicarbaldehyde and phenylhydrazine (2 mol. equiv.) give the bisphenylhydrazone, but equimolar proportions give *trans*-9,10-dihydro-10-phenylazophenanthren-9-ol (Va), resulting from cyclisation of the monophenylhydrazone. Similar cyclic products are obtained from the dialdehyde with tolyl-, halogenophenyl-, and methyl-hydrazines, but *o*- or *p*-nitrophenylhydrazine gives the monoarylhydrazone (III). 2,2'-Diacetyl-biphenyl gives mono- and bis-phenylhydrazones. The arylazo-compounds (V) are readily dehydrated to the corresponding 9-arylazophenanthrenes (VI) and they are oxidised by manganese dioxide to the corresponding 10-arylazophenanthren-9-ols (VII), which are also obtained by reaction of the arylhydrazines with 9,10-phenanthraquinone or by acidic treatment of arylhydrazones of 2'-formylbiphenyl-2-carboxylic acid. The mononitrophenylhydrazones (III) gave phenanthrene derivatives of type (VI) with acid but readily gave those of type (VII) with alkali.

IN extension of earlier work¹ this paper describes investigations of the intermediate condensation products (III)—(V), in reaction sequences leading from biphenyl-2,2'-dicarbaldehyde (I) and phenylhydrazine or its *C*-substitution products (II) to 9-arylazophenanthrenes (VI) (Scheme 1). We also report reactions with methylhydrazine (IIh) in place of the arylhydrazines, and the dicarbonyl compounds (VIII), (IX), and (XI) in place of the dialdehyde (I).

Mono- and Bis-arylhydrazones.—Reaction between equimolar quantities of phenylhydrazine and biphenyl-2,2'-dicarbaldehyde occurred rapidly in solution at ambient temperature, but, in accord with the tendency of arylhydrazones to undergo secondary reactions,² it led to a cyclised product (see below). However, reaction with 2 mol. equiv. of phenylhydrazine gave a high yield of the yellow bisphenylhydrazone (IVa), previously reported with ethanol of solvation.³ Reactions of the dialdehyde with equimolar proportions of the tolyl- and halogenophenyl-hydrazines (IIb—d) were similar to that with phenylhydrazine, but use of *o*- or *p*-nitrophenyl-

hydrazine gave the respective monoarylhydrazones (IIIe and g) almost quantitatively.

2'-Formylbiphenyl-2-carboxylic acid (IX) reacted normally either with phenylhydrazine or with *o*-nitrophenylhydrazine, giving high yields of the monoarylhydrazones (Xa and e), respectively. 2,2'-Diacetyl-biphenyl (XI) was considerably slower in reaction than the dialdehyde, but gave successively the mono- and bis-phenylhydrazones (XII) and (XIII).

10-Arylazo-(or alkylazo)-9,10-dihydrophenanthren-9-ols.—The reaction between equimolar quantities of biphenyl-2,2'-dicarbaldehyde and phenylhydrazine (*e.g.* in benzene-light petroleum or aqueous ethanol) yielded a cyclised isomer of the monophenylhydrazone as a yellow crystalline precipitate. On the basis of n.m.r. and i.r. spectral evidence (see Experimental section), this product is formulated as *trans*-9,10-dihydro-10-phenylazophenanthren-9-ol, with the conformation (Va). The cyclisation may be represented (Scheme 2) as an intramolecular nucleophilic addition, catalysed by base (*e.g.*, the reagent arylhydrazine) or by acid (as when

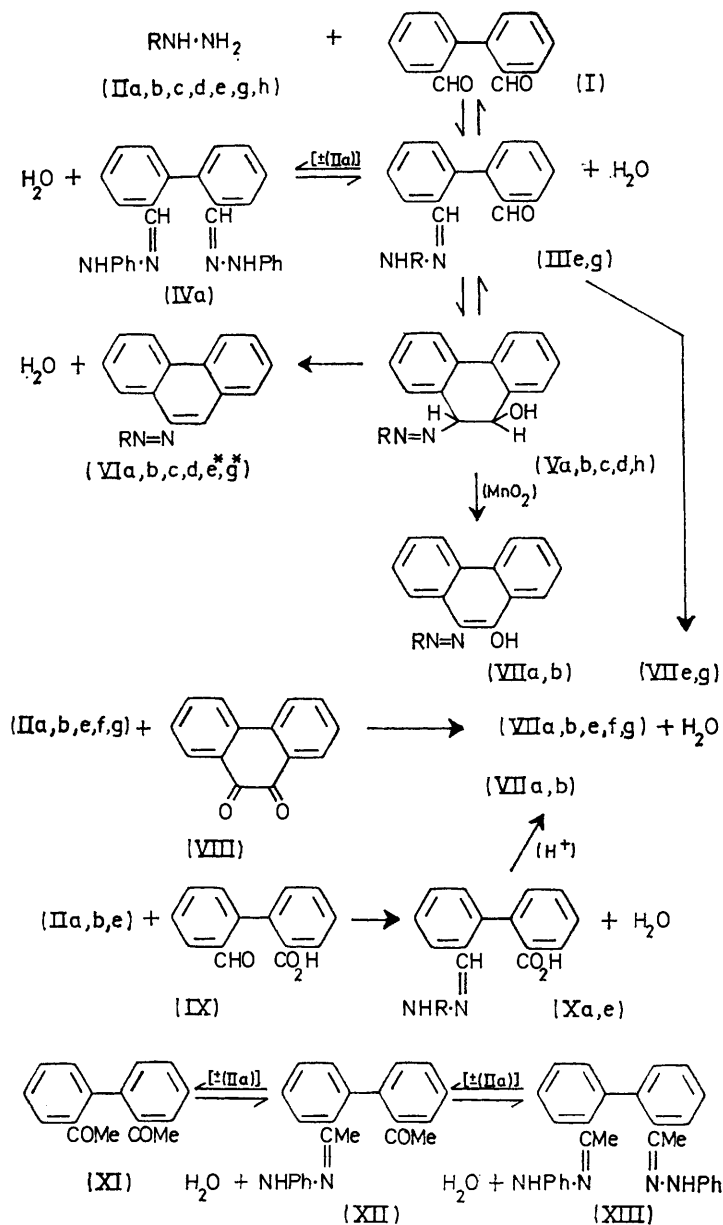
¹ Part IV, B. J. Auret, R. G. R. Bacon, R. Bankhead, D. C. H. Bigg, and J. S. Ramsey, preceding paper.

² J. Buckingham, *Quart. Rev.*, 1969, **23**, 37.

³ J. Kenner and E. G. Turner, *J. Chem. Soc.*, 1911, **99**, 2101.

acetic acid is used as solvent, or an arylhydrazine hydrochloride is employed¹). Under acidic conditions a dihydrophenanthrenol derivative (V) was not isolated owing to its ready dehydration (see below).

substituent in reducing the nucleophilicity of the ArNH·N=CH- group. Under the acidic conditions needed to promote cyclisation of these nitrophenylhydrazones (see below) dehydration followed.



R = a, Ph; b, *p*-C₆H₄Me; c, *p*-C₆H₄Cl; d, *p*-C₆H₄Br; e, *o*-C₆H₄NO₂; f, *m*-C₆H₄NO₂; g, *p*-C₆H₄NO₂; h, Me

* Formed directly from (IIIe, g).

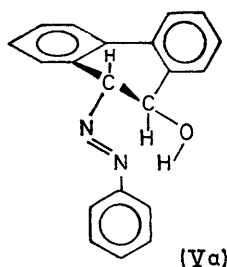
The products analogously obtained with tolyl- or halogenophenyl-hydrazines were also identified as *trans*-10-aryazo-9,10-dihydrophenanthren-9-ols (Vb—d). Likewise, methylhydrazine gave *trans*-9,10-dihydro-10-methylazophenanthren-9-ol (Vh). The reaction of nitrophenylhydrazines under similar conditions, giving the arylhydrazones (IIIe and g) and not their cyclised isomers, is attributed to the effect of the *o*- or *p*-nitro-

Transformations (III) → (V) exemplify the ease of cyclisation common to *oo'*-disubstituted biaryls.⁴ Reactions between biphenyl-2,2'-dicarbonyl compounds and hydrazine, giving phenanthrene or its derivatives,⁵ could be interpreted as in

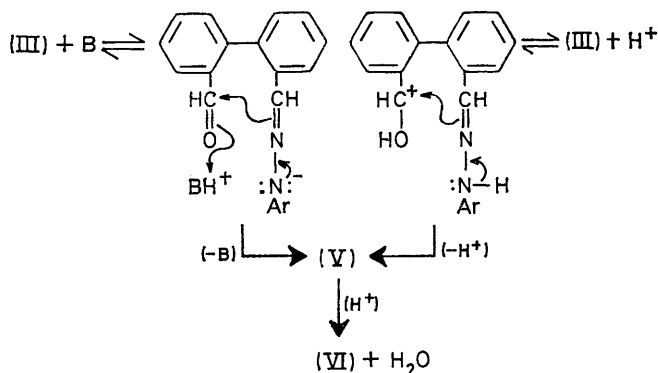
⁴ R. E. Buntrock and E. C. Taylor, *Chem. Rev.*, 1968, **68**, 209.

⁵ (a) R. G. R. Bacon and W. S. Lindsay, *J. Chem. Soc.*, 1958, 1375, 1382; (b) R. G. R. Bacon and R. Bankhead, *ibid.*, 1963, 839.

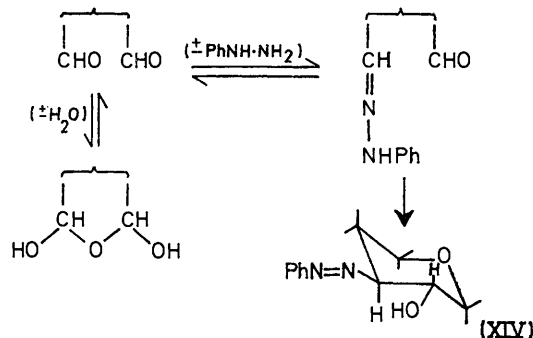
Scheme 2, but the resulting di-imides, $\text{ArN}:\text{NH}$, would decompose with loss of nitrogen.⁶



Also, analogous cyclisations may occur when nucleophiles react with dialdehydes obtained by oxidation of monosaccharides; hydration gives hemialdals,⁷ and reactions with phenylhydrazine give phenylazodeoxy-sugars (XIV)⁸ (Scheme 3), analogous to the products



(V). Our findings concerning spectral and conformational features of compounds of type (V), and also our observations on effects of varying the substituent R (in the reagent $\text{NH}_2\cdot\text{NHR}$) are in agreement with those of Guthrie and his co-workers on compounds of type (XIV).⁸



9-Arylazophenanthrenes.—As would be expected from the presence of a secondary benzylic alcohol function in a dihydrophenanthrene system, the compounds (V) underwent ready dehydration, giving 9-arylazophenanthrenes (VI)¹ when R was aryl (but tarry products when R was methyl):

⁶ E. M. Kosower, *Accounts Chem. Res.*, 1971, **4**, 193.

⁷ R. D. Guthrie and J. Honeyman, *J. Chem. Soc.*, 1959, 2441; R. D. Guthrie, J. Honeyman, and M. A. Parsons, *ibid.*, p. 2449.

(i) Depending upon the time and temperature employed, partial or complete dehydration could ensue during preparations of compounds (V) in ethanol or benzene (see Table).

(ii) The products (V) could be chromatographically purified on silica gel columns, but dehydration readily occurred on alumina (see Table).

(iii) Acid-catalysed dehydration was observed when the reaction between the dialdehyde and an arylhydrazine was carried out in acetic acid, or when the products (V) were warmed with ethanolic hydrochloric acid, and it was the terminal stage in the reaction of dialdehyde nitrophenylhydrazones (IIIe and g) with acid.

(iv) Base-catalysed dehydration was observed when compound (Va) was treated with sodium in benzene.

Reaction of biphenyl-2,2'-dicarbaldehyde (I) (2.5 mmol) with phenylhydrazine (IIa) (2.5 mmol), giving 9,10-dihydro-10-phenylazophenanthren-9-ol (Va) and 9-phenylazophenanthrene (VIa).

Solvent *	Time (h)	Temp. (°C)	Isol. method †	(Va) (%)	(VIa) (%)
(i) EtOH-H ₂ O (2 : 3) (50 ml)	16	20	A	35	0
(ii) LP-C ₆ H ₆ (4 : 1) (50 ml)	48	20	A	52	0
(iii) C ₆ H ₆ (20 ml)	3	20	B	70	0
(iv) C ₆ H ₆ (20 ml)	16	20	C	75	9
(v) C ₆ H ₆ (20 ml)	3	80	C	51	42
(vi) C ₆ H ₆ (20 ml)	3	80	D	0	90
(vii) AcOH (20 ml)	6	118	D	0	54

* LP = light petroleum. † A, precipitation; B, evaporation (20°); C, chromatography (SiO₂); D, chromatography (Al₂O₃).

10-Arylazophenanthren-9-ols.—Further evidence for the structure of the compounds (V) was provided by their oxidation with manganese dioxide to the corresponding 10-arylazophenanthren-9-ols (VII). These products are tautomers of the monoarylhya zones of 9,10-phenanthraquinone (VIII),⁹ and samples thus obtained proved to be identical with those resulting from oxidation.

The dialdehyde nitrophenylhydrazones (IIIe and g) showed some peculiarities. In warm ethanolic solution containing a little hydrochloric acid they were dehydrated, as expected, to the phenanthrene derivatives (VIe and g), but in alkaline ethanol they readily gave the corresponding oxidation products, the phenanthrenols (VIIe and g). A possible explanation is that part of the nitrophenylhydrazine is acting oxidatively; there are examples of such oxidations, *e.g.* in reactions with deoxybenzoin or with 9-phenanthrol.¹⁰

A third route to the 10-arylazophenanthren-9-ols (VI) was from 2'-formylbiphenyl-2-carboxylic acid (IX) via the arylhydrazones (X). Cyclisation of the $\text{ArNH}\cdot\text{N}:\text{CH}$ -group on to the $-\text{CO}_2\text{H}$ group in (X) occurred less readily than on to the $-\text{CHO}$ group in (III); refluxing acetic acid was the reaction medium. The mechanism

⁸ R. D. Guthrie and L. F. Johnson, *J. Chem. Soc.*, 1961, 4166; G. J. F. Chittenden and R. D. Guthrie, *ibid.*, 1963, 3658; G. J. F. Chittenden, R. D. Guthrie, and J. F. McCarthy, *Carbohydrate Res.*, 1965, **1**, 196.

⁹ (a) T. Zincke, *Ber.*, 1883, **16**, 1563; (b) A. Werner, *Annalen*, 1902, **321**, 248; (c) K. Auwers, *ibid.*, 1911, **378**, 210.

¹⁰ D. A. Kinsley and S. G. P. Plant, *J. Chem. Soc.*, 1956, 4814.

may be analogous to that suggested for the acid-catalysed cyclisation in Scheme 2. A reaction of related type occurs (possibly *via* an unstable di-imide) between 4-formylphenanthrene-5-carboxylic acid and hydrazine in acetic acid, giving pyren-5-ol.¹¹

EXPERIMENTAL

Sources of reagents were as previously described.¹ The C-substituted phenylhydrazines were freshly generated from their hydrochlorides by treatment with aqueous sodium carbonate and were recrystallised. Chromatographic alumina was Spence type E, silica gel was Sorbsil type M60. M.p.s were determined on a Kofler hot-stage apparatus. Electronic absorption spectra were obtained (solvent ethanol unless otherwise stated) with a Unicam SP 700C instrument, n.m.r. spectra (solvent deuteriochloroform unless otherwise stated) with a Varian HR-100 instrument (tetramethylsilane as internal standard), and mass spectra with an A.E.I. MS 902 instrument.

Arylhydrazones.—(a) *From biphenyl-2,2'-dicarbaldehyde* (I). A mixture of the dialdehyde (1.25 mmol) and phenylhydrazine (2.5 mmol) in light petroleum–benzene (7 : 3) (25 ml) at ambient temperature (1 h) gave the yellow *bisphenylhydrazone* (IVa) (86%), m.p. 150–151° (Found: C, 80.1; H, 6.0; N, 14.5. $C_{26}H_{22}N_4$ requires C, 80.0; H, 5.7; N, 14.4%), λ_{max} (benzene) 357 nm (log ϵ 4.68), τ 0.5 (s, 2 NH) and 1.7–3.2 (m, aromatic H and –CH=).

A similar reaction (48 h) between the dialdehyde (2.5 mmol) and *o*-nitrophenylhydrazine (2.5 mmol) in light petroleum–benzene (4 : 1) (50 ml) furnished the orange *mono-o-nitrophenylhydrazone* (IIIe) (94%), m.p. 184–185° (decomp.) (Found: C, 69.3; H, 4.7; N, 11.9. $C_{20}H_{15}N_3O_3$ requires C, 69.6; H, 4.4; N, 12.2%), λ_{max} (CHCl₃) 250 (log ϵ 4.59), 285 (4.11), 336 (4.23), and 475 nm (4.04), ν_{max} (KBr) 1680 and 3220 cm⁻¹ (3300 cm⁻¹ in CHCl₃), τ –0.8 (NH, eliminated by D₂O), 0.2 (CHO), and 1.8–3.3 (m). *p*-Nitrophenylhydrazine likewise furnished the *mono-p-nitrophenylhydrazone* (IIIg) (100%), m.p. 142–143° (decomp.) (Found: C, 69.2; H, 4.2; N, 12.4%), λ_{max} (CHCl₃) 250 (log ϵ 4.46), 297 (3.95), 400 (4.60), and 408 nm (4.60), ν_{max} (KBr) 1680 and 3220 cm⁻¹ (3340 cm⁻¹ in CHCl₃), τ –0.3 (NH), 0.2 (CHO), and 1.7–2.9 (m).

(b) *From 2,2'-diacetyl biphenyl* (XI). A solution of equimolar quantities of the diketone^{5a} and phenylhydrazine in ethanol was refluxed (6 h) and cooled; the *monophenylhydrazone* (XII) separated (40%). Recrystallisation from light petroleum gave rods, m.p. 140–141°, which became discoloured in air (Found: M^+ , 328.1574. $C_{22}H_{20}N_2O$ requires M , 328.1575), λ_{max} (benzene) 298 (log ϵ 4.15) and 324 nm (4.18), ν_{max} 3300 cm⁻¹, τ 2.1–3.3 (m, aromatic H + NH), 7.9 (s, MeCO), and 8.2 (s, MeC=N). Preparations carried out for short periods gave products contaminated with unchanged diketone. Prolonged heating resulted in diminished yield and oily decomposition products. Only slight improvement resulted from reaction under nitrogen.

Reaction (4 h) between the diketone (or its monophenylhydrazone) and an excess (3–10 mol) of phenylhydrazine in refluxing ethanol, or in acetic acid at ambient temperature, gave a precipitate of the bisphenylhydrazone (XIII) (50–75%), which formed colourless rods, m.p. 172–173° (from ethanol) (lit.,¹² yellow crystals, m.p. 178°)

¹¹ H. Vollmann, H. Becker, M. Corell, and H. Streeck, *Annalen*, 1937, **531**, 1.

(Found: C, 80.5; H, 6.6; N, 13.4. Calc. for $C_{28}H_{26}N_4$: C, 80.4; H, 6.3; N, 13.4%), λ_{max} 304 (log ϵ 4.54) and 320 nm (4.57), ν_{max} 3300 cm⁻¹, τ 2.4–3.3 (m, aromatic H + NH) and 8.4 (s, MeC=N).

(c) *From 2'-formylbiphenyl-2-carboxylic acid* (IX). The acid (IX) was prepared from phenanthrene.¹³ A mixture with an equimolar quantity of phenylhydrazine in ethanol was refluxed (3 h), then evaporated, and the residue was triturated with light petroleum, furnishing the *phenylhydrazone* (Xa) (75–80%), m.p. 182–183° (from ethanol or ether–light petroleum) (Found: N, 8.8%; M^+ , 316.1209. $C_{20}H_{16}N_2O_2$ requires N, 8.9%; M , 316.1212), λ_{max} 300 (log ϵ 4.26) and 356 nm (4.62), τ 0.7 (s, NH) and 1.8–3.4 (m). It was also obtained as a precipitate (85–90%) from reaction (0.5–3 h) in benzene–light petroleum (1 : 1).

A solution of 2'-formylbiphenyl-2-carboxylic acid (1 mmol) and *o*-nitrophenylhydrazine hydrochloride (1 mmol) in acetic acid (10 ml) was refluxed (3 h), then concentrated and cooled. This gave the *o-nitrophenylhydrazone* (Xe) (80%), m.p. 226–230° (raised to 231.5–232.5° by repeated recrystallisation from nitromethane) (Found: C, 66.6; H, 4.3; N, 11.5. $C_{20}H_{15}N_3O_4$ requires C, 66.5; H, 4.2; N, 11.6%), λ_{max} 212 (log ϵ 4.64), 228 (4.63), 330 (4.38), and 455 nm (4.00), τ –1.0 (s, NH) and 1.8–3.2 (13H, m).

10-Arylazo-9,10-dihydrophenanthren-9-ols.—Reactions were carried out between biphenyl-2,2'-dicarbaldehyde and phenylhydrazine under the various conditions summarised in the Table. The products from experiments (i)–(iii), purified by chromatography on silica, furnished yellow crystals of *trans-9,10-dihydro-10-phenylazophenanthren-9-ol* (Va), m.p. 124–125° (Found: C, 80.0; H, 5.5; N, 9.5. $C_{20}H_{16}N_2O$ requires C, 80.0; H, 5.4; N, 9.3%), λ_{max} 213 (log ϵ 4.65), 270 (4.44), and 398 nm (2.38), ν_{max} 3500 cm⁻¹, τ 1.9–2.8 (m, aromatic H), 4.5 (q, 9-H), 5.0 (d, 10-H), and 7.7 (d, OH) ($J_{9,10}$ 8.5, $J_{9,OH}$ 5.5 Hz; on shaking with D₂O the signal at τ 7.7 disappeared and the quartet at τ 4.5 became a doublet, J 8.5 Hz). Chromatography of the mixed products from experiments (iv) and (v) gave the red compound (VIa), eluted by benzene, followed by the yellow compound (Va), eluted by benzene–chloroform; the latter was further purified by precipitation with petroleum from benzene solution.

The following procedure gave C-substituted analogues of (Va), likewise as yellow crystals. A mixture of *p*-tolylhydrazine, m.p. 64–65° (2.5 mmol) and biphenyl-2,2'-dicarbaldehyde (2.5 mmol) in light petroleum–benzene (4 : 1) (50 ml) was stirred for 48 h at ambient temperature. More light petroleum was added and *trans-9,10-dihydro-10-p-tolylazophenanthrene* (Vb) (38%), m.p. 113–115° (decomp.), was filtered off; dissolution in benzene and reprecipitation with pentane raised the m.p. to 115–116° (decomp.) (Found: M^+ , 314.1418. $C_{21}H_{18}N_2O$ requires M , 314.1419), λ_{max} 212 (log ϵ 4.67), 274 (4.46), and 398 nm (2.49), τ 2.1–2.9 (m), 4.6 (d, 9-H), 5.1 (d, 10-H) ($J_{9,10}$ 9 Hz; the OH signal overlapped with that of CH₃ at τ 7.6). *p*-Chlorophenylhydrazine, m.p. 89–90°, gave *trans-10-p-chlorophenylazo-9,10-dihydrophenanthren-9-ol* (Vc) (67%), m.p. 113–114° after reprecipitation (Found: M^+ , 334.0869. $C_{20}H_{15}ClN_2O$ requires M , 334.0873), λ_{max} 211 (log ϵ 4.58), 268 (4.48), and 363 (2.76), τ 2.1–3.2 (m), 4.6 (d, 9-H), 5.0 (d, 10-H), 7.7br (OH) ($J_{9,10}$ 8 Hz). *p*-Bromophenylhydrazine, m.p. 105–106°, gave *trans-10-p-bromophenylazo-9,10-dihydrophenanthren-9-ol* (Vd) (77%), m.p. 124–125°,

¹² T. Zincke and W. Tropp, *Annalen*, 1908, **363**, 302.

¹³ P. S. Bailey, *J. Amer. Chem. Soc.*, 1956, **78**, 3811.

after reprecipitation [mass spectrum showed dehydration product (VId)], λ_{\max} 212 (log ϵ 4.68), 274 (4.48), and 398 nm (2.60), τ 2.1—3.0 (m), 4.6 (d, 9-H), 5.0 (d, 10-H), and 7.7 (OH) ($J_{9,10}$ 9 Hz).

9,10-Dihydro-10-methylazophenanthren-9-ol (Vh).—A solution of biphenyl-2,2'-dicarbaldehyde (5 mmol) and methylhydrazine (5 mmol) in light petroleum-benzene (5 : 1) (100 ml), stirred at ambient temperature, gave a precipitate (60% after 2 h; only slightly augmented after 60 h); the yield was similar from reaction in ethanol. The product formed needles, m.p. 137—138° (from benzene-light petroleum) (Found: C, 75.8; H, 6.0; N, 11.6. $C_{15}H_{14}N_2O$ requires C, 75.6; H, 5.9; N, 11.8%), λ_{\max} 272 (log ϵ 4.26) and 360 nm (1.43), τ 2.1—2.9 (m, aromatic H), 4.8 (q, 9-H), 5.3 (d, 10-H), 6.1 (s, Me), 7.7 (d, OH) ($J_{9,10}$ 8, $J_{9,OH}$ 6 Hz; on shaking with D_2O the signal at τ 7.7 disappeared and the quartet at τ 4.8 became a doublet).

9-Phenylazophenanthrene (VIa).—The red azo-compound, m.p. 156—157°, λ_{\max} 246 (log ϵ 4.76), 271sh, 296 (4.23), 308 (4.18), 380 (4.00), and 470sh nm, identical with samples previously described,¹ was obtained: (i) directly from biphenyl-2,2'-dicarbaldehyde and phenylhydrazine, as summarised in the Table; (ii) by dissolving 9,10-dihydro-10-phenylazophenanthren-9-ol (Va) in the minimum quantity of benzene and adding the solution to an alumina column; the colour changed from yellow to red and compound (VIa) was eluted (91%) by benzene; (iii) by refluxing a solution of compound (Va) in benzene for 12 h, concentrating, and isolating the product (VIa) (92%) by chromatography on silica; (iv) by maintaining a solution of compound (Va) at ca. 60° in aqueous ethanolic 0.4N-hydrochloric acid and filtering off the precipitated product (VIa) (85%) after 40 min; in the absence of acid the compound was stable in ethanol over the same period at 60°; (v) by attempting alkoxide formation; addition of sodium to a solution of compound (Va) in benzene resulted in a red colour and the product (VIa) (85%) was isolated.

9-(Substituted phenyl)azophenanthrenes.—Samples prepared, as follows, from hydroxy-compounds (V) or mono-arylhydrazones (III) were identical with corresponding products previously obtained¹ directly from the dialdehyde (I) and arylhydrazines (II).

9,10-Dihydro-10-p-tolylazophenanthren-9-ol (Vb) was dissolved in a few ml of ethanol containing a drop of 4N-hydrochloric acid and refluxed; the mixture became orange-red. Concentration, cooling, and filtration gave 9-p-tolylazophenanthrene (VIb) (90%), m.p. 138—139° (from ethanol), λ_{\max} 248 (log ϵ 4.68), 255sh, 272sh, 296 (4.22), 308 (4.20), 380 (4.08), and 470sh nm. Likewise, the *p*-chloro-compound (Vc) gave the *p*-chloro-compound (VIc) (74%), m.p. 157—158°, λ_{\max} 248 (log ϵ 4.71), 254 (4.67), 272 (4.53), 288 (4.36), 298 (4.40), 310 (4.36), 383 (4.27), 390 (4.28), and 407sh nm, and the *p*-bromo-compound (Vd) gave the *p*-bromo-compound (VId) (86%), m.p. 168—169°, λ_{\max} 247 (log ϵ 4.67), 253sh, 272 (4.47), 288 (4.36), 298 (4.40), 310 (4.36), 383 (4.30), 3.92 (4.30), and 407 nm (4.25). Similar acidic treatment of the mono-*o*-nitrophenylhydrazones (IIIe) yielded the *o*-nitro-compound (VIe), m.p. (after repeated recrystallisation from ethanol-benzene) 163—165° (not depressed by admixture with an authentic sample,¹ m.p. 164—166°) (Found: M^+ , 327.1009. Calc.

for $C_{20}H_{13}N_3O_2$: M , 327.1008), λ_{\max} 246 (log ϵ 4.66), 252sh, 272, 286, 299, 310, and 405 nm (4.08). Similar treatment of the *p*-nitrophenylhydrazones (IIIg) gave 9-*p*-nitrophenylazophenanthrene (63%), m.p. 211—212° (from ethanol-benzene) (Found: C, 73.1; H, 4.3; N, 13.0. $C_{20}H_{13}N_3O_2$ requires C, 73.4; H, 4.0; N, 12.8%), λ_{\max} 245 (log ϵ 4.66), 290, 296 (4.32), 315, and 410 nm (4.20).

10-Phenylazophenanthren-9-ol (VIIa).—The following methods gave identical products, m.p. 164—165° (lit.,^{9c} 165°) (Found: C, 80.5; H, 5.0; N, 9.5. Calc. for $C_{20}H_{14}N_2O$: C, 80.5; H, 4.7; N, 9.4%), λ_{\max} (CHCl₃) 248 (log ϵ 4.34), 254 (4.43), 260 (4.48), 268 (4.60), 296 (4.28), 415sh, and 487 nm (4.48):

(i) A solution of 9,10-dihydro-10-phenylazophenanthren-9-ol (Va) (0.5 mmol) in ether was stirred for 25 h at ambient temperature with activated manganese dioxide (5 mmol).¹⁴ Filtration, evaporation, and recrystallisation from benzene-methanol gave the product (VIIa) (63%).

(ii) A solution of 2'-formylbiphenyl-2-carboxylic acid (IX) (1 mmol) and phenylhydrazine (1 mmol) in acetic acid (20 ml) was refluxed (6 h). The solvent was removed and the crude product chromatographed with benzene on silica or alumina, giving compound (VIIa) (26%). The yield was not improved by using an excess of phenylhydrazine. Similar reaction in refluxing propionic or butyric acid gave yields of 35—40%.

(iii) A solution of the phenylhydrazones (Xa) of 2'-formylbiphenyl-2-carboxylic acid in acetic acid was refluxed (3 h). The solvent was removed and the product chromatographed, yielding compound (VIIa) (36%). The yield was little changed when a few drops of hydrochloric acid were included in the solution.

(iv) A solution of 9,10-phenanthraquinone (IX) (10 mmol) and phenylhydrazine hydrochloride (10 mmol) in acetic acid (40 ml) was refluxed for 1 h, concentrated, and filtered; the crude product (88%), recrystallised from ethanol, gave pure (VIIa).

10-p-Tolylazophenanthren-9-ol (VIIb).—(i) Oxidation of the dihydro-compound (Vb), as described in the case of (Va), gave compound (VIIb) (60%) as red needles, m.p. 171—172° (lit.,¹⁵ 169°) (Found: C, 80.8; H, 5.4; N, 9.0. Calc. for $C_{21}H_{16}N_2O$: C, 80.8; H, 5.2; N, 9.0%); the u.v. spectrum was almost identical with that of (VIIa).

(ii) Compound (VIIb) was prepared (48%) as described for (VIIa) from 2'-formylbiphenyl-2-carboxylic acid and *p*-tolylhydrazine hydrochloride in acetic acid.

(iii) Compound (VIIb) was prepared (51%) as described for (VIIa) from phenanthraquinone and *p*-tolylhydrazine hydrochloride.

10-o-Nitrophenylazophenanthren-9-ol (VIIe).—(i) Biphenyl-2,2'-dicarbaldehyde mono-*o*-nitrophenylhydrazones (IIIe) was dissolved in ethanol, a drop of 4N-sodium hydroxide was added, and the solution was refluxed for 10 min and cooled, giving a precipitate of compound (VIIe) (66%), as red needles, m.p. 255—256° (from ethanol-benzene) (lit.,¹⁰ 246—249°) (Found: C, 70.0; H, 3.9; N, 12.0%; M^+ , 343.0954. Calc. for $C_{20}H_{13}N_3O_3$: C, 70.0; H, 3.8; N, 12.2%; M , 343.0956), λ_{\max} 248sh, 254 (log ϵ 4.63), 264sh, 290, 410sh, and 500 nm (4.48).

(ii) Compound (VIIe) was prepared (90%) as described for (VIIa) from phenanthraquinone and *o*-nitrophenylhydrazine hydrochloride.

10-m-Nitrophenylazophenanthren-9-ol (VIIf).—Reaction of phenanthraquinone and *m*-nitrophenylhydrazine gave compound (VIIf) (91%), m.p. 219—220° (from ethanol-

¹⁴ J. Attenburrow, A. F. B. Cameron, J. H. Chapman, R. M. Evans, B. A. Hems, A. B. A. Jansen, and T. Walker, *J. Chem. Soc.*, 1952, 1094.

¹⁵ G. Charrier and G. Ferreri, *Gazzetta*, 1914, 44, 228.

benzene) (lit.,¹⁶ 196—197°) (Found: C, 70.1; H, 3.9; N, 12.1%; M^+ , 343.0954).

10-*p*-Nitrophenylazophenanthren-9-ol (VIIg).—The following procedures gave identical samples of the compound as red needles, m.p. 256—257°, after repeated crystallisation from ethanol-benzene (lit.,¹⁶ 185°; lit.,¹⁷ 245°) (Found: M , 343.0954; C, 69.9; H, 3.6; N, 12.1%), λ_{\max} . 256 (log ϵ 4.47), 294, 425sh, and 497 nm (4.47).

(i) A solution of biphenyl-2,2'-dicarbaldehyde (2.5 mmol) and *p*-nitrophenylhydrazine (2.5 mmol) in ethanol (15 ml), stirred at ambient temperature for 3 days, gave compound (VIIg) (21% after purification) as a precipitate.

¹⁶ G. Charrier, *Gazzetta*, 1922, **52**, 261.

¹⁷ E. Hyde, *Ber.*, 1899, **32**, 1810.

(ii) A suspension of biphenyl-2,2'-dicarbaldehyde mono-*p*-nitrophenylhydrazone (IIIg) in ethanol became intensely violet when treated with one drop of 4*N*-sodium hydroxide. The mixture was shaken for 5 min at ambient temperature, poured into water, and extracted with chloroform, giving compound (VIIg) (47%).

(iii) The compound was prepared (67%) from phenanthraquinone and *p*-nitrophenylhydrazine as described for (VIIa).

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