

Cyclisations with Hydrazine and its Derivatives. Part IV.¹ 9-Arylazophenanthrenes and Related Reduction Products from Reactions of Biphenyl-2,2'-dicarbaldehyde with Arylhydrazines

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9-Arylazophenanthrenes are the main end products (yields up to *ca.* 90%) from condensation and cyclisation reactions in organic solvents between biphenyl-2,2'-dicarbaldehyde and arylhydrazines. 9-Phenylazophenanthrene, thus obtained with phenylhydrazine, is converted by various reducing agents into 9-phenanthrylamine or into *N*-9-phenanthryl-*N'*-phenylhydrazine, which readily rearranges to give dibenzo[*a,c*]carbazole or 10-(*o*-aminophenyl)-9-phenanthrylamine. Reductants for 9-phenylazophenanthrene include phenylhydrazine; use of this leads mainly to the dibenzocarbazole, which consequently may be a by-product in preparations of the azo-compound.

PREVIOUS papers^{1,2} have described cyclisation reactions in organic solvents between hydrazine and biaryls containing a formyl or an oxo-substituent *ortho* to the internuclear linkage in each ring. The resulting polycyclic compounds may possess either an additional benzo-component or a 1,2-diazocine ring. We now report the reactions of arylhydrazines with biphenyl-2,2'-dicarbaldehyde, from which neither of the foregoing types of product would be expected.

Under mild conditions the reaction gave condensation products varying in character with the nature of the *N*-substituent and with the reaction conditions. This initial phase of the reaction sequence is discussed in the following paper.³ In refluxing solvents, *e.g.* benzene or ethanol, the reaction went further; phenylhydrazine thus gave 70–90% yields of 9-phenylazophenanthrene (II) (see Scheme) in a process involving overall elimination of 2 molecules of water. Compound (II) has been prepared previously⁴ from 9-phenanthrylmagnesium bromide. Examining 9-phenanthrylamine (VI)⁵ as yet another precursor, we were unsuccessful in effecting its condensation with nitrosobenzene (such reactions are known to be difficult outside the benzene series⁶), and a synthesis from the amine *via* the *N*-sulphonylamine⁶ (previously used for the 2- and 3-isomers⁷) gave 9-phenylazophenanthrene only in very poor yield.

Reactions of a selection of *C*-substituted phenyl-

hydrazines, $H_2N \cdot NH \cdot C_6H_4X$, in refluxing ethanol with an equimolar proportion of biphenyl-2,2'-dicarbaldehyde were studied similarly. Corresponding 9-arylazophenanthrenes were obtained in yields of 60–90% when X was *o*- or *p*-Me, *o*-OMe, *p*-Cl, or *p*-Br, but in poor yield (*ca.* 30% or less) when X was *o*- or *m*-NO₂. There was no disadvantage in using hydrochlorides in the reactions instead of the free arylhydrazines. The azo-compounds were obtained as red crystals, showing similarity in their electronic spectra.³ A low-intensity peak at 1600 cm⁻¹ in their i.r. spectra is attributed⁸ to N=N stretching.

During purification of the various arylazo-compounds on alumina columns other products were observed, but examination of these was confined to the mixtures resulting from the preparations with phenylhydrazine. In these cases a feature of some of the chromatographic separations was the appearance of a second band of 9-phenylazophenanthrene after the main fraction had been eluted. This occurred when a reaction was incomplete; the surviving intermediate condensate then underwent transformation on the alumina.³ A second end product was dibenzo[*a,c*]carbazole (IV), identical with an authentic sample prepared from 9-phenanthrol (VII) by a variation⁹ on a Borsche-type carbazole synthesis whereby compound (IV) was first obtained.¹⁰

¹ Part III (under the general title 'Cyclisations with Hydrazine'), R. G. R. Bacon and R. Bankhead, *J. Chem. Soc.*, 1963, 839.

² R. G. R. Bacon and W. S. Lindsay, *J. Chem. Soc.*, 1958, 1375, 1382.

³ R. G. R. Bacon and D. C. H. Bigg, following paper.

⁴ J. W. Barton, A. M. Rogers, and M. E. Barney, *J. Chem. Soc.*, 1965, 5537.

⁵ R. H. Altiparmakian and R. J. W. Braithwaite, *J. Chem. Soc. (C)*, 1967, 1818.

⁶ K. H. Schündehütte, 'Diarylazoverbindungen,' in Houben-Weyl, 'Methoden der Organischen Chemie,' vol. 10/3, 1965, pp. 219–465.

⁷ O. M. Friedman, R. M. Gofstein, and A. M. Seligman, *J. Amer. Chem. Soc.*, 1949, 71, 3010.

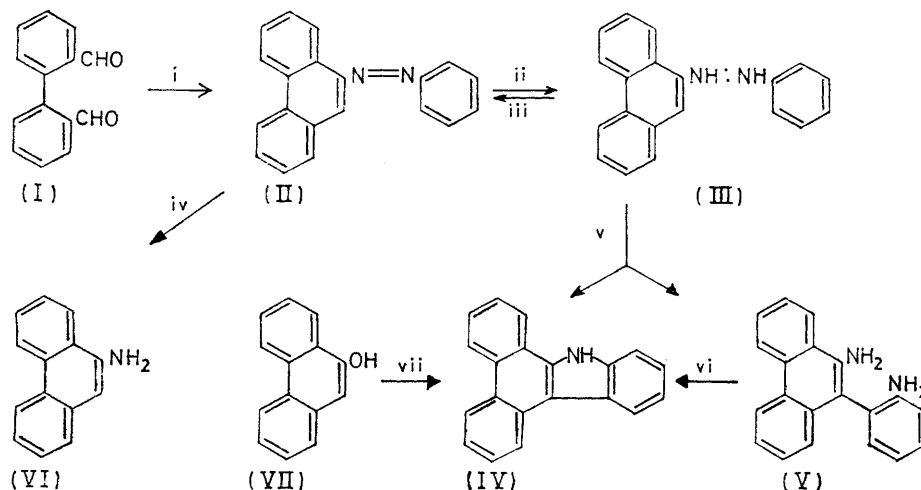
⁸ L. J. Bellamy, 'The Infra-red Spectra of Complex Molecules,' Methuen, London, 2nd edn., 1958.

⁹ E. Campaigne, L. Ergener, J. V. Hallum, and R. D. Lake, *J. Org. Chem.*, 1959, 24, 487.

¹⁰ F. R. Japp and A. Findlay, *J. Chem. Soc.*, 1897, 71, 1115.

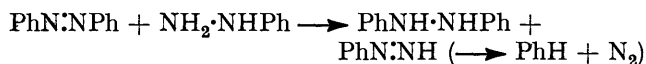
Only a trace of the dibenzocarbazole resulted when equimolar quantities of the dialdehyde and phenylhydrazine were employed, but if the proportion of phenylhydrazine was increased, the yield of the azo-compound progressively fell, while the yield of the dibenzocarbazole rose to a maximum of *ca.* 20%. Form-

where has given divergent results,¹¹ gave the dibenzocarbazole almost quantitatively. The hydrazo-compound (III), which is the intermediate in production of (IV) and (V), was isolated in good yield by reducing the azo-compound in ether with lithium aluminium hydride and a catalytic amount of iron(III) chloride.¹⁵



Reagents: i, $\text{NH}_2\cdot\text{NPh}$ in refluxing EtOH or C_6H_6 ; ii, $\text{LiAlH}_4\text{-FeCl}_3\text{-Et}_2\text{O}$; iii, HgO-CCl_4 ; iv, $\text{Ni-H}_2\text{-C}_6\text{H}_6$; v, from (III) in refluxing EtOH; or from (II) *via* (III) at reflux temperature with $\text{SnCl}_2\text{-HCl-MeOH}$, or $\text{Na}_2\text{S}_2\text{O}_4\text{-aq. MeOH}$, or $\text{NH}_2\cdot\text{NPh-EtOH}$; vi, refluxing EtOH- H_2SO_4 ; vii, refluxing $\text{NH}_2\cdot\text{NPh-EtOH-HCl}$

ation of isomeric dibenzocarbazoles is a feature of both thermal and acid-catalysed benzidine-type rearrangements of *NN'*-dinaphthylhydrazines.^{11,12} Correspondingly, the precursor of the dibenzocarbazole (IV) is considered to be the hydrazo-compound, *N*-9-phenanthryl-*N'*-phenylhydrazine (III), formed by hydrogen transfer from phenylhydrazine to the azo-compound; this type of reduction is known, for example in the case of azobenzene:¹³



In view of this result, effects of reducing agents on samples of the azo-compound (II) were examined. Treatment with an excess of phenylhydrazine in hot ethanol gave varying yields of the dibenzocarbazole (IV), accompanied by minor amounts of a second rearrangement product, the diamine (V). These two products appeared to be produced independently (*cf.* ref. 11), since the diamine was stable under the reaction conditions. It was converted into the dibenzocarbazole in hot acidic ethanol.

Sodium dithionite, which has been used for converting an azo- into a hydrazo-compound,¹⁴ likewise gave the dibenzocarbazole, accompanied by the hydrazo-compound (III). Acidic tin(II) chloride, which else-

It was highly susceptible to oxidation and to rearrangement and was quantitatively reconverted to the azo-compound by mercury(II) oxide. Rearrangement occurred in boiling ethanol, giving the dibenzocarbazole and the diamine in the ratio *ca.* 5 : 1.

Unlike azobenzene, the azo-compound (II) was unresponsive to hydrogenation under mild conditions over palladium, but Raney nickel was effective for its reductive cleavage,¹⁶ giving 9-phenanthrylamine (VI) in good yield. Dissolving-metal reduction with zinc, under non-acidic conditions effective with azonaphthalenes^{11,12} was unsuccessful in converting the azo-compound (II) into the hydrazo-compound (III), although a procedure of similar type is reported⁴ to have given, after acidification, the diamine (V) and a trace of the dicarbazole (IV).

EXPERIMENTAL

Biphenyl-2,2'-dicarbaldehyde (I) (65–85%), m.p. 64–65°, was prepared¹⁷ by ozonolysis of phenanthrene in methanol at –25° and recrystallisation from light petroleum. Phenylhydrazine was freshly redistilled and the *C*-substituted phenylhydrazines were freshly generated from their hydrochlorides with aqueous sodium carbonate.

9-Phenylazophenanthrene (II).—(a) Reaction between biphenyl-2,2'-dicarbaldehyde (5–10 mmol) and phenylhydrazine (1–2.5 equiv.) in refluxing ethanol (50–125 ml) re-

¹³ R. Walther, *J. prakt. Chem.*, 1896, **53**, 433.

¹⁴ *E.g.*, R. J. W. Cremllyn, *J. Chem. Soc.*, 1964, 6235.

¹⁵ G. A. Olah, *J. Amer. Chem. Soc.*, 1959, **81**, 3165.

¹⁶ *E.g.*, L. Horner and U. Schwenk, *Annalen*, 1953, **579**, 204.

¹⁷ P. S. Bailey, *J. Amer. Chem. Soc.*, 1956, **78**, 3811; *Org. Synth.*, 1961, **41**, 41.

¹¹ D. V. Banthorpe, E. D. Hughes, and Sir Christopher Ingold, *J. Chem. Soc.*, 1962, 2386, 2402, 2407; 1964, 2849, 2854.

¹² H. J. Shine, *J. Amer. Chem. Soc.*, 1956, **78**, 4807; H. J. Shine and J. C. Trisler, *ibid.*, 1960, **82**, 4054; H. J. Shine, F.-T. Huang, and R. L. Snell, *J. Org. Chem.*, 1961, **26**, 380.

sulted in rapid development of a red colour. The azo-compound (yields up to ca. 80% after 5 h refluxing) was isolated by evaporation of solvent and chromatography on a column of alumina (Spence type H). Results were not significantly different if reactions were carried out under nitrogen. The yield from a reaction with hydrochloric acid present was 82%. In a typical case, reaction (5 h) between the dialdehyde (5 mmol) and phenylhydrazine (5 mmol) in ethanol (50 ml) gave a red gum, yielding fairly pure azo-compound, m.p. 155–157°, on elution with benzene. After an interval, during which reaction intermediates were transformed on the column, benzene eluted a further small quantity of azo-compound; later fractions were oils. The bulked 9-phenylazophenanthrene was rechromatographed, giving red needles (72%), m.p. 158–159° (from ethanol) (lit.,⁴ 160–161.5°) (Found: C, 84.9; H, 4.9; N, 9.7. Calc. for C₂₀H₁₄N₂: C, 85.1; H, 5.0; N, 9.9%). Similar preparations, carried out in benzene, gave yields of ca. 90%. Lower yields resulted from reaction in acetic acid.

(b) 9-Phenanthrylamine (VI)⁵ yielded resins when treated with nitrosobenzene in acetic acid.⁶ Treatment of the amine in benzene with thionyl chloride, followed by *N*-phenylhydroxylamine,^{6,7} gave a product yielding various chromatographic fractions, one of which was 9-phenylazophenanthrene (3%), identical in m.p. and spectral properties with samples obtained as in (a).

Other 9-Arylazophenanthrenes.—The following compounds were prepared by reaction (5 h) between biphenyl-2,2'-dicarbaldehyde (2.5 mmol) and a *C*-substituted phenylhydrazine (2.5 mmol) in refluxing ethanol (50–80 ml). The products were obtained as red needles after chromatographic purification with benzene on alumina and recrystallisation from benzene or light petroleum: 9-(*o*-tolylazo)phenanthrene (80%; 86% when *o*-tolylhydrazine hydrochloride used), m.p. 151–152° (Found: C, 84.9; H, 5.2; N, 9.7. C₂₁H₁₆N₂ requires C, 85.1; H, 5.4; N, 9.4%); 9-(*p*-tolylazo)phenanthrene (78%), m.p. 137–138° (Found: C, 85.1; H, 5.5; N, 9.2%); 9-(*o*-methoxyphenylazo)phenanthrene (75%), m.p. 199–200° (Found: C, 80.5; H, 5.3; N, 8.7. C₂₁H₁₆N₂O requires C, 80.7; H, 5.1; N, 8.9%); 9-(*p*-chlorophenylazo)phenanthrene (73%), m.p. 157–158° (Found: C, 75.9; H, 3.7; N, 8.6. C₂₀H₁₃ClN₂ requires C, 75.8; H, 4.1; N, 8.8%); 9-(*p*-bromophenylazo)phenanthrene (59%), m.p. 168–169° (Found: Br, 22.5; N, 7.7. C₂₀H₁₃BrN₂ requires Br, 22.1; N, 7.5%); 9-(*o*-nitrophenylazo)phenanthrene (6%), m.p. 164–166° (*M*⁺, 327.1009. C₂₀H₁₃N₃O₂ requires *M*, 327.1008) [accompanied by substantial amounts of 10-(*o*-nitrophenylazo)phenanthren-9-ol,³ m.p. 255–256°]; 9-(*m*-nitrophenylazo)phenanthrene (33%), m.p. 190–191° (Found: C, 73.7; H, 4.2; N, 13.0. C₂₀H₁₃N₃O₂ requires C, 73.4; H, 4.0; N, 12.8%).

*Dibenzo[*a,c*]carbazole* (IV).—(a) A series of reactions carried out (5 h) between biphenyl-2,2'-dicarbaldehyde (5 mmol) and increasing proportions of phenylhydrazine in refluxing ethanol (50 ml), yielded the dibenzocarbazole as a second product (see Table). The products were separated chromatographically on alumina; the dibenzocarbazole was eluted after the azo-compound, e.g., with benzene-ether (4:1), as white crystals, m.p. 190–191° (from benzene-light petroleum) (lit.,⁴ 193–194°; lit.,¹⁰ 188–

189°). Purification, as in the case of the parent carbazole,¹⁸ was difficult (Found: C, 89.5; H, 5.0; N, 5.5. Calc. for C₂₀H₁₃N: C, 89.9; H, 4.9; N, 5.2%).

Phenylhydrazine (mol. equiv.)	Azo-compound (II) (%)	Dibenzocarbazole (%)
1	69	Trace
2	68	4
4	67	5
7	22	14
12	13	16
20	10	20

(b) 9-Phenanthrol (VII)¹⁹ (2 mmol) in 70% aqueous ethanol (10 ml) containing hydrochloric acid (0.25 ml) was mixed with phenylhydrazine (2.3 mmol) in ethanol (5 ml). The solution was refluxed (4 h) and evaporated, and the product chromatographed on alumina, yielding dibenzo[*a,c*]carbazole (60%), m.p. 190–191°.

(c) An excess (4 g) of tin(II) chloride in concentrated hydrochloric acid (12 ml) was added to a solution of 9-phenylazophenanthrene (1 mmol) in methanol (50 ml). Dibenzo[*a,c*]carbazole (96%), m.p. 192–193°, was precipitated when the resulting colourless solution was treated with water.

(d) 9-Phenylazophenanthrene (1 mmol), suspended in refluxing methanol-water (2:1; 150 ml) was treated with portions of aqueous sodium dithionite (4 mmol in all) until the mixture became colourless. Extraction with ether and addition of light petroleum to the extract precipitated a small amount of the hydrazo-compound (III). Evaporation of the filtrate and chromatography on silica gel gave the azo-compound (II) (30%) (formed by oxidation of the hydrazo-compound during work-up), followed by the dibenzocarbazole (50%).

N-9-Phenanthryl-*N'*-phenylhydrazine (III).—A mixture of 9-phenylazophenanthrene (2 mmol), an excess (10 mmol) of lithium aluminium hydride, and a trace of iron(III) chloride, in ether (50 ml), was stirred for 1 h and refluxed for 2 h. After decomposition with wet ether and dilute hydrochloric acid, the pale yellow ethereal solution was evaporated and the residue purified by precipitation from benzene solution with light petroleum. All the operations were carried out under nitrogen. *N*-9-Phenanthryl-*N'*-phenylhydrazine was thus obtained (65–95%) as colourless crystals, m.p. 126–127°, which gradually turned orange in air; concordant results in combustion analysis were difficult to obtain (Found: *M*⁺, 284.1319. C₂₀H₁₆N₂ requires *M*, 284.1313; *m/e* 282 (*M* – 2H) and 267 (*M* – NH₃); τ 3.78 (s, C₁₄H₉NH) and 4.34 (s, PhNH); cf. hydrazobenzene, τ 4.35 (s, PhNH).

When subjected to chromatography with deoxygenated benzene on a column of silica gel, the hydrazo-compound was recovered practically quantitatively, but its m.p. was slightly depressed. Extensive change occurred on a column of alumina, giving 9-phenylazophenanthrene and other compounds. The hydrazo-compound was reoxidised by stirring at ambient temperature, under nitrogen, in deoxygenated carbon tetrachloride, with an excess (3 equiv.) of yellow mercury(II) oxide; evaporation and chromatography on silica gel yielded 9-phenylazophenanthrene (94%).

10-(*o*-Aminophenyl)-9-phenanthrylamine (V).—(a) Rearrangement of *N*-9-phenanthryl-*N'*-phenylhydrazine was

¹⁸ W. C. Sumpter and F. M. Miller, 'Heterocyclic Compounds with Indole and Carbazole Systems,' Interscience, New York, 1954.

¹⁹ R. G. R. Bacon and S. C. Rennison, *Chem. and Ind.*, 1966, 812.

effected by maintaining an ethanolic solution, under oxygen-free conditions, for 2 days at the b.p. T.l.c. of the product indicated a complex mixture. Elution with benzene from a column of silica gel gave 9-phenylazophenanthrene (2%), followed by dibenzo[*a,c*]carbazole (45%); benzene-ethyl acetate (4:1) then gave colourless, fluorescent crystals of 10-(*o*-aminophenyl)-9-phenanthrylamine (8%), m.p. 201–202° (lit.,⁴ 202–203°), *m/e* 284 (*M*) and 267 (*M* – NH₃). A sample of the diamine kept for 2 days in refluxing ethanol was recovered unchanged. Repetition of the operation with a trace of sulphuric acid present gave dibenzo[*a,c*]carbazole (96%), m.p. 191–192°.

(*b*) Samples of 9-phenylazophenanthrene (2 mmol) were treated with an excess (20–40 mmol) of phenylhydrazine in refluxing ethanol (30 ml) for 10–20 h. After removal of phenylhydrazine with acetic acid, chromatography on silica gel gave azo-compound (40–50%) and reduction products (20–40%); in a typical case the unchanged azo-compound (46%) was followed by dibenzo-

[*a,c*]carbazole (20%), m.p. 192–193°, and then by 10-(*o*-aminophenyl)-9-phenanthrylamine (5%), m.p. 201–202°.

9-Phenanthrylamine (VI).—A solution of 9-phenylazophenanthrene in benzene or cyclohexane was shaken with hydrogen, at ambient temperature and atmospheric pressure, in the presence of W2 Raney nickel. Aniline was removed from the product by steam distillation, leaving 9-phenanthrylamine, which was treated in ether solution with gaseous hydrogen chloride; basification of the precipitated hydrochloride gave the free amine (70%), m.p. 137–138° (from ether-light petroleum) (lit.,⁵ 133–135°; lit.,²⁰ 137.5–138.5°) (Found: *M*, 193.0891. Calc. for C₁₄H₁₁N: *M*, 193.0891); picrate, m.p. 192–193° (from ethanol-benzene) (lit.,²¹ 190°). Treatment of the azo-compound with an excess of Raney nickel in the absence of hydrogen gave the amine in 57% yield.

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²⁰ L. F. Fieser, R. P. Jacobsen, and C. C. Price, *J. Amer. Chem. Soc.*, 1936, **58**, 2163.

²¹ J. Schmidt and M. Strobel, *Ber.*, 1901, **34**, 1461.