Rearrangements of Aromatic Carbonyl Arylhydrazones of Benzene, Naphthalene, and Azulene

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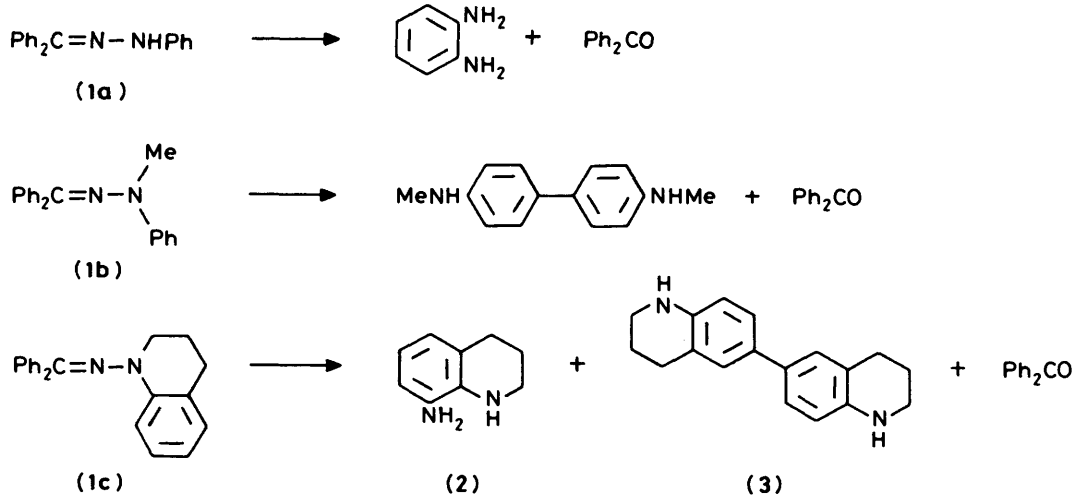
Aromatic carbonyl arylhydrazones have been shown to undergo two kinds of rearrangement in polyphosphoric acid both involving nitrogen–nitrogen bond cleavage. The first proceeds *via* insertion of the imine portion in the position *ortho* to the second nitrogen atom to give *o*-phenylenediamine intermediates: their evolution depends on the nature of the starting substrate. This reaction has been employed for synthesizing the quinoxalines (**5**) and the phenanthridines (**11**), and was demonstrated to be intramolecular. The second reaction path is a [5,5]sigmatropic rearrangement exclusive to electron-rich aromatic carbonyl hydrazones.

Previous work on rearrangements in acid media of aromatic carbonyl arylhydrazones focussed on substrates resulting from electron-rich systems, in which at least one strong electron-donating substituent was present in the position *para* to the original carbonyl function.[1] This was a feature responsible for several reaction paths, a few being novel and of general significance; of particular value is a [5,5]sigmatropic rearrangement which affords biaryls.[1a,b]

The subject of this paper is the behaviour of unsubstituted aromatic carbonyl arylhydrazones in hot polyphosphoric acid (PPA).

Results and Discussion

The following benzophenone arylhydrazones (**1a**—**c**) were converted into benzophenone and *o*-phenylenediamine or benzidine derivatives in fairly good yields (Scheme 1).

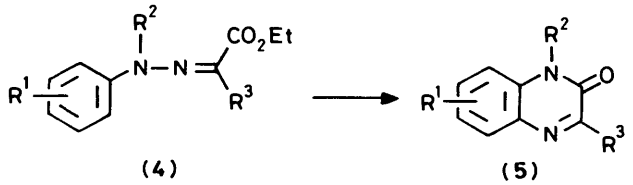


Scheme 1.

o-Phenylenediamine formation was not unexpected, acid treatment of aliphatic carbonyl phenylhydrazones having given similar results;[2] a detailed investigation of the mechanism of this reaction is described later. Although no fully satisfying explanation for the formation of benzidines already noted by us,[1c] can be given, a homolytic N–N bond cleavage was probably involved.

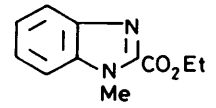
o-Phenylenediamine formation was extended to the α-oxo ester arylhydrazones (**4a**—**g**) which gave the quinoxalin-2(3*H*)-ones (**5a**—**f**) in variable, but generally modest yield [(**4f**) and (**4g**) gave the same product (**5f**)]. The structures of the reaction products (**5**) were confirmed by comparing physical and spectral data of the already known products (**5a**—**d**) with those obtained from authentic samples; (**5e**) and (**5f**) were independently prepared by the condensation of 3,6-dimethyl-*o*-phenylenediamine with ethyl *p*-tolyl glyoxylate and ethyl phenylglyoxylate, respectively. For the substrate (**4d**) the reaction afforded (**5d**) together with ethyl 1-methylbenzimidazole-2-carboxylate (**6**). Formation of benzimidazoles had already been observed during the treatment of aliphatic carbonyl phenylhydrazones with zinc chloride at 180—190 °C;[2] the gain in resonance stabilization accompanying the formation of the imidazole nucleus has been suggested as providing the driving force for the C–C bond cleavage involved in the reaction.[2b,3]

The hydrazone (**4e**) gave (**5e**) and (**8**) as by-products, the main reaction product being the biphenyl (**7**), resulting from the [5,5]sigmatropic rearrangement cited earlier[1a,b] and typical of electron-rich aromatic carbonyl arylhydrazones. Hyperconjugation is probably responsible for such variation in the reaction course. The indazole (**8**) formed in trace amounts, had analytical and spectral data (see Experimental section)

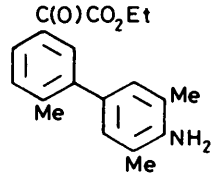


(4) (5)

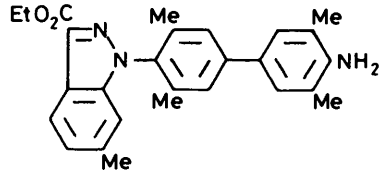
	R^1	R^2	R^3		R^1	R^2	R^3
	H	H	Ph	**a**	H	H	Ph
	H	Me	Ph	**b**	H	Me	Ph
	H	Ph	Ph	**c**	H	Ph	Ph
	H	Me	CO_2Et	**d**	H	Me	CO_2Et
	2,6-Me_2	H	4-MeC_6H_4	**e**	5,8-Me_2	H	4-MeC_6H_4
	2,5-Me_2	H	Ph	**f**	5,8-Me_2	H	Ph
	2,6-Me_2	H	Ph	**g**			
	H	Me	Bz	**h**			



(6)

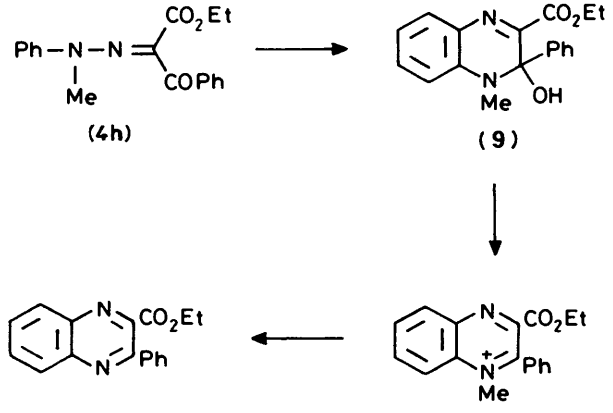


(7)



(8)

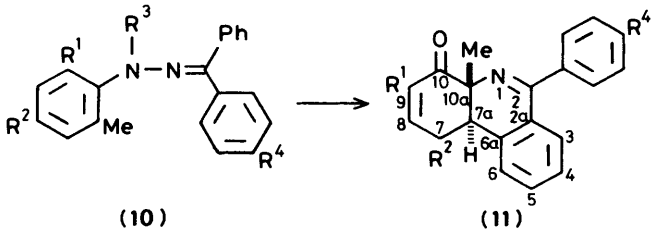
compatible only with this structure: a possible mechanistic interpretation will be given later. As expected, the hydrazones (**4f**) and (**4g**) gave the same product (**5f**), a 1,2-shift of a methyl group[4] occurring in the last mentioned case in which both termini of the migration are occupied by methyl groups. Behaviour in line with that seen before was shown by the substrate (**4h**) which gave the dihydroquinoxaline (**9**) in good yields; the structural assignment was based on the transformation sequence reported in Scheme 2. A new and surprising



(4h) (9)

Scheme 2.

reaction course was observed with benzophenone arylhydrazones (**10a—d**) in which at least one of the positions *ortho* to the hydrazine entity of the substrate is occupied by a methyl group, the phenanthridines (**11a—c**) being the main reaction products: (**10a**) and (**10d**) gave the same product (**11a**) [or (**11d**)], while (**10b**) and (**10c**) gave (**11b**) and (**11c**) respectively. No satisfactory reaction was found for the chemical demonstration of structures (**11**) although the structural assignments were strongly supported by ^1H and ^{13}C n.m.r. spectral results (see Experimental section: Table 1). Selective decoupling experiments showed that C-6a is coupled with 7-H and 7a-H and 10a-Me, and J(C-6a, 7-H) = 3 Hz was determined. Furthermore, comparison of the spectra of substrates (**11a**) and (**11c**) showed that 7-Me in (**11c**) produces a γ-effect (−1.4 p.p.m.) on C-6a; this ruled out any other possible isomeric structure.[5]



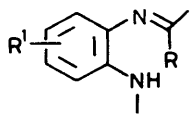
(10) (11)

	R^1	R^2	R^3	R^4
a	Me	H	H	H
b	Me	H	H	Cl
c	H	Me	H	H
d	Me	H	Me	H

All the reaction products depicted above [except for the benzidine derivatives (**7**) and (**8**)], can be derived from formal N–N bond cleavage of the substrate followed by attack of the imine entity at the position *ortho* to the other nitrogen atom. Although an intermolecular process has been suggested,[2a] it seems reasonable to assign a non-concerted intramolecular process to formation of the quinoxalines (**5**) and (**9**), the phenanthridines (**11**), and the *o*-phenylenediamines. In order to define unequivocally the true path governing this rearrangement, the substrate (**12**) labelled with deuterium both on the carbonyl and hydrazine moieties was synthesized (see Experimental section): the reaction with PPA of equimolar amounts of the labelled and unlabelled hydrazone (**4b**) gave a mixture of the two quinoxalines (**5b**) and (**13**), any scrambling between the ketone and hydrazine portions being totally excluded on the basis of the mass spectroscopic data.

(12) (13)

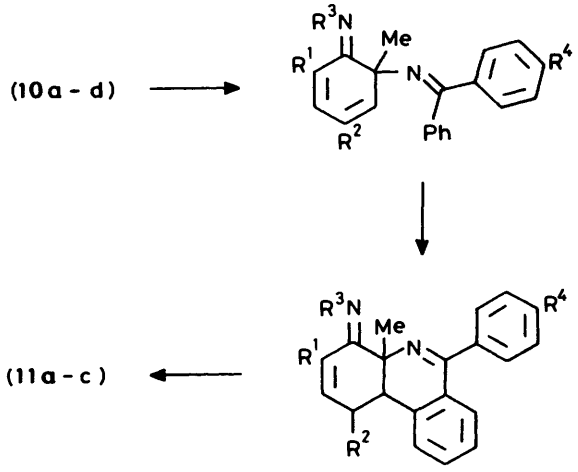
These results unequivocally demonstrated the intramolecularity of the process, this *ortho*-semidine-like rearrangement involving the Schiff base (**I**) as an intermediate, which could either undergo hydrolysis to the starting carbonyl compound



(I)

and to *o*-phenylenediamine or cyclize to the quinoxalines (**5**) and (**9**) when R is a carbonyl function.[6]

The behaviour of the hydrazones (**10a—d**) can be easily interpreted in terms of the same reaction scheme: the methyl group does not allow the rearomatization of the cyclohexadienone imine system, which evolves as an electrophile on the electron richer phenyl ring of the benzophenone imine entity;



the driving force for this process could be the formation of a stable anellated system. A rather different reactivity was shown instead by the 2,6-dimethylphenylhydrazones of ethyl 1- and 2-naphthylglyoxylates (**14**) and (**17**) which rearranged in hot PPA to give rather complex reaction mixtures, from which the products reported in Scheme 3 were isolated pure by chromatography.

The quinoxalines (**15**) and (**18**) were prepared by an independent synthesis by condensation of the 3,6-dimethyl-*o*-phenylenediamine with 1- and 2-naphthylglyoxylic acid ester respectively. Structural assignments to (**16**) and (**19**) are based on analytical data and on their ^1H and ^{13}C n.m.r. spectra.

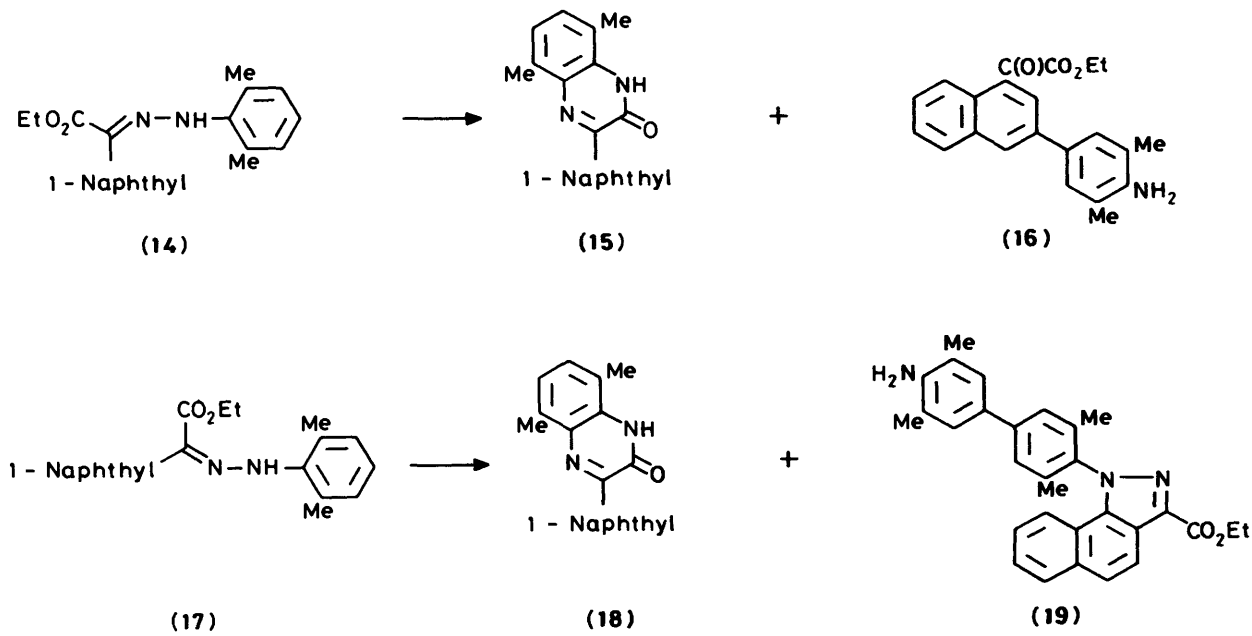
Formation of compounds (**15**) and (**18**) must be interpreted on the basis of the same *ortho*-semidine-like rearrangement discussed earlier; in these cases a 1,2-shift of a methyl group is involved, as already seen for analogous substrates of the benzenoid series. The product (**16**) instead arises through a reaction path which involves the [5,5]sigmatropic rearrangement. The indazole derivative (**19**), like (**8**), must derive from the combination of two processes: the first one would be a homolytic N–N bond cleavage of the protonated hydrazones to produce electrophilic anilinium radicals which combine with the most electron-rich site of the substrates, namely the *para* position of the xylidine residue. The second step should be the oxidative cyclization to indazoles, which is not unexpected having been often observed during rearrangements of arylhydrazones in acid media.[5,7] This reaction occurs readily for compound (**17**) where an electron-rich α-position of the naphthalene ring is involved.

It is interesting to note that the hydrazone (**14**) exhibits behaviour which ranges from that typical of the electron-rich substrates (sigmatropic rearrangements) to that characteristic for the electron-poor hydrazones (*ortho*-semidine-like rearrangement) both concurrent in this case. This observation fits with the better electronic availability of the naphthalene compared with benzene. The validity of this hypothesis was clearly shown by the results of the rearrangement of azulene-2-carbaldehyde 2,6-xylylhydrazone (**20**) in PPA: the amino aldehyde (**21**) was the sole product, isolated in a 60% yield. The identity of compound (**21**) was established on the basis of ^1H n.m.r. evidence.

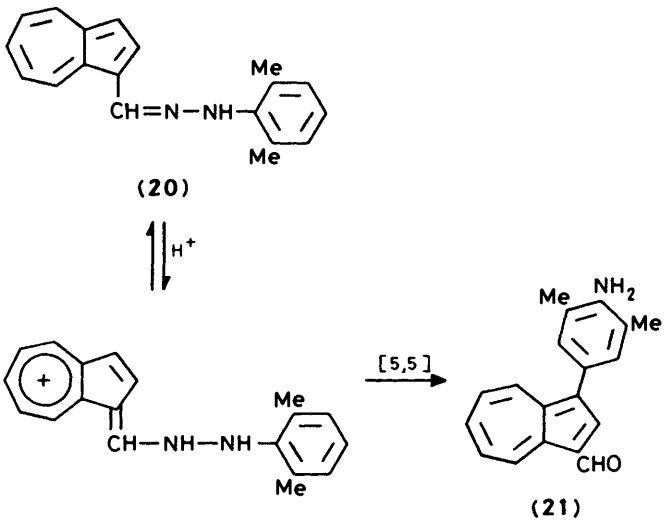
A [5,5]sigmatropic rearrangement involving a terminal five-membered ring has already been observed by us in the heterocyclic series;[1b] the geometrical constraints on the suprafacial shift do not seem too different from those predictable for a six-membered system.

Experimental

M.p.s are uncorrected. ^1H and ^{13}C N.m.r. spectra were recorded on Varian 3M-390 and Varian XL 300 spectrometers with deuteriochloroform as a solvent unless otherwise stated and with tetramethylsilane as an internal standard. Chemical shifts



Scheme 3.



are given in δ units and refer to the centre of the signal: coupling constants are given in Hz.

Carbonyl Compounds.—The only unknown compound was the ethyl pentadeuteriophenylglyoxylate, which was prepared by reaction of ethyl oxalyl chloride (15.5 g, 0.113 mol) and hexadeuteriobenzene (9.5 g, 0.113 mol) in the presence of anhydrous aluminium chloride (30 g, 0.225 mol) in carbon disulphide solution (80 ml) at 10 °C. After work-up of the reaction mixture, the product was purified by distillation under reduced pressure (15.7 g); δ_H 4.45 (2 H, q, CH_2CH_3) and 1.38 (3 H, t, CH_2CH_3). The other carbonyl compounds were prepared according to methods described in the literature.

Hydrazines.—The only unknown compound was the *N*-methyl-*N'*-(2,6-xylyl)hydrazine, prepared by reduction of the *N*-methyl-*N*-nitroso-2,6-xylidine[8] either with lithium aluminium hydride in THF solution[9] or with Zn dust in acetic acid solution according to known experimental procedures.[10] The other arylhydrazines were prepared according to methods described in the literature, references being given when necessary.

N-*Methyl*-N'-(2,6-*xylyl*)*hydrazine.* A very careful distillation procedure was necessary to completely remove the *N*,2,6-trimethylaniline, which is the main reaction product. The title hydrazine is an oil, b.p. 108—111 °C at 18 mmHg: yield 15%. The purity of the product was checked by the integrals of the ^{1}H n.m.r. signals: δ_H 2.86 (NH_2NCH_3) and 2.63 ($NHCH_3$).

Hydrazones.—The hydrazones (**1a**) and (**1b**) were already known in the literature. The hydrazones (**4d**) and (**4h**) were prepared by methylation of diethyl mesoxalate phenylhydrazone[11] and ethyl 2-benzoylphenylhydrazonoacetate[12] respectively, according to the procedure described below. The other hydrazones were generally prepared by treating equimolar amounts of the hydrazine with the appropriate carbonyl compound in alcohol solution in the presence of some acetic acid as a catalyst or directly in aqueous acetic acid solution. The product either crystallized from the reaction mixture or was extracted with diethyl ether after dilution with water or after evaporation of the solvent; the organic extract was washed with a 5% hydrochloric acid and, then with a 5% aqueous sodium hydrogen carbonate. The residue was either crystallized when solid, or chromatographed on a silica gel column, or, in few cases, directly submitted to the reaction with PPA without any further purification, when it was recognised to be a mixture of two *E*/*Z* interconverting stereoisomers.[13]

Benzophenone 1,2,3,4-*Tetrahydroquinolin*-1-*ylhydrazone* (**1c**).—The reaction of benzophenone with 1-amino-1,2,3,4-tetrahydroquinoline[14] was carried out in refluxing ethanol solution for 12 h; the hydrazone (**1c**) directly crystallized on cooling (yield 92%), m.p. 108 °C (Found: C, 84.35; H, 6.35; N, 8.8. $C_{22}H_{20}N_2$ requires C, 84.58; H, 6.45; N, 8.97%).

Ethyl phenylhydrazono(*phenyl*)*acetate* (**4a**). The reaction was carried out in the absence of any solvent; the title compound is a yellow solid, m.p. 94 °C (from hexane) (yield 79%) (Found: C, 71.35; H, 5.9; N, 10.3. $C_{16}H_{16}N_2O_2$ requires C, 71.62; H, 6.01; N, 10.44%).

Ethyl methyl(*phenyl*)*hydrazono*(*phenyl*)*acetate* (**4b**). The reaction was carried out in 50% acetic acid; the title compound was a yellow oil which was found to be a mixture of two stereoisomers (yield 75%); δ_H 7.32 (10 H, m, ArH), 4.35 (2 H, q, CH_2CH), 3.42 (3 H, s, CH_3N), and 1.4 (3 H, t, CH_2CH_3).

Ethyl diphenylhydrazono(*phenyl*)*acetate* (**4c**). The reaction of *N*,*N*-diphenylhydrazine[15] and ethyl phenylglyoxylate was carried out in the absence of solvent and the crude reaction product was chromatographed on a silica gel column with chloroform. From the first fractions eluted a light yellow solid was obtained (11.5 g) which was crystallized from hexane to give a stereoisomer of (**4c**) in a pure state, m.p. 63 °C [Found: C, 76.85; H, 5.85; N, 8.15%; *M* (mass spectrum), 344. $C_{22}H_{20}N_2O_2$ requires C, 76.72; H, 5.85; N, 8.13%; *M*, 344]. The ^{1}H n.m.r. spectrum showed that the equilibration of this stereoisomer was fast in deuteriochloroform solution: 7.68 (2 H, m, ArH in position *ortho* to the hydrazonic function), 7.4—6.8 (13 H, m, ArH), 3.45 (2 H, q, CH_2), and 1.1 (3 H, t, CH_3). From the following fractions the second stereoisomer of (**4c**) was obtained (3.2 g), m.p. 112 °C (from hexane) [Found: C, 76.7; H, 5.55; N, 8.15%; *M* (mass spectrum), 344. $C_{22}H_{20}N_2O_2$ requires C, 76.72; H, 5.85; N, 8.13%; *M*, 344]; δ_H 7.2—6.8 (15 H, m, ArH), 4.35 (2 H, q, CH_2), and 1.35 (3 H, t, CH_3)].

Diethyl mesoxalate methyl(*phenyl*)*hydrazone* (**4d**). A mixture of diethyl mesoxalate phenylhydrazone[11] (26 g, 0.1 mol), potassium carbonate (19 g, 0.15 mol), dimethyl sulphate (14 g, 0.11 mol), and acetonitrile (50 ml) was stirred and heated under reflux for 8 h, after which equivalent amounts of dimethyl sulphate and potassium carbonate to those used originally were added; heating was then continued for 12 h. Salts were filtered off and the solution evaporated to dryness to give the title compound in a pure state (15 g) as a solid, m.p. 48 °C (from hexane) (Found: C, 64.5; H, 5.95; N, 13.65. $C_{11}H_{12}N_2O_2$ requires C, 64.70; H, 5.88; N, 13.72%); δ_H 1.20 and 1.42 (2 × 3 H, 2 t, 2 $CO_2CH_2CH_3$), 3.65 and 3.33 (3 H, s, NCH_3), 4.25 and 4.40 (2 × 2 H, 2 q, 2 $CO_2CH_2CH_3$), and 7.0—8.0 (5 H, m, C_6H_5).

Ethyl 2,6-*xylylhydrazono*(p-*tolyl*)*acetate* (**4e**). The reaction between the *p*-tolylglyoxylate and the 2,6-xylylhydrazine[16] was carried out in ethanol solution to give in a quantitative yield an oily mixture of two stereoisomeric hydrazones (**4e**) (Found: C, 73.15; H, 7.15; N, 8.7. $C_{19}H_{22}N_2O_2$ requires C, 73.52; H, 7.14; N, 9.02%); δ_H 12.50 (1 H, br s exchanging with D_2O, NH), 8.2—7.1 (9 H, m, ArH), 4.50 (2 H, m, CH_2CH_3), 2.50 (s, 3 CH_3 on aromatic rings), and 1.40 (3 H, m, CH_2CH_3).

Ethyl 2,5-*xylylhydrazono*(*phenyl*)*acetate* (**4f**). The reaction between the phenyl glyoxylate and the 2,5-xylylhydrazine[17] was carried out in refluxing alcohol. A mixture of two stereoisomeric hydrazones separated on cooling (yield 76%), m.p. 190 °C.

Ethyl 2,6-*xylylhydrazono*(*phenyl*)*acetate* (**4g**). The reaction between ethyl phenylglyoxylate and the 2,6-xylylhydrazine[16] was carried out in refluxing ethanol solution. The title compound separated on cooling of the solution (yield 95%); m.p. 47 °C (from hexane) (Found: C, 73.45; H, 6.75; N, 9.2. $C_{18}H_{20}N_2O_2$ requires C, 73.60; H, 6.76; N, 9.45%); δ_H 12.30 (1 H, br s exchanging with D_2O, NH), 7.5 (5 H, m, C_6H_5), 7.0 (3 H, s, C_6H_3), 4.45 (2 H, q, CH_2CH_3), 2.45 (6 H, s, 2 CH_3), and 1.35 (3 H, t, CH_2CH_3).

Ethyl methyl(phenyl)hydrazono(benzoyl)acetate (**4h**). The methylation of the ethyl phenylhydrazono(benzoyl)acetate[12] was performed according to the method described above for (**4d**), with the difference that, in this case, the reaction was slower and a third addition of potassium carbonate and dimethyl sulphate had to be made, the reaction time, thereby, being increased. The oily reaction product (yield 80%) was found to be a *ca.* 1:1 mixture of two interconverting stereoisomers and was submitted to the reaction with PPA in a crude state.

Benzophenone 2,6-*xylylhydrazone* (**10a**). The reaction between benzophenone and 2,6-xylylhydrazine hydrochloride[16] was carried out in ethanol solution in the presence of an equimolar amount of sodium acetate. The title compound crystallized on cooling of the solution (yield 90%); m.p. 115 °C (from hexane) (Found: C, 83.6; H, 6.55; N, 9.0. $C_{29}H_{20}N_2$ requires C, 83.96; H, 6.71; N, 9.32%); δ_H 7.7—6.8 (14 H, 1 H exchanging with D_2O, ArH and NH) and 2.28 (6 H, s, 2 CH_3).

4-*Chlorobenzophenone* 2,6-*xylylhydrazone* (**10b**). The reaction between the 4-chlorobenzophenone and the 2,6-xylylhydrazine[16] was carried out in refluxing alcohol solution. The title compound separated on cooling of the solution (yield 82%); m.p. 85 °C (from ethanol) (Found: C, 75.4; H, 5.8; N, 8.4. $C_{21}H_{21}ClN_2$ requires C, 75.34; H, 5.68; N, 8.37%); δ_H 7.3 (13 H, exchanging with D_2O, ArH and NH) and 2.28 (6 H, s, 2 CH_3).

Benzophenone 2,4-*xylylhydrazone* (**10c**). The reaction between benzophenone and 2,4-xylylhydrazine[18] was carried out in refluxing alcoholic solution (yield 75%); m.p. 117 °C (from ligroin) (Found: C, 83.65; H, 6.75; N, 9.35. $C_{21}H_{20}N_2$ requires C, 83.96; H, 6.71; N, 9.32%).

Benzophenone 2,6-*xylyl(methyl)hydrazone* (**10d**). The reaction between benzophenone and the *N*-(2,6-xylyl)-*N*-methylhydrazine described above was carried out in refluxing alcohol solution. Work-up gave an oily residue which became solid with time (yield 37%); m.p. 122 °C (from methanol) (Found: C, 84.0; H, 8.0; N, 8.9. $C_{22}H_{22}N_2$ requires C, 84.03; H, 7.05; N, 8.91%); δ_H 7.6—6.8 (10 H, m, 2 C_6H_5), 6.70 (3 H, s, C_6H_3), 2.23 (3 H, s, NCH_3), and 2.12 (6 H, s, 2 CH_3).

Ethyl trideuteriomethyl(phenyl)hydrazono(pentadeuteriophenyl)acetate (**12**). The reaction was carried out according to the procedure reported above for (**4b**), using the labelled starting materials described before; δ_H 7.3 (5 H, m, C_6H_5), 4.35 (2 H, q, CH_2CH_3), and 1.35 (3 H, t, CH_2CH_3).

Ethyl 1-*naphthylglyoxylate* 2,6-*xylylhydrazone* (**14**). The reaction between the ethyl 1-naphthylglyoxylate[19] and 2,6-xylylhydrazine[16] was carried out in refluxing alcoholic solution in the presence of a trace of acetic acid. The title compound separated on cooling of the solution (yield 86%); m.p. 94 °C (from ethanol) (Found: C, 76.15; H, 6.45; N, 8.15. $C_{22}H_{22}N_2O_2$ requires C, 75.86; H, 6.89; N, 8.05%); δ_H 7.85 (3 H, m, 2-, 4-, 8-naphthalene H), 6.90 (3 H, m, xylidine H), 4.22 (2 H, q, CH_2CH_3), 1.12 (3 H, t, CH_2CH_3), and 12.55 (1 H, s, exchanging with D_2O, NH).

Ethyl 2-*naphthylglyoxylate* 2,6-*xylylhydrazone* (**17**). The reaction between the ethyl 2-naphthylglyoxylate[19] and 2,6-xylylhydrazine[16] was carried out in refluxing alcohol solution in the presence of a trace of acetic acid for 3 h. The oily residue resulting after work-up was chromatographed on a silica gel column with chloroform: the main product eluted was the title hydrazone which was obtained as a viscous yellow oil, containing traces of (**14**) as impurity (yield 45%) (Found: C, 75.9; H, 6.7; N, 7.75. $C_{22}H_{24}N_2O_2$ requires C, 75.86; H, 6.89; N, 8.05%); δ_H 8.14 (1 H, s, 1-naphthalene H), 7.82 and 7.43 (4 H and 2 H, naphthalene H), 7.0 (3 H, m, C_6H_3), 4.40 (2 H, q, CH_2CH_3), 2.52 (6 H, s, 2 CH_3), 1.45 (3 H, t, CH_2CH_3), and 12.41 (1 H, s exchanging with D_2O, NH).

Azulene-2-*carbaldehyde* 2,6-*xylylhydrazone* (**20**). The reaction between azulene-2-carbaldehyde[20] and the 2,6-xylylhydrazine[16] was carried out in alcoholic solution in the presence of a trace of acetic acid at room temperature. Removal of the solvent left a residue which, after work-up, gave the title compound as a green solid (yield 49%); m.p. 69 °C (from isopropyl alcohol) (Found: C, 82.85; H, 6.8; N, 9.85. $C_{19}H_{18}N_2$ requires C, 83.21; H, 6.57; N, 10.21%); δ_H 8.70 (1 H, d, 8-ArH, *J* 10 Hz), 8.14 (1 H, d, 4-ArH, *J* 10 Hz), 8.05 (2 H, s and d, 2-ArH and CHN), 7.47 (1 H, t, 6-ArH, *J* 10 Hz), 7.25—6.80 (7 H one of which exchanging with D_2O, m, ArH and NH), and 2.40 (6 H, s, 2 CH_3).

Reactions of Hydrazones with PPA.—The hydrazones were added portionwise with stirring to PPA (10-fold excess in weight) preheated at *ca.* 90 °C; in a few cases an exothermic reaction occurred. The temperature was raised to 110—130 °C and maintained there until starting material had disappeared. The reaction mixture was cooled, poured onto ice–water, and then neutralised with concentrated ammonium hydroxide solution. The organic material separated was extracted with diethyl ether or chloroform to give a crude product which was generally chromatographed on a silica gel column. In a few cases an acid-base treatment was performed.

Reaction of the hydrazone (**1a**) *with PPA.* The reaction was carried out at 150 °C for 5 min; an acid-base treatment of the crude reaction product was performed. The neutral fraction was distilled *in vacuo* to give benzophenone (yield 37%) and unchanged starting hydrazone (yield 17%). The basic fraction was also distilled *in vacuo* (b.p. 110—115 °C at 0.01 mmHg) to give *o*-phenylenediamine, which was purified by crystallization from ligroin (yield 63%).

Reaction of the hydrazone (**1b**) *with PPA.* The experimental procedure was the same as that described for (**1a**). The neutral fraction gave only benzophenone (yield 45%); the basic fraction gave *N*,*N*′-dimethylbenzidine after distillation *in vacuo* (b.p. 180 °C at 0.07 mmHg) and crystallization of the distillate from ligroin; m.p. 91 °C (yield 27%).[21]

Reaction of the hydrazone (**1c**) *with PPA.* The experimental procedure was similar to that described for (**1a**). The neutral fraction gave only benzophenone (yield 47%); the basic fraction was a complex mixture of products which was first chromatographed on a silica gel column with chloroform to remove some tarry products. The combined fractions eluted were rechromatographed on a silica gel column with benzene–ethyl acetate (85:15). The first product eluted was the 8-*amino*-1,2,3,4-*tetrahydroquinoline* (**3**), as a yellow oil easily oxidised in air, which was purified by distillation *in vacuo* (b.p. 130 °C at 0.3 mmHg) (Found: C, 72.95; H, 8.35; N, 18.95. $C_9H_{12}N_2$ requires C, 72.94; H, 8.16; N, 18.90%); $\delta_H(CCl_4)$ 6.32 (3 H, s, ArH), 3.2 (2 H, m, NCH_2), 3.12 (3 H, br s exchanging with D_2O, NH_2 and NH), 2.68 (2 H, t, benzylic CH_2), and 1.83 (2 H, m, CH_2 on unsaturated carbons). The final product eluted was the 1,1′,2,2′,3,3′,4,4′-octahydro-6,6′-biquinolyl (**3**), m.p. 125 °C (from hexane–benzene) (Found: C, 81.75; H, 7.9; N, 10.25. $C_{18}H_{20}N_2$ requires C, 81.78; H, 7.63; N, 10.60%); δ_H 6.8 (3 H, m, ArH), 3.7 (1 H, s exchanging with D_2O, NH), 3.28 (2 H, t, NCH_2), 2.79 (2 H, t, benzylic CH_2), and 1.9 (2 H, m, CH_2 on saturated carbons).

Reaction of the hydrazone (**4a**) *with PPA.* The reaction was exothermic. After work-up the crude reaction product was dissolved in warm 10% aqueous sodium hydroxide: the solvent was removed under reduced pressure and the residue was treated with water and diethyl ether. The aqueous layer was made acid with 10% hydrochloric acid and the solid precipitate was extracted with chloroform and crystallized from alcohol to give the 3-*phenylquinoxalin*-2(1H)-*one* (**5a**) (yield 20%); m.p. 246 °C.[22]

Reaction of the hydrazone (**4b**) *with PPA.* The reaction of the hydrazone (**4b**) (4.1 g) was carried out at 105 °C for 30 min. Work-up gave a solid (2.8 g) and this was triturated with diisopropyl ether and filtered off. The filtrate was evaporated to

dryness and the residue refluxed with 10% aqueous sodium hydroxide for 5 min. Solvent was removed under reduced pressure and the residue was treated with water: the undissolved material was filtered off and combined with the solid recovered earlier; it was then chromatographed on a silica gel column with chloroform. The 1-*methyl*-3-*phenylquinoxalin*-2(1H)-*one* (**5b**) was eluted as a light yellow solid (0.73 g), m.p. 137 °C (from isopropyl alcohol), identical with an authentic sample;[23] δ_H 8.35 (2 H, m, ArH in position *ortho* to the C_6H_5 group), 7.95 (1 H, m, 5-ArH), 7.45 (6 H, m, ArH), and 3.8 (3 H, s, CH_3); *M* (mass spectrum), 236.

Reaction of the hydrazone (**4c**) *with PPA*. The reaction was carried out at 105 °C for 30 min and the crude reaction product was chromatographed on a silica gel column with benzene–ethyl acetate (9:1). The main product eluted was 1,3-*diphenylquinoxalin*-2-(1H)-*one* (**5c**) (yield 20%), m.p. 187 °C (from ethanol)[24] (Found: C, 80.85; H, 4.75; N, 9.5. $C_{20}H_{14}N_2O$ requires C, 80.53; H, 4.69; N, 9.39%); δ_H 8.45 (2 H, m, ArH in the position *ortho* to C_6H_5), 7.95 (1 H, m, 5-ArH), 6.69 (1 H, m, 8-ArH), and 7.2—7.8 (10 H, m, ArH); *M* (mass spectrum), 298.

Reaction of the hydrazone (**4d**) *with PPA*. Reaction of the hydrazone (**4d**) (0.7 g) was carried out at 90 °C for 10 min. The crude reaction product was purified through an acid-base treatment. The neutral fraction was treated with isopropyl alcohol and the insoluble solid was filtered off and crystallized from the same solvent to give pure *ethyl* 1,2-*dihydro*-1-*methyl*-2-*oxoquinoxaline*-3-*carboxylate* (**5d**), m.p. 121 °C;[25] δ_H 7.92 (1 H, dd, 8-ArH), 7.65 (1 H, m, 6-ArH), 7.38 (1 H, m, 7-ArH), 7.30 (1 H, m, 5-ArH), 4.47 (2 H, q, CH_2CH), 3.75 (3 H, s, CH_3), and 1.42 (3 H, t, CH_2CH_3); *M* (mass spectrum), 232. The basic fraction was chromatographed on a silica gel column with dichloromethane and the main product eluted was purified by distillation *in vacuo* to give *ethyl* 1-*methylbenzimidazole*-2-*carboxylate* (**6**) (b.p. 140 °C at 0.1 mmHg)[26] [Found: C, 64.5; H, 5.95; N, 13.65%; *M* (mass spectrum), 204. $C_{11}H_{12}N_2O_2$ requires C, 64.70; H, 5.88; N, 13.72%; *M*, 204]; δ_H 7.85 (1 H, m, 4-ArH), 7.3 (3 H, m, ArH), 4.5 (2 H, q, CH_2CH_3), 4.2 (3 H, s, CH_3), and 1.50 (3 H, t, CH_2CH_3).

Reaction of the hydrazone (**4e**) *with PPA*. The reaction of the two stereoisomeric hydrazones (**4e**) (10.0 g) was carried out at 100 °C for 30 min. The brown oily crude product was treated with diethyl ether to give 5,8-*dimethyl*-3-(p-*tolyl*)*quinoxalin*-2(1H)-*one* (**5e**) as a light green solid (0.50 g), m.p. 281 °C (Found: C, 75.9; H, 5.75; N, 10.2. $C_{17}H_{16}N_2O$ requires C, 76.27; H, 6.06; N, 10.60%); δ_H 7.70 (6 H, m, ArH), 2.65 (3 H, s, CH_3), and 2.45 (6 H, s, 2 CH_3). The ethereal solution was chromatographed on a silica gel column with chloroform; the first fraction eluted gave ethyl *p*-tolylglyoxylate (3.1 g). The following fractions gave the *ethyl* 4′-*amino*-3′,5′,6-*trimethylbiphenyl*-3-*ylglyoxylate* (**7**) as a light brown solid which was crystallized from di-isopropyl ether (1.8 g) [Found: C, 73.2; H, 6.7; N, 4.6%; *M* (mass spectrum), 311. $C_{19}H_{21}NO_3$ requires C, 73.29; H, 6.80; N, 4.50%; *M*, 311]; δ_H 7.70 (2 H, m, 2-, 4-ArH), 7.88 (1 H, d, 5-ArH), 6.85 (2 H, s, 2′-, 6′-ArH), 4.36 (2 H, q, CH_2CH_3), 3.60 (2 H, br s exchanging with D_2O, NH_2), 2.35 (3 H, s, 6-CH_3), 2.20 (6 H, s, 2 CH_3), and 1.40 (3 H, t, CH_2CH_3). The last fractions of the chromatography gave the *ethyl* 1-(4′-*amino*-3,5,3′,5′-*tetramethylbiphenyl*-4-*yl*)-6-*methylindazole*-3-*carboxylate* (**8**) (0.050 g), m.p. 211 °C [Found: C, 75.55; H, 6.65; N, 9.55%; *M* (mass spectrum), 427. $C_{27}H_{29}N_3O_2$ requires C, 75.87; H, 6.79; N, 9.83%; *M*, 427]; δ_H 7.35 and 7.25 (each 2 H, 2 s, 2,2′,6,6′-biphenyl H), 7.15 and 8.20 (each 1 H, dd, 4-, 5-indazole H), 6.90 (1 H, s, 7-indazole H), 4.55 (2 H, q, CH_2CH_3), 4.65 (2 H, br s exchanging with D_2O, NH_2), 2.45 (3 H, s, 6-indazole CH_3), 2.25 (6 H, s, 2 CH_3), and 1.95 (6 H, s, 2 CH_3). The ester (**7**) (1.1 g) gave upon reaction with refluxing sodium hydroxide in alcohol solution and then treatment with hydrogen peroxide, the 4′-*amino*-3′,5′,6-*trimethylbiphenyl*-3-*carboxylic acid* (0.52 g), m.p. 248 °C (from ethanol) (Found: C, 76.6; H, 6.45; N, 5.4. $C_{16}H_{17}NO_2$ requires C, 76.40; H, 6.36; N, 5.24%); δ_H(DMSO) 7.85 (1 H, s, 2-ArH), 7.45 and 7.95 (each 1 H, dd, 4-, 5-ArH), 6.95 (2 H, s, 2′-, 6′-ArH), 2.80—6.80 (3 H, br s exchanging with D_2O, NH_2 and CO_2H), and 2.10 (6 H, s, 2 CH_3).

Reaction of the hydrazone (**4f**) *with PPA*. The reaction of a mixture of the two stereoisomeric hydrazones (**4f**) (3.3 g) was carried out at 130 °C for 1 h. The crude reaction product (1.6 g) was treated with isopropyl alcohol to give the 5,8-*dimethyl*-4-*phenylquinoxalin*-2(1H)-*one* (**5f**) (0.30 g), m.p. 259 °C (from isopropyl alcohol) (Found: C, 76.5; H, 5.7; N, 11.0. $C_{16}H_{14}N_2O$ requires C, 76.78; H, 5.64; N, 11.19%); δ_H(DMSO) 7.50 (5 H, m, C_6H_5), 7.20 and 8.40 (2 H, dd, 6-, 7-ArH), and 2.60 and 2.40 (each 3 H, 2 s, 2 CH_3).

Reaction of the hydrazone (**4g**) *with PPA*. The reaction of the hydrazone (**4g**) (11.1 g) with PPA was carried out at 110 °C for 50 min. The crude reaction product was directly crystallized from isopropyl alcohol to give pure 5,8-dimethyl-4-phenylquinoxalin-2(1H)-one (**5f**) (0.7 g). Physical and spectral data were identical with those shown by a sample of (**5f**) obtained from the reaction of (**4f**) with PPA.

Reaction of the hydrazone (**4h**) *with PPA*. The reaction of the hydrazone (**4h**) was carried out at 120 °C for 15 min; the reaction mixture was poured into water and the pH was adjusted to 6 with a 35% aqueous sodium hydroxide. The insoluble solid was extracted with diethyl ether and crystallized from benzene to give the *ethyl* 1,2-*dihydro*-2-*hydroxy*-1-*methyl*-2-*phenylquinoxaline*-3-*carboxylate* (**9**) (33%), m.p. 107 °C [Found: C, 69.75; H, 5.85; N, 8.8%; *M* (mass spectrum), 310. $C_{18}H_{18}N_2O_3$ requires C, 69.66; H, 5.85; N, 9.03%; *M*, 310]; δ_H 6.8—7.5 (9 H, m, ArH), 5.08 (1 H, s exchanging with D_2O, OH), 4.23 (2 H, q, CH_2CH_3), 3.82 (3 H, s, CH_3), and 2.25 (3 H, t, CH_2CH_3).

Reaction of the hydrazone (**10a**) *with PPA*. The reaction of the hydrazone (**10a**) (27.0 g) with PPA was exothermic and was carried out at 100 °C for 30 min. An acid-base treatment of the crude reaction product gave benzophenone (11.5 g) and a brown basic residue (13.3 g) which was chromatographed on a silica gel column with chloroform: some more benzophenone (6.0 g) was recovered from the first fractions eluted; the 9,10a-*dimethyl*-2-*phenyl*-7,7a-*dihydrophenanthridin*-10(10aH)-*one* (**11a**) was recovered when chloroform–ethyl acetate (9:1) was employed (0.61 g), m.p. 136 °C [Found: C, 83.4; H, 6.4; N, 4.55%; *M* (mass spectrum), 301. $C_{21}H_{19}NO$ requires C, 83.69; H, 6.35; N, 4.65%; *M*, 301]; δ_H 7.70 (9 H, m, ArH), 6.78 (1 H, m, vinylic H), 3.20 (1 H, dd, axial 7a-CH), 2.22 (2 H, m, CH_2), 1.85 (3 H, s, CH_3 on unsaturated carbon), and 1.21 (3 H, s, CH_3 on saturated carbon); δ_C chemical shifts are reported in the Table.

Reaction of the hydrazone (**10b**) *with PPA*. The hydrazone (**10b**) (13.9 g) was allowed to react at 150 °C for 90 min after which the reaction mixture was poured into water and the pH adjusted to 5.0 with concentrated aqueous sodium hydroxide. The separated material was extracted with methylene dichloride to remove some precipitated 4-chlorobenzophenone; the pH of the aqueous layer was then adjusted to 8.5 with concentrated aqueous ammonium hydroxide and the separated solid was extracted with diethyl ether. Evaporation of the extract left a residue which was directly crystallized from di-isopropyl ether to give the 2-(4-*chlorophenyl*)-9,10a-*dimethyl*-7,7a-*dihydrophenanthridin*-10(10aH)-*one* (**11b**), as colourless crystals (0.65 g), m.p. 175 °C (Found: C, 74.85; H, 5.4; N, 4.15. $C_{21}H_{18}ClNO$ requires C, 75.11; H, 5.36; N, 4.17%); δ_H 7.3 (8 H, m with an emerging A_2X_2 system, ArH), 6.65 (1 H, m, vinylic H), 3.20 (1 H, m, NCH), 2.45 (2 H, m, CH_2), 1.85 (3 H, m, CH_3 on unsaturated carbon), 1.18 (3 H, s, CH_3 on saturated carbon); δ_C chemical shifts are reported in the Table. The pH of the aqueous solution was adjusted to 9.5 with concentrated aqueous sodium

Table. ^{13}C Chemical shifts for compounds (**11**)

Carbon	Compound (**11a**)	(**11b**)	(**11c**)
2	166.9	165.85	167.1
2a	127.03	126.63	127.0
3,4,5,6	131.51, 128.68, 127.3 (2 carbons)	131.79, 128.32, 127.44, 127.4	130.92, 128.75, 128.4, 127.57
6a	139.98	139.98	138.6
7	30.58	30.47	34.25
7a	42.3	42.16	49.60
8	145.11	145.15	156.04
9	135.83	135.78	129.29
10	198.07	197.89	197.88
10a	63.41	63.45	63.16
7-Me			17.88
9-Me	16.85	16.83	
10a-Me	19.12	19.16	18.45
meta	129.07	130.51	129.01
ortho	128.17	128.41	128.2
para	129.51	135.64	129.64
ipso	138.45	136.99	138.19

hydroxide, and the resulting mixture was stirred and treated with benzoyl chloride and then extracted with methylene dichloride. Concentration of the extract gave a residue which was triturated with diethyl ether, dried, and then extracted with boiling water in order to remove benzamide. The undissolved material was chromatographed on a silica gel column with ethyl acetate. From the first fractions eluted some 4-chlorobenzophenone was obtained; final fractions gave the *N,N'*-dibenzoyl-2,6-dimethyl-*p*-phenylenediamine (0.240 g), m.p. 292 °C; its physical and spectral properties were identical with those shown by an authentic sample prepared by reaction of 2,6-dimethyl-*p*-phenylenediamine with benzoyl chloride;[27] δ_H 10.20 (1 H, s exchanging with D_2O, NH), 9.65 (1 H, s exchanging with D_2O, NH), 8.00 (4 H, m, ArH), 7.60 (8 H, m, ArH), and 2.22 (6 H, s, 2 CH_3).

Reaction of the hydrazone (**10c**) *with PPA.* The hydrazone (**10c**) (8.0 g) was allowed to react at 130 °C for 30 min after which the reaction mixture was poured into water and the insoluble material, mostly benzophenone, was extracted with diethyl ether. The pH of the aqueous layer was adjusted to 8.5 with a 26% aqueous ammonium hydroxide and the precipitate was extracted with chloroform. Concentration of the extract left a residue (6.0 g) which was chromatographed on a silica gel column with chloroform. The first fractions eluted gave further benzophenone (3.3 g); on adding ethyl acetate to the eluant (10%), the 7,10a-*dimethyl*-2-*phenyl*-7,7a-*dihydrophenanthridin*-10(10a*H*)-*one* (**11c**) was eluted, as a colourless solid (0.42 g), m.p. 178 °C (from isopropyl alcohol [Found: C, 83.65; H, 6.35; N, 4.65%; *M* (mass spectrum), 301. $C_{21}H_{19}NO$ requires C, 83.69; H, 6.35; N, 4.65%; *M*, 301]; δ_H 7.2—7.7 (9 H, m, ArH), 6.75 (1 H, dd, *J* 12 Hz and 2 Hz, 8-vinylic H), 6.17 (1 H, dd, *J* 12 and 3 Hz, 9-vinylic H), 2.75 (1 H, d, *J* 10 Hz, 7a-CH), 2.45 (1 H, m, 7-CH), 1.15 (3 H, d, *J* 10 Hz, $CHCH_3$), 1.07 (3 H, s, 10a-CH_3); δ_C chemical shifts are reported in the Table.

Reaction of the hydrazone (**10d**) *with PPA.* The hydrazone (**10d**) (5.0 g) was allowed to react at 120 °C for 40 min; after work-up followed by an acid-base treatment, benzophenone (1.4 g) was recovered from the neutral fraction; the basic fraction gave, by removal of the solvent, an oily residue (2.90 g) which was chromatographed on a silica gel column with benzene. The first fraction eluted gave further benzophenone (0.95 g); on adding ethyl acetate to the eluant (10%) 9,10a-dimethyl-2-phenyl-7,7a-dihydrophenanthridin-10(10a*H*)-one (**11a**) was eluted (1.1 g), identical with the product obtained by reaction of (**10a**) with PPA, described above.

Reaction of the hydrazone (**12**) *with PPA.* The hydrazone (**12**) was allowed to react following the procedure described above for the reaction of the unlabelled compound (**4b**). 3-Pentadeuteriophenyl-1-trideuteriomethylquinoxalin-2(1H)-one (**13**) was the only product isolated; δ_H 7.95 (1 H, m, 5-ArH), 7.45 (3 H, m, 6-, 7-, 8-ArH); *M* (mass spectrum), 244.

Reaction of an equimolar mixture of (**4b**) *and* (**12**) *with PPA.* Reaction of an equimolar mixture of the hydrazones (**4b**) and (**12**) was carried out following the procedure described above for the reaction of the unlabelled compound (**4b**). An equimolar mixture of the quinoxalines (**5b**) and (**13**) was isolated, the mass spectrum showing only peaks at 236 and 234: there were no peaks at 239 and 241, possibly deriving from scrambling of unlabelled and labelled fragments.

Reaction of the hydrazone (**14**) *with PPA.* Reaction of the hydrazone (**14**) (4 g) with PPA was slightly exothermic; work-up of the reaction mixture gave a deep-green oil which was treated with diethyl ether to provide 5,8-*dimethyl*-3-(1-*naphthyl*)-*quinoxalin*-2(1H)-*one* (**15**) which was recrystallized from acetic acid (0.45 g); it had m.p. 268 °C [Found: C, 79.95; H, 5.55; N, 9.2%; *M* (mass spectrum), 300. $C_{20}H_{16}N_2O$ requires C, 80.00; H, 5.33; N, 9.33%; *M*, 300]; δ_H(DMSO) 8.2—7.8 (3 H, m, 2-, 4-, 8-naphthyl H), 7.7—7.3 (4 H, m, naphthyl H), 7.17 (2 H, dd, quinoxaline H), 2.65 and 2.50 (2 × 3 H, 2 s, 2 CH_3), and 11.1 (1 H, br s exchanging with D_2O, NH). The ethereal solution was saturated with dry hydrogen chloride and the crystalline precipitate was filtered off and treated with 10% aqueous sodium hydroxide: an oily product separated which was extracted with diethyl ether and chromatographed on a silica gel column with dichloromethane; the main product eluted was purified by crystallization from hexane to give *ethyl* 3-(4-*amino*-3,5-*dimethylphenyl*)*naphthylglyoxylate* (**16**), as orange crystals (0.24 g), m.p. 123 °C (Found: C, 76.15; H, 6.2; N, 3.9. $C_{22}H_{21}NO_3$ requires C, 76.08; H, 6.05; N, 4.03%); δ_H 9.0 (1 H, m, 8-ArH), 8.22 (2 H, s, 2-, 4-ArH), 7.93 (1 H, m, 5-ArH), 7.60 (2 H, m, 6-, 7-ArH), 7.30 (2 H, s, C_6H_2), 4.51 (2 H, q, CH_2CH_3), 3.75 (2 H, br s exchanging with D_2O, NH_2), 2.34 (6 H, s, 2 CH_3), and 1.48 (3 H, t, CH_2CH_3). Only ethyl 1-naphthylglyoxylate could be recovered from the ethereal acid mother liquors.

Reaction of the hydrazone (**17**) *with PPA.* A solution of the hydrazone (**17**) (2.4 g) in PPA (50 g) was heated at 110 °C for 90 min and work-up of the reaction mixture gave a residual brown oil; this was dissolved in diethyl ether and saturated with dry hydrogen chloride to give the hydrochloride of the basic products; the free bases were then regenerated and chromatographed on a silica gel column with benzene–ethyl acetate (9:1) to give *ethyl* 1-(4'-*amino*-3,5,3',5'-*tetramethylbiphenyl*-4-*yl*)-*benz*[g]*indazole*-3-*carboxylate* (**19**) as the main product eluted (0.30 g), m.p. 235 °C (from di-isopropyl ether) [Found: C, 77.6; H, 6.5; N, 8.7%; *M* (mass spectrum), 463. $C_{30}H_{29}N_3O_2$ requires C, 77.72; H, 6.31; N, 9.07%; *M*, 463]; δ_H 8.32 (1 H, d, 4-ArH), 7.97 (1 H, d, 9-ArH), 7.68 (1 H, d, 5-ArH), 7.60—7.32 (7 H, m with an emerging s at 7.45 of the C_6H_2 group, ArH), 4.58 (2 H, q, CH_2CH_3), 3.82 (2 H, br s exchanging with D_2O, NH_2), 2.33 (6 H, s, 2 xylidine CH_3), 1.98 (6 H, s, 2 xylyl CH_3), and 1.55 (3 H, t, CH_2CH_3). From the neutral fraction 5,8-*dimethyl*-3-(2-*naphthyl*)*quinoxalin*-2(1H)-*one* (**18**) was obtained as a colourless solid, m.p. 195 °C (from acetic acid); *M* (mass spectrum), 300. Analytical and spectral data were identical with those obtained from an authentic sample obtained by independent synthesis.

Reaction of the hydrazone (**20**) *with PPA.* The reaction, carried out at 60 °C, was complete in 20 min and work-up of the mixture gave a crude product which was chromatographed on a silica gel column with chloroform. This afforded 3-(4-*amino*-3,5-*dimethylphenyl*)*azulene*-1-*carbaldehyde* (**21**), as deep-green crystals (57%), m.p. 210 °C (from toluene) [Found: C, 82.55;

H, 6.15; N, 4.8%; *M* (mass spectrum), 275. $C_{19}H_{18}N_2O$ requires C, 82.90; H, 6.18; N, 5.09%; *M*, 275]; δ_H 10.43 (1 H, s, CHO), 9.53 (1 H, d, 8-ArH, *J* 9 Hz), 8.66 (1 H, d, 4-ArH, *J* 9 Hz), 8.30 (1 H, s, 2-ArH), 7.80 (1 H, t, 6-ArH, *J* 9 Hz), 7.60 (1 H, t, 7-ArH, *J* 9 Hz), 7.43 (1 H, t, 5-ArH, *J* 9 Hz), 7.20 (2 H, s, C_6H_2), 3.70 (2 H, s exchanging with D_2O, NH), and 2.30 (6 H, s, 2 CH_3).

5,8-*Dimethyl*-3-*phenylquinoxalin*-2(1H)-*one* (**5f**).—A mixture of ethyl phenylglyoxylate (0.6 g) and 3% aqueous sodium hydroxide (20 ml) was refluxed for 10 min and to the clear solution was added 3,6-dimethyl-*o*-phenylenediamine hydrochloride[28] (0.56 g); the pH was then adjusted to 6 with 5% aqueous hydrochloric acid. The resulting solution was refluxed for 1 h to give a brown precipitate which was filtered off and crystallized to afford the title compound, whose physical and spectral data were identical with those shown by the product isolated from the reaction of compounds (**4**) and (**4g**) with PPA.

5,8-*Dimethyl*-3-(p-*tolyl*)*quinoxalin*-2(1H)-*one* (**5e**).—The reaction between ethyl *p*-tolylglyoxylate and 3,6-dimethyl-*o*-phenylenediamine was carried out following the procedure described above for the synthesis of compound (**5f**). Physical and spectral data for the product were identical with those shown by the product isolated from the reaction of (**4e**) with PPA.

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Received 4*th August* 1987; *Paper* 7/1437