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THERMAL INDOLIZATION OF ARYLHYDRAZONES

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ABSTRACT

Thermal cyclization of arylhydrazones in the absence of acid catalyst has been investigated. Indole was not obtained from acetaldehyde phenylhydrazone; aniline, N-ethylaniline, and an unidentified compound were isolated. Phenylhydrazones of cyclohexanone and cyclopentanone and their 2-substituted derivatives were cyclized, often in good yield, to the indole and indolenine; the nature of the substituent markedly influences the ratio of the two products. Gas–liquid chromatographic analysis of the reaction mixture from indolization of two arylhydrazones revealed no crossed products. Nitrophenylhydrazones do not cyclize in good yield, but thermal indolization of some pyridylhydrazones is a good method for the preparation of pyrrolopyridines.

One of the most useful methods available for the preparation of indoles is the acid-catalyzed cyclization of phenylhydrazones discovered by Fischer (1). Many Brønsted and Lewis acids have been used as catalysts. The mechanism of the reaction was investigated by Robinson and the proposed intramolecular cyclization process has been accepted by later workers, with some slight modification. A review of the mechanism and some aspects of the synthetic utility of the reaction has appeared recently (2).

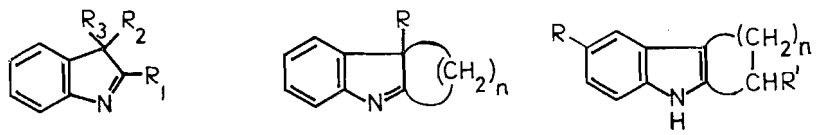
Early work led to the idea that an acid catalyst and a high temperature were essential for a successful Fischer indole synthesis. However, later work (3) has shown that the acid may assist in the first stage of the reaction, i.e. the tautomerization of the hydrazone to the enehydrazine, but is not generally essential for this or later stages of the cyclization. The early ideas may explain why an observation (4) that distillation of acetophenone phenylhydrazone gave some 2-phenylindole was ignored, until Fitzpatrick and Hiser (5) reported several phenylhydrazones were converted into the corresponding indoles on boiling a solution of the phenylhydrazone in a suitable high-boiling solvent. The reaction occurred in the absence of any acid catalyst and, indeed, in one case, in the presence of sodium hydroxide. The examples quoted by Fitzpatrick and Hiser were somewhat limited in variety. Since the reaction has obvious interest and application due to the experimental simplicity, we have investigated this thermal indolization reaction.

Indole cannot be prepared by the acid-catalyzed cyclization of acetaldehyde phenylhydrazone, though propionaldehyde and higher aldehyde phenylhydrazones do give the 3-alkylindoles (2). Fitzpatrick and Hiser (5) report the thermal cyclization of propionaldehyde *p*-tolylhydrazone but make no mention of attempts to cyclize acetaldehyde phenylhydrazone. Our efforts to obtain indole in this way were unsuccessful, though ammonia was evolved from the reaction mixture. The product consisted of a steam-volatile fraction and a nonvolatile black residue. Fractional distillation of the volatile material yielded N-ethylaniline, aniline, and an unidentified component. Since our experiments were completed, Robinson (2) has recorded that he was unable to obtain indole by this technique, though the formation of ammonia was again noted. The evolution of ammonia (possibly accompanied by other basic gas) is not a reliable indication of the formation of an indole, nor is the rate of evolution of the basic gas always a trustworthy criterion on which to judge the optimum reaction time. It seems likely that, in certain cases, two competing reactions may occur; one leading to the indole and the other giving polymeric products. Both reactions involve the evolution of basic gas.

TABLE I

Phenylhydrazone of:	Thermal cyclization		Acetic acid (7)	Sulfuric acid (7)
	Indolenine (II) (%)	Indole (III) (%)	Indole (%)	Indole (%)
Cyclohexanone	0	100	100	100
2-Methylcyclohexanone	51	49	9	68
2-*n*-Propylcyclohexanone	28	72	—	—
2-Phenylcyclohexanone	13	87	28	73
2-Cyclohexylcyclohexanone	4	96	10	63

Acid-catalyzed cyclization of phenylhydrazones from aldehydes or ketones having only one hydrogen on the α-carbon atoms give indolenines (I). Robinson (6) has used the thermal cyclization technique to prepare such compounds. Pausacker (7) has shown that the ratio of 1,2,3,4-tetrahydrocarbazolenine (II, $n = 4$, R = alkyl or aryl) to 1,2,3,4-tetrahydrocarbazole (III, $n = 3$, R = H, R′ = alkyl or aryl), formed by acid-catalyzed cyclization of 2-substituted cyclohexanone phenylhydrazones, depends on the nature of the acid catalyst: glacial acetic acid favored the formation of the tetrahydrocarbazolenine, while dilute sulfuric acid gave the tetrahydrocarbazole preferentially. We find that 1,2,3,4-tetrahydrocarbazole (III, $n = 3$, R = R′ = H) (83% yield) is obtained by boiling a solution of cyclohexanone phenylhydrazone in diethylene glycol. Thermal cyclization of 2-methyl-, 2-*n*-propyl-, 2-phenyl-, and 2-cyclohexyl-cyclohexanone phenylhydrazones gave mixtures of the corresponding 1,2,3,4-tetrahydrocarbazolenine (II, $n = 4$, R = CH_3, C_3H_7, C_6H_5, and C_6H_{11}) and 1,2,3,4-tetrahydrocarbazole (III, $n = 3$, R = H, R′ = CH_3, C_3H_7, C_6H_5, and C_6H_{11}) in the proportions shown in Table I. The high proportion of tetrahydrocarbazole resembles the results for the dilute sulfuric acid catalyzed cyclizations (7), but the steric size of the substituent has a more marked effect on the ratio of products from the thermal cyclizations than in the acid-catalyzed indolization.



I II III

When an indole shows exceptional acid sensitivity, the thermal cyclization technique appeared to offer advantages over the acid-catalyzed procedure. For example, 1,2,3,4-tetrahydrocyclopent[*b*]indole (III, $n = 2$, R = R′ = H) rapidly forms a red gum in the presence of an acid, and previous preparations (8) have used dilute sulfuric acid catalyzed indolization of cyclopentanone phenylhydrazone and extraction of the indole from the gum. 8*b*-Alkyl-1,2,3,8*b*-tetrahydrocyclopent[*b*]indoles (II, $n = 3$, R = alkyl) were not known; a reported attempt to cause indolization of 2-ethylcyclopentanone phenylhydrazone by acid-catalyzed procedure failed (9). 1,2,3,8*b*-Tetrahydrocyclopent[*b*]indole (III, $n = 2$, R = R′ = H) was now obtained in high yield by the thermal cyclization technique and was more stable than that obtained by the acid-catalyzed process. Further, 1,2,3,8*b*-tetrahydro-8*b*-methylcyclopent[*b*]indole (II, $n = 3$, R = CH_3) and the indole (III, $n = 2$, R = H, R′ = CH_3) were obtained, though in poor yield, by thermal cyclization of 2-methylcyclopentanone phenylhydrazone, while attempts to cause indolization

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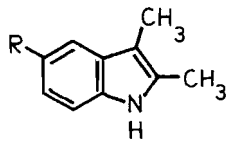
in the presence of glacial acetic acid, dilute sulfuric acid or zinc chloride gave only intractable material. However, attempts to obtain 1,4-dihydro-4-methyl-1-phenylcyclopent[*b*] indole (V) by thermal cyclization of 3-phenylcyclopent-2-en-1-one α-methylphenylhydrazone failed.



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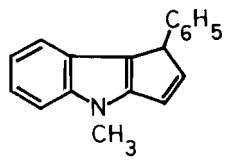
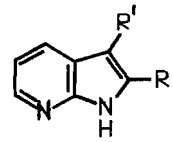


V



VI

It has been suggested (10), on the basis of the isolation of crossed products, that the acid-catalyzed formation of indoles may occur by a free radical mechanism. This idea was later shown to be erroneous (11): crossed products having been formed by hydrolysis of the arylhydrazones and formation of crossed arylhydrazones, or direct transhydrazonation (12), and subsequent cyclization. Any tendency towards a free radical type of mechanism would be expected to be favored by the purely thermal cyclization technique. Consequently we have analyzed the products of the thermal cyclization of two separate pairs of arylhydrazones.

1,2,3,4-Tetrahydrocarbazole (III, $n = 3$, R = R′ = H), 1,2,3,4-tetrahydro-6-methylcarbazole (III, $n = 3$, R = CH_3, R′ = H), 1,2,3,8*b*-tetrahydrocyclopent[*b*]indole (III, $n = 2$, R = R′ = H) were prepared in high yield by thermal cyclization of the corresponding arylhydrazones. An analytical separation of these three was achieved by gas–liquid chromatography, but (III, $n = 2$, R = CH_3, R′ = H) was not separated from (III, $n = 3$, R = R′ = H). Gas–liquid chromatographic analysis of the reaction product from the thermal indolization of a mixture of cyclopentanone phenylhydrazone and cyclohexanone *p*-tolylhydrazone in diethylene glycol showed the presence of neither (III, $n = 2$, R = CH_3, R′ = H) nor (III, $n = 3$, R = R′ = H), only the expected (III, $n = 2$, R = R′ = H) and (III, $n = 3$, R = CH_3, R′ = H) were found. A similar experiment involving the indolization of cyclohexanone phenylhydrazone and ethyl methyl ketone *p*-tolylhydrazone in the same reaction mixture gave only 2,3,5-trimethylindole (IV, R = CH_3) and 1,2,3,4-tetrahydrocarbazole, no 2,3-dimethylindole (IV, R = H) or 1,2,3,4-tetrahydro-6-methylcarbazole (III, $n = 3$, R = CH_3, R′ = H) were present: in this experiment all four possible products were resolved by gas–liquid chromatography. These results, together with the high yields frequently obtained, indicate that thermal indolization of arylhydrazones does not proceed by free radical mechanism.

Arylhydrazones containing an electron-deficient aromatic nucleus undergo acid-catalyzed indolization much less rapidly than the corresponding phenylhydrazones (2). Thus, nitrophenylhydrazones cyclize with some difficulty and the choice of catalyst is critical (13). We find that thermal cyclization of cyclohexanone *p*-nitrophenylhydrazone to the nitrotetrahydrocarbazole (III, $n = 3$, R = NO_2, R′ = H) occurs in only poor yield. Addition of cuprous chloride to the reaction mixture caused a more rapid evolution of ammonia, but no increase in the yield of (III, $n = 3$, R = NO_2, R′ = H).

Pyridylhydrazones also contain an electron-deficient nucleus, but have the additional feature that in acid solution further deactivation occurs due to protonation of the pyridyl nucleus. Attempts to use acid catalysts in the cyclization of these compounds have had little success, and Robison (14) concluded that only those 2-pyridylhydrazones cyclize

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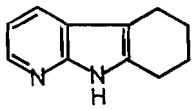
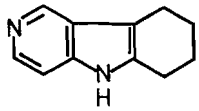


VII



VIII

to the pyrrolo[2,3-*b*]pyridine (VI, R = R′ = H), where the corresponding phenylhydrazones cyclize with extreme ease. Cyclohexanone and benzyl phenyl ketone 2-pyridylhydrazones have been cyclized, using polyphosphoric acid as catalyst, to 6,7,8,9-tetrahydro-α-carboline (VII) and 2,3-diphenylpyrrolo[2,3-*b*]pyridine (VI, R = R′ = C_6H_5); the yields were 53% and 12%. Thermal cyclization in diethylene glycol gave yields of 70% and 56% respectively.

Indolization of pyridylhydrazones by fusion with zinc chloride has been reported in some cases, the product being first obtained as the chlorozincate. Mann *et al.* (15) obtained a chlorozincate (2.8 g) on fusion of cyclohexanone 4-pyridylhydrazone (2 g) with an excess of zinc chloride, and then obtained 6,7,8,9-tetrahydro-γ-carboline (VIII) in unspecified yield. Thermal cyclization afforded the tetrahydro-γ-carboline (VIII) directly in 95% yield. The high yields obtained in these thermal cyclizations of pyridylhydrazones are surprising, and in marked contrast to the results with nitrophenylhydrazones. Details of further applications of thermal indolization to the preparation of pyrrolopyridines will be reported elsewhere.

EXPERIMENTAL

Infrared spectra were recorded on a Grubb Parsons GS3 spectrophotometer. Gas–liquid chromatography apparatus was a Pye Argon Chromatograph.

Attempted Indolization of Acetaldehyde Phenylhydrazone

Acetaldehyde phenylhydrazone (65 g) in diethylene glycol (300 ml) was boiled under reflux for 5 days. Ammonia was evolved during this time and the mixture darkened. The mixture was steam distilled to give a volatile fraction and much residual black tar, which was not investigated further. The distillate was extracted with ether and dried (Na_2SO_4), the ether removed, and the pale yellow oil (11.4 g) fractionally distilled to give fraction (i), b.p. 44–50° at 2.5 mm (3.7 g), redistilled and collected over the range 64–66° at 8 mm, n_D^{21} 1.5840, and identified as aniline by conversion to acetanilide; fraction (ii), b.p. 62–68° at 2.5 mm (5.5 g), was found to contain basic and neutral components. The basic compound was separated by extraction with acid in the usual way and distilled, b.p. 86–90° at 10 mm (0.6 g), n_D^{23} 1.5536, and identified as mainly N-ethylaniline by formation of a picrate and melting point mixed melting point with an authentic sample, 130–132°. The non-basic component was distilled, b.p. 84–88° at 10 mm (1.7 g) n_D^{21} 1.5998.

Anal. Calcd. for C_6H_6N: C, 78.3; H, 6.5; N, 15.2. Found: C, 78.2; H, 6.3; N, 15.2.

The infrared spectrum showed absorption at 3 413 cm^{-1}. The Ehrlich test was positive, but the compound was not investigated further.

Thermal Indolization of Phenyl- and p-Tolylhydrazones

The general method adopted was to prepare the arylhydrazone from the corresponding arylhydrazine and ketone by standard procedure, and to purify the product by distillation under reduced pressure or crystallization. A 10–20% solution of the arylhydrazone, in ethylene glycol or diethylene glycol, was boiled under reflux for a few hours and then poured into ice water. The solid was filtered off and recrystallized. Reaction conditions and yields are recorded in Table II. The indoles, with one exception (III, *n* = 2, R = CH_3, R′ = H), were known compounds and had melting points in accordance with the literature values.

1,2,3,4-Tetrahydro-7-methylcyclopent[b]indole (III, n = 2, R = CH_3, R′ = H) crystallized from petroleum ether (b.p. 60–80°) as colorless prisms, m.p. 116–118°.

Anal. Calcd. for $C_{12}H_{13}N$: C, 84.3; H, 7.6. Found: C, 84.6; H, 7.8.

It gave a *picrate* as brown needles from aqueous ethanol, m.p. 145–147° (decomp.).

Anal. Calcd. for $C_{18}H_{16}N_4O_7$: C, 54.0; H, 4.0. Found: C, 53.6; H, 4.2.

Indolization of 2-Substituted Cyclohexanone Phenylhydrazones

Phenylhydrazones of 2-methyl-, 2-*n*-propyl-, 2-phenyl-, and 2-cyclohexyl-cyclohexanone were prepared from the corresponding 2-substituted cyclohexanones and phenylhydrazine. The indolization procedure

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TABLE II

$R.C_6H_4.NH.NH_2$	Ketone	Solvent*	Time (h)	Product	Yield (%)
R = H	Cyclohexanone	DEG	1	III, n = 3, R = R′ = H	83†
R = H	Cyclopentanone	DEG	1	III, n = 2, R = R′ = H	78‡
R = H	Ethyl methyl ketone	EG	3	IV, R = H	65‡
R = *p*-CH_3	Cyclohexanone	DEG	12	III, n = 3, R = CH_3, R′ = H	73‡
R = *p*-CH_3	Cyclopentanone	DEG	1	III, n = 2, R = CH_3, R′ = H	56‡
R = *p*-CH_3	Ethyl methyl ketone	EG	3	IV, R = CH_3	68‡

*Abbreviations: EG = ethylene glycol; DEG = diethylene glycol.
†Crystallization from ethanol.
‡Crystallization from light petroleum.

adopted was that a phenylhydrazone (10 g), in diethylene glycol (30 ml), was gently boiled under reflux for 2 h. After pouring into water, the mixture was extracted with ether, and the ethereal solution washed with dilute hydrochloric acid (3 × 25 ml). The acid washings were added to an excess of ice-cold, dilute sodium hydroxide solution. Any solid product was filtered off and recrystallized. When an oil was formed, it was extracted with ether and the indolenine distilled under reduced pressure. The above acid-washed, ethereal solution was washed with water, dried (Na_2SO_4), and filtered, the ether distilled off, and the indole crystallized.

2-Methylcyclohexanone phenylhydrazone gave 1,2,3,4-tetrahydro-11-methylcarbazolenine (II, $n = 4$, $R = CH_3$) (3.5 g), b.p. 120–126° at 1 mm, crystallized from alcohol, m.p. 68–69° (lit. m.p. 69° (9)) and 1,2,3,4-tetrahydro-1-methylcarbazole (III, $n = 3$, R = H, R′ = CH_3) (3.4 g), recrystallized from aqueous ethanol, m.p. 66–68° (lit. m.p. 69° (7)).

2-*n*-Propylcyclohexanone phenylhydrazone yielded 1,2,3,4-tetrahydro-11-*n*-propylcarbazolenine (II, $n = 4$, R = *n*-C_3H_7) (1.2 g), b.p. 120–144° at 0.5–1 mm, crystallized from petroleum ether (b.p. 60–80°), m.p. 137–139° (lit. m.p. 139° (10)) and *1,2,3,4-tetrahydro-1-n-propylcarbazole (III, n = 3, R = H, R′ =* *n*-C_3H_7) (3.1 g), recrystallized as colorless needles from benzene, m.p. 151–152°.

Anal. calcd. for $C_{15}H_{19}N$: C, 84.6; H, 8.9. Found: C, 84.5; H, 8.9.

Picrate crystallized as brown plates from ethanol, m.p. 116–118°.

Anal. Calcd. for $C_{21}H_{22}N_4O_7$: C, 57.1; H, 5.0. Found: C, 56.8; H, 4.8.

2-Phenylcyclohexanone phenylhydrazone afforded 1,2,3,4-tetrahydro-11-phenylcarbazolenine (II, $n = 4$, R = C_6H_5), b.p. 175–186° at 1.5 mm (0.6 g), crystallized from petroleum ether (b.p. 60–80°), m.p. 122–124° (lit. m.p. 125° (7)) and 1,2,3,4-tetrahydro-1-phenylcarbazole (III, $n = 3$, R = H, R′ = C_6H_5) (3.9 g), recrystallized from petroleum ether (b.p. 40–60°), m.p. 97–99° (lit. m.p. 99° (7)).

2-Cyclohexylcyclohexanone phenylhydrazone gave 11-cyclohexyl-1,2,3,4-tetrahydrocarbazolenine (II, $n = 4$, R = C_6H_{11}) (0.2 g), recrystallized from petroleum ether (b.p. 60–80°), m.p. 76–78° (lit. m.p. 79° (7)) and 1-cyclohexyl-1,2,3,4-tetrahydrocarbazole (III, $n = 3$, R = H, R′ = C_6H_{11}) (4.9 g), b.p. 201–206° at 1 mm, crystallized from petroleum ether (b.p. 60°–80°) m.p. 137–139° (lit. m.p. 140° (7)).

1,2,3,8b-Tetrahydro-8b-methylcyclopent[b]indole (II, n = 3, R = CH_3) and 1,2,3,4-tetrahydro-3-methylcyclopent[b]indole (III, n = 2, R = H, R′ = CH_3)

2-Methylcyclopentanone (2.64 g) and phenylhydrazine (2.9 g) were mixed, and, after the initial exothermic reaction had slackened, the mixture was warmed on a water bath for 30 min. The water produced was removed by azeotropic distillation with benzene. The hydrazone, in diethylene glycol (20 ml), was boiled under reflux for 2 h and then poured into ice water. The oil was extracted with ether and quickly separated into basic and neutral fractions by extraction with dilute hydrochloric acid in the usual way. The basic fraction was distilled, b.p. 94–96° at 0.5 mm, as a colorless oil (0.57 g). Treatment with ethanolic picrolonic acid afforded *1,2,3,8b-tetrahydro-8b-methyl-cyclopent[b]indole picrolonate* as yellow prisms, m.p. 219–221° (decomp.).

Anal. Calcd. for $C_{22}H_{21}N_5O_5$: C, 60.1; H, 4.8; N, 16.1. Found: C, 59.7; H, 5.0; N, 15.6. The neutral fraction was distilled, b.p. 116–124° at 0.8 mm, as a colorless oil (0.12 g). Addition of ethanolic picric acid gave *1,2,3,4-tetrahydro-3-methylcyclopent[b]indole picrate*, recrystallized as dark-red needles from aqueous ethanol, m.p. 132–134°.

Anal. Calcd. for $C_{18}H_{16}N_4O_7$: C, 54.0; H, 4.0. Found: C, 54.2; H, 4.1.

Attempted Preparation of 1,4-Dihydro-4-methyl-1-phenylcyclopent[b]indole (V)

3-Phenylcyclopent-2-en-1-one (3.2 g) and α-methylphenylhydrazine (2.4 g) were mixed and, after the addition of glacial acetic acid (2 drops), warmed on a water bath for 30 min. Benzene was added and the water removed by azeotropic distillation. The *phenylhydrazone* was crystallized from ethanol as yellow prisms (4.4 g), m.p. 113–114°.

Anal. Calcd. for $C_{18}H_{18}N_2$: C, 82.5; H, 6.8. Found: C, 82.2; H, 7.0.

When a solution of this phenylhydrazone in ethylene glycol (or diethylene glycol) was boiled under reflux in a nitrogen atmosphere a basic gas was evolved, but, after pouring the reaction mixture into water, the only product isolated was a black, friable amorphous solid.

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Indolization of Mixtures of Arylhydrazones

(i) A mixture of freshly prepared cyclopentanone phenylhydrazone (1 g) and cyclohexanone *p*-tolylhydrazone (1 g), in diethylene glycol (10 ml), was boiled under reflux for 1 h and then poured into water. The oil was extracted with benzene, washed with water, and dried (Na_2SO_4). The benzene solution was submitted to gas–liquid chromatography in a column of 4% silicone oil on celite 545 (80–100 mesh) at 150°, packed in 4 ft of 5 mm (outside diameter) glass tubing, and using argon as the carrier gas at a flow rate of 20 ml/min. Retention times were measured relative to that for 1,2,3,4-tetrahydrocarbazole (III, $n = 3$, R = R′ = H) (15 min). The two peaks obtained had relative retention time (r.r.t.) of 0.68 and 1.54 and were shown to be due to 1,2,3,4-tetrahydrocyclopent[b]indole (III, $n = 2$, R = R′ = H) and 1,2,3,4-tetrahydro-6-methylcarbazole (III, $n = 3$, R = CH_3, R′ = H). 1,2,3,4-Tetrahydro-7-methylcyclopent[b]indole (III, $n = 2$, R = CH_3, R′ = H) had r.r.t. 1.02.

(ii) A similar reaction was performed with a mixture of cyclohexanone *p*-tolylhydrazone and ethyl methyl ketone phenylhydrazone. Gas–liquid chromatography in a column of 4% Apiezon L on celite 545 at 200°, in a tube of the dimensions mentioned above and at the same gas flow rate, gave two peaks, r.r.t. 0.23 and 1.27, identified as due to 1,2,3,4-tetrahydro-6-methylcarbazole (III, $n = 3$, R = CH_3, R′ = H) and 2,3-dimethylindole (IV, R = H). 1,2,3,4-Tetrahydrocarbazole had a retention time of 22.5 min and 2,3,5-trimethylindole (IV, R = CH_3) had r.r.t. 0.59.

1,2,3,4-Tetrahydro-6-nitrocarbazole (III, $n = 3$, R = NO_2, R′ = H)

Cyclohexanone *p*-nitrophenylhydrazone (3 g), in diethylene glycol (20 ml), was boiled under reflux until evolution of ammonia ceased (10 h) and then poured into water. The solid (2.1 g) was extracted with boiling benzene (2 × 50 ml). The benzene solution was passed down an alumina column and afforded an upper brown band and a lower yellow band. The latter was eluted with more benzene, and the benzene solution concentrated to give yellow prisms (0.1 g), m.p. 176–178° (lit. m.p. 177° (13)).

6,7,8,9-Tetrahydro-α-carboline (VII)

Cyclohexanone 2-pyridylhydrazone (14) (4.25 g) in diethylene glycol (20 ml) was boiled under reflux for 7 h. Ammonia was evolved and the solution became red-brown. After cooling, the mixture was poured into ice water and the solid (2.7 g) filtered off. Recrystallization from petroleum ether (b.p. 60–80°) gave pale cream needles, m.p. 153.5–154.5° (lit. m.p. 156° (14)).

2,3-Diphenylpyrrolo[2,3-b]pyridine (VI, R = R′ = C_6H_5)

Benzyl phenyl ketone 2-pyridylhydrazone (14) (6.5 g) in diethylene glycol (20 ml) was boiled under reflux for 7 h. After cooling, the solid was filtered off and washed with water. The dry solid (3.4 g, 56%) was sublimed, 230° at 1.5 mm, to give a pale cream solid m.p. 293–295° (lit. m.p. 293.5° (14)).

6,7,8,9-Tetrahydro-γ-carboline (VIII)

Cyclohexanone 4-pyridylhydrazone (15) (3 g), in diethylene glycol (20 ml), was boiled under reflux for 11 h. After cooling, the mixture was poured into water and the solid filtered off. The light brown solid (2.6 g, 95%) was recrystallized from aqueous ethanol (charcoal) to give colorless prisms, m.p. 268.5–270° (lit. m.p. 272° (15)).

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