305. *The Synthesis of Indolo(2' : 3'-1 : 2)- and Indolo(3' : 2'-1 : 2)-carbazole.*

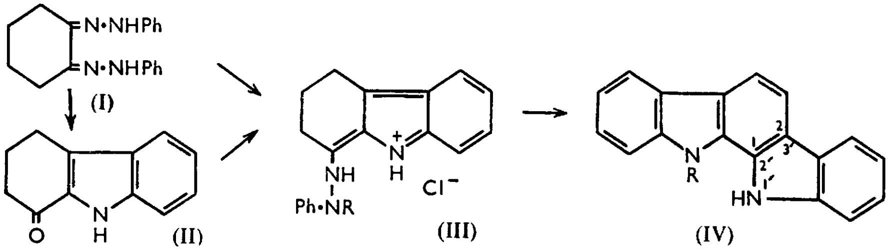
By Frederick G. Mann and Trevor J. Willcox.

It is shown that 1 : 2 : 3 : 4-tetrahydro-1-oxocarbazole, which is feebly basic, forms a very unstable phenylhydrazone but a stable yellow phenylhydrazone hydrochloride, which when heated under reduced pressure or in acetic acid solution, undergoes indolisation and dehydrogenation to give indolo(2' : 3'-1 : 2)carbazole.

Tetrahydro-4-oxocarbazole is more strongly basic and its pure crystalline hydrochloride can be isolated. It also forms a stable colourless phenylhydrazone hydrochloride, which when similarly heated gives indolo(3' : 2'-1 : 2)carbazole.

The structures of the two oxocarbazoles, their salts and their phenylhydrazone hydrochlorides are discussed.

It has been shown by Plancher, Cecchetti, and Ghigi [1] that hot dilute sulphuric acid reacts with *cyclo*hexane-1 : 2-dione bisphenylhydrazone (I), causing indolisation of one hydrazone unit and hydrolysis of the other, to form 1 : 2 : 3 : 4-tetrahydro-1-oxocarbazole (II) a detailed study of this production of the oxo-carbazole (II) has been made by Bloink and Pausacker.[2] The indolo(2' : 3'-1 : 2)carbazole system was first synthesised as the 9-methyl derivative (IV; R = Me) by Brunton, Drayson, Plant, and Tomlinson [3] using a less direct route.



Bhide, Tikotkar, and Tilak,[4] in a recent preliminary note, have shown that the oxo-carbazole (II) reacts with phenylhydrazine in boiling acetic acid, undergoing indolisation and dehydrogenation, to furnish the parent indolo(2' : 3'-1 : 2)carbazole (IV; R = H).

We have also investigated the formation of the ring-system (IV), and find that an ethanolic solution of the bisphenylhydrazone (I), when heated with hydrogen chloride, readily deposits stable yellow crystals of composition corresponding to tetrahydro-oxo-carbazole phenylhydrazone hydrochloride. The free phenylhydrazone is markedly unstable and apparently has not been recorded, but a solution of the colourless oxo-carbazole and phenylhydrazine in ethanolic hydrogen chloride when heated also deposits the yellow crystalline hydrochloride. Since, however, it is highly improbable that 1-oxocarbazole phenylhydrazone would form a stable coloured salt by simple proton addition to any of the nitrogen atoms, there is little doubt that the hydrochloride has the structure (III; R = H), and that both the colour and the stability are associated with the conjugated system so produced. The infrared spectrum of the hydrochloride shows the bands at 3140 and 2600 cm.$^{-1}$, indicating the presence of the =NH and the $\equiv$NH$^+$ group respectively: although this evidence does not preclude the structure (V; R = H), the contribution by this form is probably for the above reasons almost negligible.

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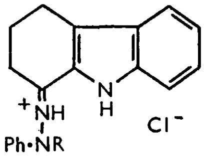
[1] Plancher, Cecchetti, and Ghigi, *Gazzetta*, 1929, **59**, 346.
[2] Bloink and Pausacker, *J.*, 1950, 1328.
[3] Brunton, Drayson, Plant, and Tomlinson, *J.*, 1956, 4783.
[4] Bhide, Tikotkar, and Tilak, *Chem. and Ind.*, 1957, 363.

Tetrahydro-1-oxocarbazole (II) reacts similarly with *N*-methyl-*N*-phenylhydrazine in ethanolic hydrogen chloride to give the yellow hydrochloride (III; R = Me), which, like the previous salt, can be recrystallised unchanged from ethanol: its infrared spectrum also shows bands at 3140 and 2600 cm.$^{-1}$.

In contrast to these results, the oxocarbazole (II) gives a normal, purple 2 : 4-dinitrophenylhydrazone (VI). When hydrogen chloride is passed into a suspension of this compound in cold acetone, a clear yellow solution is slowly obtained, but dilution with ether then rapidly restores the purple colour. The yellow colour is probably that of an unstable hydrochloride, which dissociates on dilution of the hydrogen chloride solution. It is noteworthy that an ethereal solution of the oxocarbazole (II), when treated with hydrogen chloride, deposits a yellow crystalline hydrochloride (VII), which rapidly dissociates when separated from the solution. Plant, Mears, and Oakeshott [5] have reported that both the oxocarbazole (II) and its colourless 6-bromo-derivative give yellow hydrobromides, too unstable for isolation: these salts undoubtedly have a similar structure.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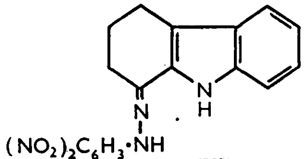
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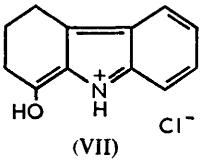
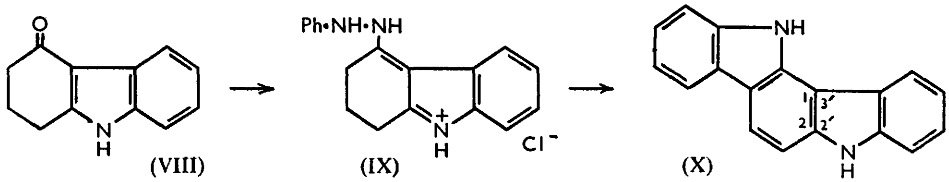

(VII)

The phenylhydrazone hydrochloride (III; R = H), when heated at 320°/0·2 mm., undergoes indolisation and dehydrogenation, affording indolo(2′ : 3′-1 : 2)carbazole (IV; R = H) as a colourless crystalline sublimate: the same process occurs when a solution of the hydrochloride in acetic acid is boiled for 5 hours. The dehydrogenation was confirmed by the infrared spectrum of the product, which showed no band corresponding to a $>CH_2$ group. The methylphenylhydrazone hydrochloride (III; R = Me) when similarly heated furnishes 9-methylindolo(2′ : 3′-1 : 2)carbazole (IV; R = Me).

Indolo(2′ : 3′-1 : 2)carbazole (IV; R = H) with methyl sulphate affords 1′ : 9-dimethylindolo(2′ : 3′-1 : 2)carbazole. The melting points of the carbazole (IV; R = H) and its 9-methyl and 1′ : 9-dimethyl derivatives (370°, 245°, and 209°, respectively) decrease with increasing methylation: this may be caused by the methyl groups progressively decreasing the degree of hydrogen-bonding, or even forcing the molecule out of the planar configuration.

1 : 2 : 3 : 4-Tetrahydro-4-oxocarbazole (VIII), when heated with phenylhydrazine in ethanol with the addition initially of a trace of acetic acid and later of ethanolic hydrogen chloride, gives colourless crystals of the phenylhydrazone hydrochloride (IX), which is also sufficiently stable to be recrystallised from ethanol. This salt differs in structure from its yellow isomer (III; R = H) in having a shorter conjugated chain and no *o*-quinonoid ring, and it is these factors which are responsible for its absence of colour.


(VIII) (IX) (X)

The hydrochloride (IX), when heated at 360°/0·2 mm., similarly undergoes indolisation and dehydrogenation to give indolo(3′ : 2′-1 : 2)carbazole (X); boiling acetic acid, however, does not produce this series of reactions. The properties of our indolo(3′ : 2′-1 : 2)carbazole (X) show that it is almost certainly identical with that which Tomlinson [6] prepared by the

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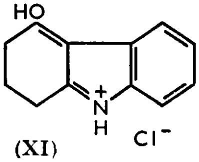
[5] Plant, Mears, and Oakeshott, *J.*, 1934, 273.

[6] Tomlinson, *J.*, 1951, 809.

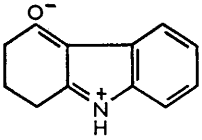
di-indolisation and subsequent dehydrogenation of bis*cyclo*hexanone *m*-phenylenedihydrazone, and afford additional evidence that her synthesis does furnish this compound and not the possible alternative indolo(2′ : 3′-2 : 3)carbazole.

Bhide *et al.*[4] report that the 4-oxocarbazole (VIII) was unaffected when its solution in acetic acid containing phenylhydrazine was boiled, and they were unable to prepare its phenylhydrazone or to indolise the phenylhydrazone of 1 : 2 : 3 : 4-tetrahydro-9-methyl-4-oxocarbazole.

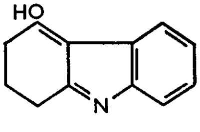
Tetrahydro-4-oxocarbazole (VIII), when treated in cold ethereal solution with hydrogen chloride, deposits a colourless hydrochloride which can be collected and kept unchanged over calcium chloride at atmospheric pressure for several days. Exposure under reduced pressure causes slow dissociation, and its melting point indicates complete dissociation on heating. There can be little doubt that the hydrochloride has the structure (XI). The 4-oxocarbazole (VIII) is, therefore, more strongly basic than the 1-oxocarbazole (II).



(XI)



(VIIIA)



(VIIIB)

It should be noted that the infrared spectra of both the 4-oxocarbazole (VIII) and its hydrochloride (XI) present indefinite features. The spectrum of the carbazole has a strong band at 1610 cm.$^{-1}$, and a rather broad band at 3060 cm.$^{-1}$. Alternative interpretations of these bands may be made: (*a*) although the band at 1610 cm.$^{-1}$ has an exceptionally low value for a >CO band, and that at 3060 cm.$^{-1}$ is unusually broad for an >NH band, these properties are consistent with existence of the carbazole as a resonance hybrid (VIII $\longleftrightarrow$ VIIIA), particularly if some additional hydrogen-bonding is present; (*b*) the bands at 1610 and 3060 cm.$^{-1}$ might be due to an >N– group and an OH group respectively, indicating the structure (VIIIB). The hydrochloride (XI) has a broad band with peaks at 2930 and 2880 cm.$^{-1}$, which may indicate an OH band partly overlaid by CH or CH_2 bands, and a band at 2230 cm.$^{-1}$ which in spite of its low value might represent the >NH$^+$ group.

In contrast, the spectrum of tetrahydro-1-oxocarbazole (II) shows a strong sharp band at 3275 cm.$^{-1}$, due to the >NH group, and a strong band at 1642 cm.$^{-1}$ attributed to the >CO group.

EXPERIMENTAL

1 : 2 : 3 : 4-*Tetrahydro*-1-*oxocarbazole Phenylhydrazone Hydrochloride* (III; R = H).—(*A*) A solution of *cyclo*hexane-1 : 2-dione bisphenylhydrazone (10 g.) in warm ethanol (225 c.c.) was treated with saturated ethanolic hydrogen chloride (20 c.c.), then heated on a steam-bath until separation of the crystalline hydrochloride was complete (10—15 min.). The mixture was cooled to 0°, and the yellow hydrochloride collected and twice recrystallised from much ethanol; it had m. p. 182—183° (decomp.), resolidifying to a reddish-brown solid which did not melt below 360° (Found: C, 69·6; H, 5·9; N, 13·7. $C_{18}H_{17}N_3$,HCl requires C, 69·35; H, 5·8; N, 13·5%). The yields of crude material were variable (50—75%) and in one experiment attained 89%. The salt is insoluble in hot water and almost insoluble in most organic solvents.

(*B*) A solution of 1-oxocarbazole (II) (0·2 g.) and phenylhydrazine (0·12 g., 1·1 mol.) in ethanol (5 c.c.) was mixed with saturated hydrogen chloride (5 c.c.), boiled under reflux for 30 min., and cooled to 0°. The deep yellow crystals of the hydrochloride (III; R = H) (0·1 g.), when collected, washed with water, and once recrystallised from ethanol, had m. p. 180—182° (decomp.), unaffected by admixture with the above product.

The hydrochloride, when treated with aqueous sodium hydroxide, gave the free hydrazone, which rapidly darkened and decomposed.

1 : 2 : 3 : 4-*Tetrahydro*-1-*oxocarbazole* N-*Methyl*-N-*phenylhydrazone Hydrochloride* (III; R = Me).—A solution of 1-oxocarbazole (1 g.) and *N*-methyl-*N*-phenylhydrazine (0·8 g., 1·2 mol.) in warm ethanol (25 c.c.), when treated with saturated ethanolic hydrogen chloride (5 c.c.),

rapidly deposited yellow crystals of the *hydrochloride hemihydrate* (0·74 g., 42%), m. p. 181—182° (decomp.) (from ethanol) (Found, on independent samples: C, 68·0, 68·4; H, 6·1, 6·0. $C_{19}H_{19}N_3$,HCl,0·5H_2O requires C, 68·2; H, 6·3%).

Tetrahydro-1-*oxocarbazole* 2 : 4-*dinitrophenylhydrazone* (VI) was readily formed in ethanol, and separated as purple crystals, m. p. 299—301° (decomp.), from much dioxan (Found: C, 59·0; H, 4·2. $C_{18}H_{15}O_4N_5$ requires C, 59·2; H, 4·1%).

Indolo(2′ : 3′-1 : 2)*carbazole* (IV; R = H).—(*A*) The hydrochloride (III; R = H) (1 g.) was heated in an inclined glass tube at 0·2 mm., the temperature being increased slowly to 320°. Sublimation was complete in *ca.* 15 min., leaving only a trace of residual yellow resin. The sublimate was washed with water, dried (yield, 0·75 g., 90%), recrystallised from ethanol, and resublimed, giving the indolocarbazole (IV; R = H) as colourless crystals, m. p. 370° (lit.,[4] 371°) (Found: C, 84·8; H, 4·6; N, 11·2. Calc. for $C_{18}H_{12}N_2$: C, 84·4; H, 4·7; N, 10·9%).

(*B*) A solution of the hydrochloride (0·2 g.) in acetic acid (10 c.c.) was boiled under reflux for 5 hr., the indolocarbazole separating after *ca.* 1 hr. The solution was concentrated and cooled, and the indolocarbazole collected and washed with water (0·1 g., 60%); after sublimation it had m. p. and mixed m. p. 370°.

The ultraviolet spectrum of the indolo(2′ : 3′-1 : 2)carbazole in ethanol showed the following characteristics (ε values in parentheses): $\lambda_{max.}$ 257 (75,600), 269 (75,510), 285 (34,100), 324 (29,750), 340 (9060), 357 (4760), $\lambda_{min.}$ 263—264 (71,600), 280·5 (29,410), 296 (7710), 335—337 (8725), 351 (3760).

The indolocarbazole was unaffected when heated with palladium–charcoal, alone or in *p*-cymene. Its ethanolic solution showed a violet fluorescence and readily gave a dipicrate, m. p. 203—204° (lit.,[4] 202°), red-brown needles (Found: N, 15·45. Calc. for $C_{18}H_{12}N_2$,2$C_6H_3O_7N_3$: N, 15·3%).

9-*Methylindolo*(2′ : 3′-1 : 2)*carbazole* (IV; R = Me).—The hydrochloride (III; R = Me), when similarly heated at 350°/0·2 mm., gave a sublimate which, when purified as before, furnished the indolocarbazole, colourless prisms, m. p. 244—245° (lit.,[3] 243—244°) (Found: C, 84·3; H, 5·4; N, 10·5. Calc. for $C_{19}H_{14}N_2$: C, 84·4; H, 5·2; N, 10·4%).

1′ : 9-*Dimethylindolo*(2′ : 3′-1 : 2)*carbazole.*—Saturated aqueous sodium hydroxide solution (0·1 c.c.) was added to a mixture of the carbazole (IV; R = H) (0·2 g.), methyl sulphate (0·22 g., 2·2 mols.), and acetone (1 c.c.), which was shaken for 30 min., rapidly giving a clear solution which then deposited crystals. The mixture was poured into water. The precipitated, colourless, almost pure *dimethylindolocarbazole* (0·2 g., 90%) formed needles, m. p. 209°, from aqueous acetone (Found: C, 84·5; H, 5·7; N, 10·15. $C_{20}H_{16}N_2$ requires C, 84·5; H, 5·7; N, 9·85%). An ethanolic solution showed a violet fluorescence in ultraviolet light.

1 : 2 : 3 : 4-*Tetrahydro*-4-*oxocarbazole Phenylhydrazone Hydrochloride* (IX).—A mixture of 4-oxocarbazole (VIII) (1·5 g.), phenylhydrazine (0·88 g., 1·1 mols.), acetic acid (0·1 c.c.), and ethanol (80 c.c.) was boiled under reflux for 24 hr., filtered hot to remove a trace of unchanged carbazole, diluted with saturated ethanolic hydrogen chloride (10 c.c.), and cooled. The colourless *hydrochloride* which separated had m. p. 233—235° after crystallisation from ethanol (Found: C, 69·4; H, 5·9; N, 13·4. $C_{18}H_{17}N_3$,HCl requires C, 69·35; H, 5·8; N, 13·5%). This hydrochloride is soluble in cold water, unlike the isomer (III; R = H), and gives a *picrate*, yellow crystals, m. p. 200—202° (immersed at 190°) (from methanol) (Found: C, 57·2; H, 3·8; N, 16·9. $C_{18}H_{17}N_3$,$C_6H_3O_7N_3$ requires C, 56·9; H, 4·0; N, 16·6%).

The infrared spectrum of the hydrochloride showed a band at 3120 cm.$^{-1}$, and a rather broad band at 2840 cm.$^{-1}$, attributed to the $>$NH and $\geqslant$NH$^+$ group respectively.

Indolo(3′ : 2′-1 : 2)*carbazole* (X).—The hydrochloride (IX) (0·5 g.), when heated to 360°/0·2 mm., gave a colourless sublimate having a pale yellow band at the lower end. The total sublimate, when washed with water, dried (yield 0·3 g., 52%), recrystallised from aqueous ethanol, and resublimed in hydrogen, furnished the indolo-carbazole (X), plates, m. p. 298° (lit.,[6] 299—300°) (Found: C, 83·7; H, 4·7. Calc. for $C_{18}H_{12}N_2$: C, 84·4; H, 4·7%). In benzene solution it showed a strong violet fluorescence in ultraviolet light.

Its ultraviolet spectrum in ethanol showed the characteristics (ε in parentheses): $\lambda_{max.}$ 2630 (40,600), 2830 (35,800), 3200 (9730), 3390 (8750), 3540 (15,180); $\lambda_{min.}$ 2720 (29,900), 3160 (8700), 3310 (4345), 3450 (6160). These values accord well with the curve obtained by Tomlinson [6] for a dioxan solution.

Tetrahydro-4-*oxocarbazole Hydrochloride* (XI).—When dry hydrogen chloride was passed into a solution of the carbazole in dry ether (in which the carbazole is only moderately soluble), the colourless crystalline *hydrochloride* rapidly separated. It was collected, washed with cold ethereal hydrogen chloride, and dried in a calcium chloride desiccator at atmospheric pressure (Found: C, 64·55; H, 5·5; N, 6·5. $C_{12}H_{11}ON,HCl$ requires C, 65·0; H, 5·4; N, 6·3%). The salt, when heated from room temperature, had m. p. 220—222°, *i.e.*, that of the oxocarbazole. When immersed at 165°, it partially melted with some effervescence, resolidified, and then melted at 220—222°: when immersed at 200°, complete fusion (with some effervescence) occurred, followed by resolidification and melting as before.

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