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SYNTHESIS OF HETEROCYCLIC STEROIDS—V*

ATTEMPTED SYNTHESIS OF B-NOR-6-AZA-6-METHYLEQUILENIN

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Abstract—Unsuccessful attempts have been made to synthesize the pyrrolo analogues of equilenin and 3-desoxyequilenin. The synthesis of several carbazole derivatives required in this connexion is described.

4-Aza[1] and 16-aza[2] analogues of steroids have been prepared by degradation of rings A and D in natural steroids and subsequent lactam formation. 17-a-Aza-D-homosteroids[3] have been prepared by Beckmann rearrangement of oximes of 17-ketosteroids. Pyridazenone analogues[4] have been synthesized by degradation of ring A in cholesterol and subsequent treatment with hydrazine, whereas the pyridyl steroids[5] have been synthesized from keto steroids by treatment with pyridyl lithium and hence the nitrogen atom does not form a part of the steroidal skeleton.[6]

Although I and II could not be synthesized, several new carbazole derivatives which were prepared in this connexion are now reported.

7-Methoxy-9-methyl-1-oxo-1,2,3,4-tetrahydrocarbazole (III), starting material for the proposed synthesis of (I), was prepared as in Chart 1. Cyclization of IV gave a mixture of two isomers (A) and (B) represented as 7-methoxy-1-oxo-1,2,3,4-tetrahydrocarbazole (V) and 5-methoxy-1-oxo-1,2,3,4-tetrahydrocarbazole (VI). Since only (A) could be isolated in small quantity, the mixture was methylated and the products separated by chromatography. The two methylated products C and D may be represented as 7-methoxy-9-methyl-1-oxo-1,2,3,4-tetrahydrocarbazole (III) and the corresponding 5-methoxy isomer (VII) respectively. Compound (A), on methylation, gives C. The latter on Wolff–Kishner–Huang-Minlon reduction gives E which on dehydrogenation with chloranil[7] yields F. Compound F has the same m.p. as 2-methoxy-9- methylcarbazole[8] (IX) and the two are identical. Consequently, compound A, C, D and E are assigned the structures V, III, VII, and VIII respectively.

In an attempt to convert III to B-nor-6-aza-6-methylequilenin (I) according to Johnson *et al.*[9], IV was converted to 9,10-dihydro-6-methoxy-4-methylcarbazolo-(2,1-d)-isoxazole (XI) through the intermediate 2-hydroxymethylene derivative (X) in the usual manner. The isoxazole (XI) was then isomerized in alkaline medium to

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* Part IV: *Tetrahedron* **10**, 223 (1960).

[1] C. C. Bolt, *Rec. Trav. Chem.* **57**, 905 (1938); R. B. Woodward, F. Sondheimer, D. Taub, K. Heusler and W. M. Mclamore, *J. Amer. Chem. Soc.* **74**, 4223 (1952).

[2] W. E. Bachmann and F. Ramirez, *J. Amer. Chem. Soc.* **72**, 2527 (1950).

[3] St. Kaufmann, *J. Amer. Chem. Soc.* **73**, 1779 (1951); B. M. Regan and F. N. Hayes, *Ibid.* **78**, 639 (1956).

[4] F. L. Weisenborn, D. C. Remy and T. L. Jacobs, *J. Amer. Chem. Soc.* **76**, 552 (1954).

[5] J. Heer and K. Hoffmann, *Helv. Chim. Acta* **39**, 1804 (1956).

[6] P. A. Plattner, P. Treadwell and C. Scholz, *Helv. Chim. Acta* **28**, 771 (1945).

[7] B. M. Barclay and N. Campbell, *J. Chem. Soc.* 530 (1945).

[8] I. F. Muth Ger. Pat. 553, 409 (1931).

[9] W. S. Johnson, J. W. Petersen and C. D. Gutsche, *J. Amer. Chem. Soc.* **69**, 2942 (1947).

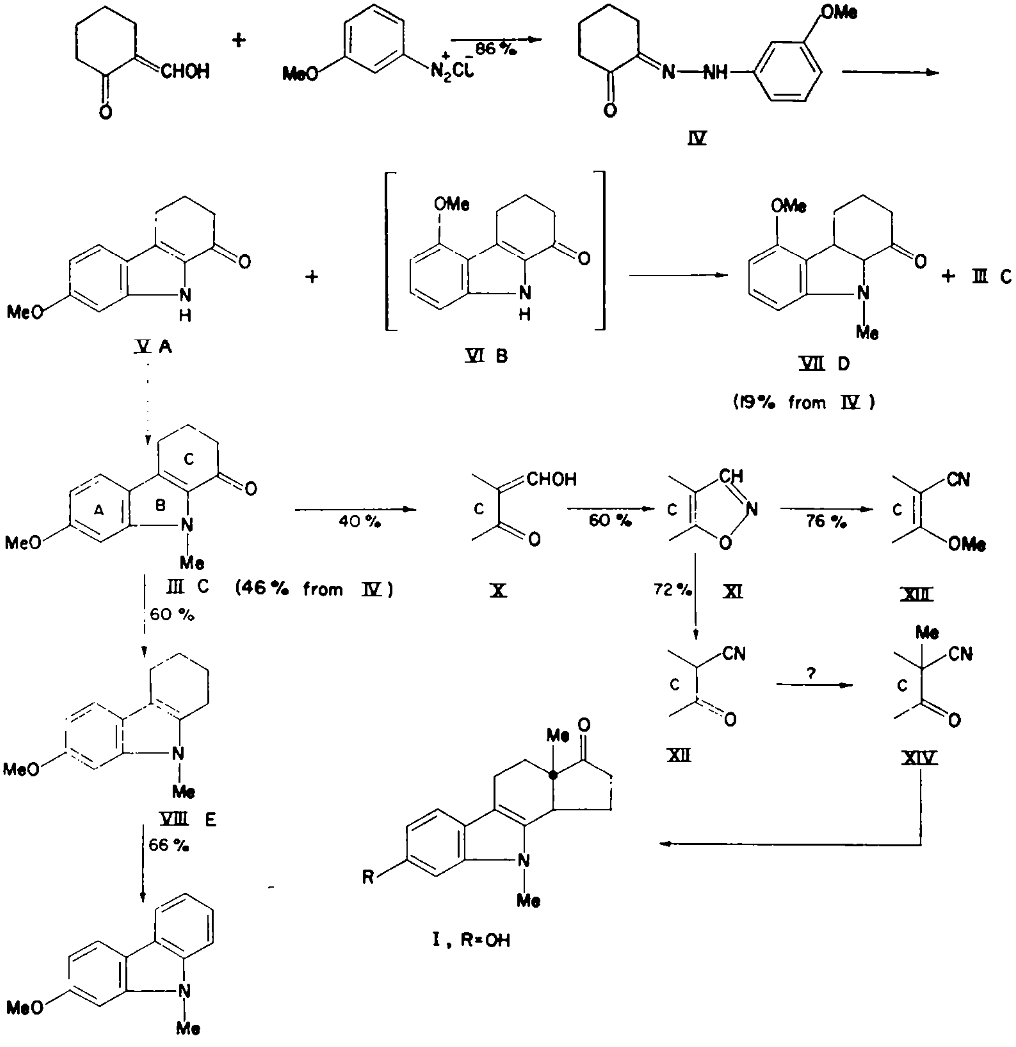

Chart I.

the alkali-soluble 2-cyano-7-methoxy-9-methyl-1-oxo-1,2,3,4-tetrahydrocarbazole (XII) and methylated *in situ* yielding only 2-cyano-1,7-dimethoxy-7-methyl-3,4-dihydrocarbazole (XIII), instead of the desired 2-cyano-2,9-dimethyl-7-methoxy-1-oxo-1,2,3,4-tetrahydrocarbazole (XIV). We erroneously reported[10] as a C-methyl derivative (XIV), but the methoxyl value and the I.R. spectrum (strong band at 2222 cm^{-1} (4·5μ) indicating presence of a nitrile group in conjugation with a double bond) leaves no doubt, that the structure of XIII is an O-methyl ether (Fig. 1). All attempts to effect C-methylation of the intermediate cyano-ketone (XII) were unsuccessful.

The failure of the isoxazole (XI) to give the C-methyl-cyanoketone (XIV) is associated with the strong enolizability imparted to the ketonic function of the intermediate cyanoketone (XII) by the electron-donating N-methyl and 7-methoxy groups.

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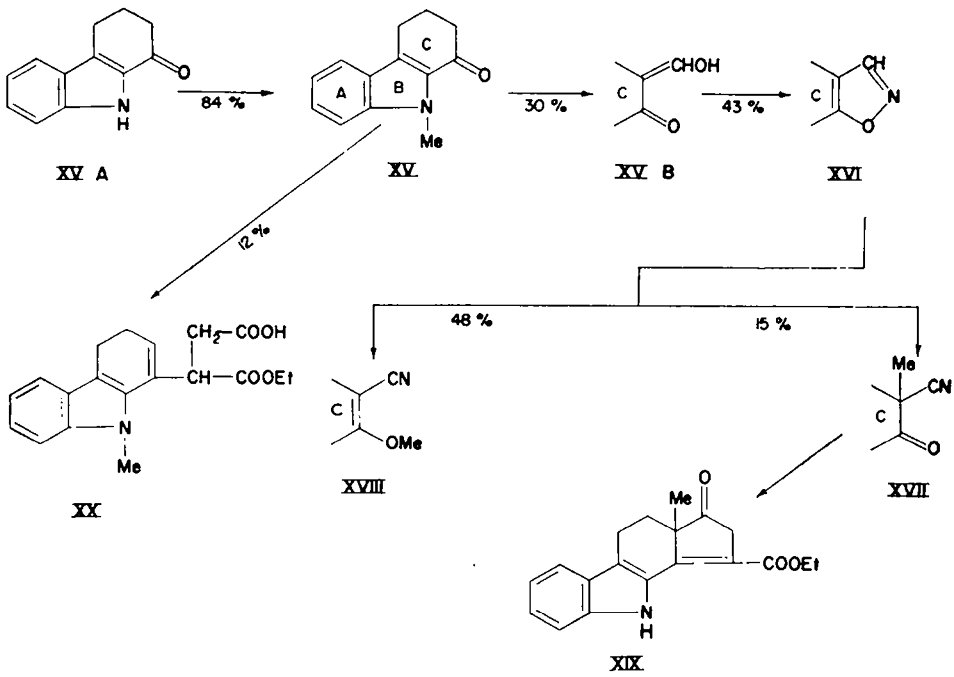
[10] G. V. Bhide, N. R. Pai, N. L. Tikotkar and B. D. Tilak, *Tetrahedron* **4**, 420 (1958).

It is interesting to record here that in the case of 1-oxo-9-methyl-1,2,3,4-tetrahydrocarbazole (XV), Stobbe reaction was successful (see later), although here the major product of methylation of isoxazole was the O-methylated derivative. It, therefore, appears that the 1-oxo function in these compounds possess pronounced enolic activity.

Attempts were made to isomerize the O-methyl derivative (XIII) to the C-methyl derivative (XIV) but without success.



In view of the formation of isomers such as V and VI, experiments were carried out earlier with 1-oxo-1,2,3,4-tetrahydrocarbazole (XV A[11]). The latter was converted to the N-methyl derivative (XV) and through Johnson's equilenin synthesis to the isoxazole (XVI). Isomerization of the latter followed by methylation *in situ* gave 2-cyano-2,9-dimethyl-1-oxo-1,2,3,4-tetrahydrocarbazole (XVII) along with the isomeric 2-cyano-1-methoxy-9-methyl-3,4-dihydrocarbazole (XVIII) in larger yield. The structure of the above products was proved by estimation of methoxyl groups and the study of their I.R. spectra. The compound XVII showed bands at 1665 and 2240 cm^{-1} characteristic of the keto group conjugated with an aromatic residue as in G and of the weak nitrile group respectively (Fig. 2). The compound XVIII, on the other hand, gave a strong band at 2230 cm^{-1} indicating the presence of a nitrile group in conjugation with a double bond as shown in H (Fig. 3).

The methyl-keto-nitrile (XVII) was then subjected to Stobbe condensation with diethyl succinate under various experimental conditions wherein the relevant factors such as the amount of condensing agent (potassium-butoxide), the time and temperature of the reaction were altered. However, the Stobbe reaction failed XVII being

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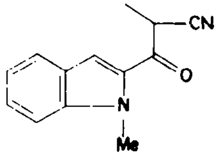
[11] A. Kent, *J. Chem. Soc.* 976 (1935).



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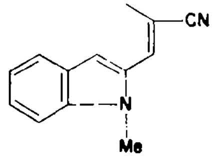

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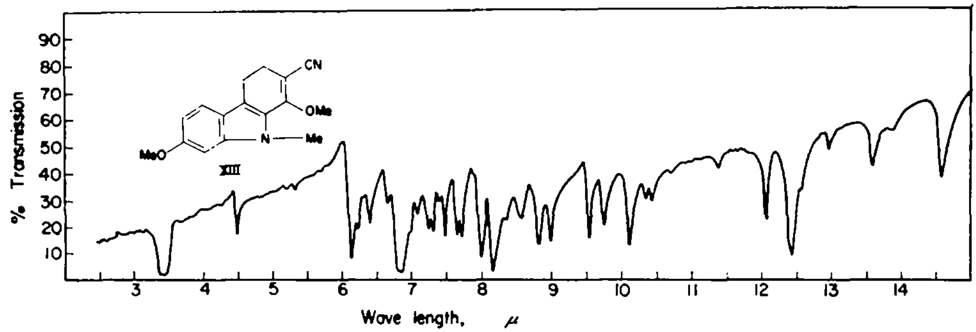
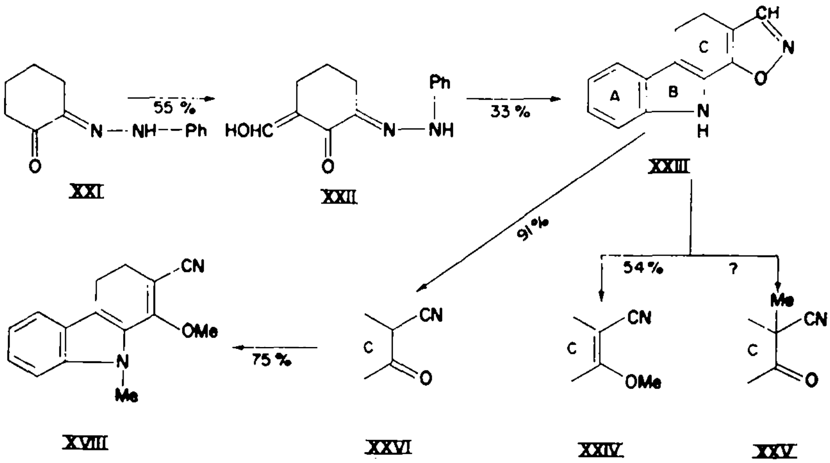


FIG. 1.

recovered unchanged. This failure may be due to the inaccessibility of the 1-oxo-group since XV undergoes a Stobbe condensation to yield β-carbethoxy-β-(3,4-dihydro-9-methylcarbazolyl-1)-propionic acid (XX) although the yield is low.



A new approach was explored wherein the N-methyl group in XVII was deleted, making the 1-oxo-group more accessible for the Stobbe condensation. Formylation of cyclohexane-1,2-dione-monophenylhydrazone[12] (XXI) yielded 3-hydroxymethyl-ene-2-oxo-cyclohexanone-phenylhydrazone (XXII). Interaction of the latter with hydroxylamine hydrochloride afforded 9,10-dihydrocarbazolo-(2,1-d)-isoxazole (XXIII), the isoxazole and the carbazole rings being built up simultaneously. Treatment of XXIII with potassium butoxide followed by methyl iodide gave the O-methyl

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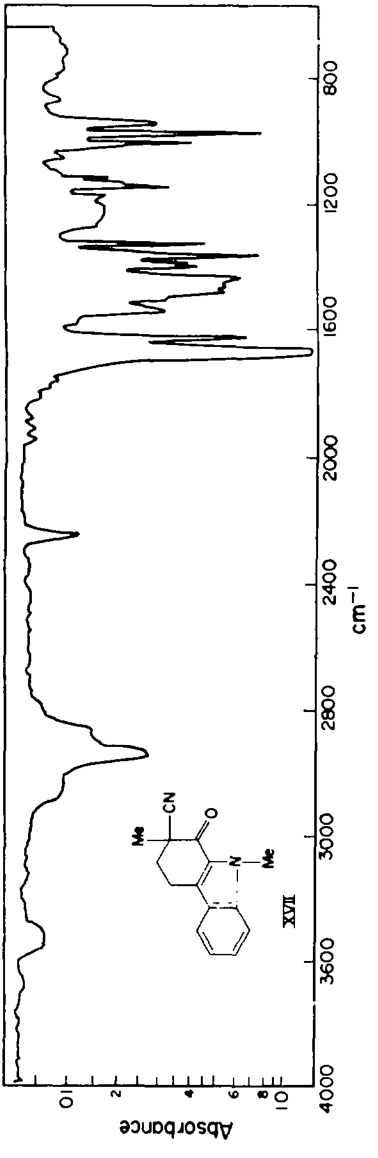
[12] H. K. Sen and S. K. Ghosh, *J. Ind. Chem. Soc.* 4, 477 (1927).


Absorbance
0·1
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·4
·6
·8
1·0
4000
3600
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2400
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1600
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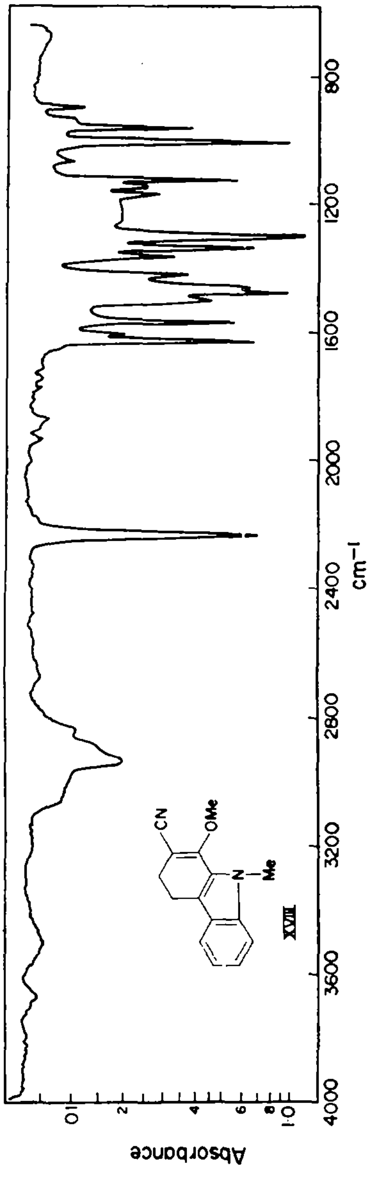
CN
O
N—Me
XVII

FIG. 2.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CN
OMe
N—Me
XVIII

FIG. 3.

derivative, 2-cyano-1-methoxy-3,4-dihydrocarbazole (XXIV) instead of the desired 2-cyano-2-methyl-1-oxo-1,2,3,4-tetrahydrocarbazole (XXV). The isoxazole (XXIII) was then isomerized to 2-cyano-1-oxo-1,2,3,4-tetrahydrocarbazole (XXVI) and treated with excess of methyl iodide yielding exclusively 2-cyano-1-methoxy-9-methyl-3,4-dihydrocarbazole (XVIII) obtained earlier.

This synthesis of II (R = H) was, therefore, also unsuccessful due to the enolizability of the ketonic function in compound XXVI.

EXPERIMENTAL

Cyclohexane-1,2-*dione-mono*-m-*methoxyphenylhydrazone* (IV). A solution of sodium acetate (25 g) in water (75 cc) was added to a solution of 2-hydroxymethylenecyclohexanone[6] (12·6 g) in methyl alcohol (150 cc). *m*-Anisidine (12·3 g) was diazotized at 0–5° with sodium nitrite (8·7 g) and conc HCl (27 cc), and the resulting solution (250 cc) added gradually during 30 min to the solution of 2-hydroxymethylene-cyclohexanone under mechanical agitation. The precipitate which separated was filtered and washed acid-free. The product crystallized from ethanol in brown needles, m.p. 173° (20 g, yield 86%) (Found: C, 67·2; H, 6·7; N, 11·7. $C_{13}H_{16}O_2N_2$ requires C, 67·2; H, 6·9; N, 12·1%).

7-*Methoxy*-1-*oxo*-1,2,3,4-*tetrahydrocarbazole* (V, A). Compound IV (2 g) was added to boiling glacial acetic acid (12 cc), conc HCl (3 cc) added through reflux condenser and the solution boiled for 5 min, and then diluted with boiling water (75 cc). The mixture was cooled and filtered and the residue washed and dried (1·6 g). The product (mixture of V and VI), on crystallization from aqueous acetone, gave a compound, m.p. 120–132°, which after repeated crystallization from aqueous acetone gave colourless needles, m.p. 156° of (V, A, 0·8 g) (Found: 72·6; H, 6·1; N, 6·2. $C_{13}H_{13}O_2N$ requires: C, 72·6; H, 6·0; N, 6·5%).

7-*Methoxy*-9-*methyl*-1-*oxo*-1,2,3,4-*tetrahydrocarbazole* (III, C) *and* 5-*methoxy*-9-*methyl*-1-*oxo*-1,2,3,4-*tetrahydrocarbazole* (VII, D). The mixture of above isomeric tetrahydrocarbazoles (2·1 g) was methylated by treatment with dimethyl sulphate (1.3 g) and fused potassium carbonate (5 g) in boiling acetone (30 cc) for 6–8 hr. The product was chromatographed over activated alumina using benzene as eluent giving two bands: one with violet and the other with green fluorescence in U.V. light. The band giving green fluorescence, on removal of benzene, gave (VII, D, 0·49 g) which crystallized from aqueous acetone in colourless needles, m.p. 104° (Found: C, 73·8; H, 6·5; N, 5·8, $C_{14}H_{15}O_2N$ requires: C, 73·4; H, 6·5; N, 5·8%). The band giving violet fluorescence gave (III, C, 1·2 g) which crystallized from aqueous acetone in colourless needles, m.p. 130° (Found: C, 73·3; H. 6·8; N, 5·9; OMe, 13·3. $C_{14}H_{15}O_2N$ requires: C, 73·4; H, 6·5; N, 5·8; OMe, 13·5%).

7-*Methoxy*-9-*methyl*-1,2,3,4-*tetrahydrocarbazole* (VIII, E). A mixture of III (C) m.p. 130° (0·46 g), potassium hydroxide (0·38 g), ethylene glycol (3 cc) and hydrazine hydrate (0·4 cc, 85%), was refluxed at 180° in an oil bath for 2 hr. Water formed in the reaction was removed by raising the temperature from 180° to 200°, in 30 min. The residual mixture was then refluxed at 200–210°, for 3 hr more. The resulting mixture was diluted with water (150 cc) and kept overnight. The reaction product crystallized from aqueous methyl alcohol in pale blue needles, m.p. 94° (0·26 g) (Found: C, 78·2; H, 8·3; N, 6·3. $C_{14}H_{17}ON$ requires: C, 78·1; H, 7·9; N, 6·5%).

2-*Methoxy*-9-*methylcarbazole* (IX, F). Chloranil (0·492 g), was added to a solution of (VIII, E, 0·215 g) in thiophene-free xylene (6 cc) and the mixture was heated under reflux at 150–160° in an oil bath for 2 hr, The reaction product on crystallization from methanol gave colourless needles, m.p. 100° of IX F, (0·14 g) (Lit,[8] m.p. 104°) (Found: C, 79·6; H, 6·1; N, 6·8. Calc. for $C_{14}H_{13}ON$: C, 79·6; H, 6·2; N, 6·6%).

2-*Hydroxymethylene*-7-*methoxy*-9-*methyl*-1-*oxo*-1,2,3,4-*tetrahydrocarbazole* (X). A solution of ethyl formate (1·4 cc) in dry ether (20 cc) was added to dry sodium methoxide (from 0·4 g of sodium). A solution of III (0·92 g) in dry ether (100 cc) was then added, the reaction flask filled with nitrogen, stoppered and the mixture shaken mechanically for 4 hr. The precipitate which separated was shaken with ether and the sodium salt of X was extracted with water (300 cc) and then with 5% NaOH (200 cc). Both water and alkaline extracts were mixed, cooled and acidified with cold dil HCl (1:1), and the precipitate filtered, washed and dried. The product, on crystallization from pet ether (b.p. 68–70°), gave shining yellow needles, m.p. 85–88° (0·41 g) (Found: 71·3; H, 6·1; N, 5.6. $C_{15}H_{15}O_3N$ requires: C, 70·0; H, 5·8; N, 5·4%).

9,10-*Dihydro-6-methoxy-4-methylcarbazolo-*(2,1-d)-*isoxazole* (XI). Dry finely powdered hydroxylamine hydrochloride (0·361 g) was added to a solution of X (0·61 g) in glacial acetic acid (12 cc) and the mixture was refluxed for 20 min by heating in an oil bath at 170–175°. After dilution with boiling water (10 cc), the mixture was cooled and more water added (40–50 cc) and left overnight in the refrigerator. Crystallization of the product from aqueous methanol gave XI as pale brown needles, m.p. 130° (0·36 g) (Found: C, 70·6; H, 5·1; N, 11·2. $C_{15}H_{14}O_2N_2$ requires: C, 70·9; H, 5·5; N, 11·0%).

2-*Cyano-*1:7-*dimethoxy-9-methyl-*3,4-*dihydrocarbazole* (XIII). To a solution of potassium (0·246 g) in t-butanol, XI (0·5 g) was added and the mixture boiled for 2 hr. After cooling, methyl iodide (0·5 cc) was added and the mixture kept at room temp for 2 hr and then refluxed gently for another 2 hr. After cooling, methyl iodide (1 cc) was added and the mixture refluxed for 2 hr, cooled and methyl iodide (0·5 cc) added and the mixture left overnight at room temp. The mixture was finally boiled for 4 hr and t-butanol removed (reduced press). The residue extracted with ether and washed with 2% aqueous sodium hydroxide. Removal of ether gave XIII (0·4 g) which crystallized from ethanol (violet fluorescence) in pale yellow needles, m.p. 156° (Found: C, 71·6; H, 6·0; N, 10·4; OMe, 30·9. $C_{16}H_{16}O_2N_2$ requires; C, 71·6; H, 6·1; N, 10·4; OMe 23·1%). The higher methoxyl value for XIII appears to be due to splitting of the N-methyl group, although methoxy group estimation in 9-methyl-1-oxo-1,2,3,4-tetrahydracarbazole (XV) and 7-methoxy-9-methyl-1-oxo-1,2,3,4-tetrahydracarbazole (III C) indicates that in these cases N-methyl group does not undergo fission during methoxy group estimation.

2-*Cyano-7-methoxy-9-methyl-*1-*oxo-*1,2,3,4-*tetrahydrocarbazole* (XII). To a solution of potassium (0·52 g) in t-butanol (40–50 cc), the isoxazole XI (1·03 g) was added and the mixture refluxed at 120–130° for 4 hr, then cooled and t-butanol removed (reduced press). The residue was extracted with ether and XII extracted with 3% aqueous sodium hydroxide (200 cc). Acidification of the alkaline extract gave a product which crystallized from aqueous methanol in pale brown needles, m.p. 221° (0·74 g, yield 72%) (Found: C, 71·4; H, 4·9; N, 10·3. $C_{15}H_{14}O_2N_2$ requires: C, 70·9; H, 5·5; N, 11·0%).

9-*Methyl-*1-*oxo-*1,2,3,4-*tetrahydrocarbazole* (XV). A mixture of dimethyl sulphate (0·77 cc), 1-oxo-1,2,3,4-tetrahydrocarbazole (XV A, 1 g),[11] anhydrous potassium carbonate (1·5 g) and acetone (25 cc) was refluxed for 6 hr. The product on crystallization from aqueous acetone, gave fine pale yellow needles of (XV, 0·9 g) m.p. 101° (Found: C, 78·8; H, 6·6; N, 6·9; OMe, 0·8. $C_{13}H_{13}ON$ requires: C, 78·4; H, 6·5; N, 7·0; OMe, nil%).

β-Carbethoxy-β-(3,4-*dihydro-9-methylcarbazolyl-*1)-*propionic acid* (XX). To a solution of potassium (0·45 g) in t-butanol (10–12 cc), diethyl succinate (3·2 cc) and XV (1 g) were added and the flask filled with nitrogen and stoppered. The mixture was shaken mechanically for 5–6 hr. The mixture was cooled and acidified in cold with dil HCl. t-Butanol was removed under reduced pressure and the residue was extracted with ether. The ether solution was washed, acid-free and then extracted twice with 15 cc portions of 2% ammonia. The ammonical extract was acidified carefully with cold dil HCl and the mixture kept overnight. The product XX was crystallized from ethanol as greenish yellow rhombic plates, m.p. 174° (0·165 g, yield 12%) (Found: C, 69·4; H, 6·1; N, 4·4. $C_{19}H_{21}O_4N$ requires: C, 69·7; H, 6·4; N, 4·3%).

2-*Hydroxymethylene-2-methyl-*1-*oxo-*1,2,3,4-*tetrahydrocarbazole* (XV B). A solution of ethyl formate (1·5 cc) in dry benzene (10 cc) was added to dry sodium methoxide (from 0·414 g of sodium). Finely powdered XV (1·2 g) was then added followed by benzene (80 cc). After replacing the air by nitrogen, the flask was stoppered and shaken for 6 hr with formation of yellowish green precipitate. The mixture was cooled, 40% aqueous sodium hydroxide (5 cc) added and the mixture extracted with ether. Ether extract was washed with water (300–400 cc) and then once with 2% aqueous sodium hydroxide (100 cc). Both the alkaline extracts were acidified with cold dil HCl. The product which separated crystallized from pet ether (b.p. 68–70°) in pale yellow needles, m.p. 81–83° (0·4 g) (Found: C, 73·3; H, 5·2; N, 6.6. $C_{14}H_{13}O_2N$ requires: C, 74·0; H, 5·1; N, 6·1%).

9,10-*Dihydro-4-methylcarbazolo-*(2,1-d)-*isoxazole* (XVI). Dry finely powdered hydroxylamine hydrochloride (0·25 g) was added to a solution of XV B (0·8 g) in glacial acetic acid (37 cc) and the mixture refluxed for 10 min at 140–155°. The mixture was cooled to 100° and immediately diluted with boiling water (100 cc), cooled and kept overnight in the refrigerator. The product was filtered, washed, extracted with ether and the extract washed with 2% aqueous sodium hydroxide till free from alkali-soluble products. The product, obtained on removal of ether, crystallized from aqueous methanol in pale brown needles, m.p. 109° (0·34 g) (Found: C, 74·3; H, 5·2; N, 12·4. $C_{14}H_{12}ON_2$ requires: C, 75·0; H, 5·4; N, 12·5%).

2-*Cyano-2,9-dimethyl-1-oxo-1,2,3,4-tetrahydrocarbazole* (XVII) and 2-cyano-1-m*ethoxy-9-methyl-3,4-dihydrocarbazole* (XVIII). To a solution of potassium (0·44 g) in t-butanol, the isoxazole (XVI, 0·83 g) was added, and the mixture boiled for 1 hr. The mixture was then treated with small portions of methyl iodide as in the synthesis of XIII using in all 3 cc of methyl iodide. t-Butanol was finally removed under reduced pressure and the residue extracted with ether. Ether extract was washed with 2% aqueous sodium hydroxide. Removal of ether and crystallization of the product from aqueous ethanol, yielded both XVII and XVIII. The mixture was chromatographed on a cellulose (Whitman, Grade 1) pulp column and the column eluted with benzene–pet ether (60–68°). Two distinct bands were obtained, one showing violet and the other pale blue fluorescence in U.V. light.

After removal of the solvent, the pale blue fluorescent band gave XVII which crystallized from aqueous ethanol in yellowish rhombs, m.p. 96° (0·12 g) (Found: C, 75·6; H, 5·7; N, 11·8; OMe, 0·8. $C_{15}H_{14}ON_2$ requires: C, 75.6; H, 5·9; N, 11·8% OMe, nil).

The band showing violet fluorescence, gave XVIII which crystallized from aqueous ethanol in shining white needles, m.p. 122° (0·42 g) (Found: C, 75·6; H, 5·7; N, 11·8; OMe, 13·8. $C_{15}H_{14}ON_2$ requires: C, 75·6; H, 5·9; N, 11·8; OMe, 13·6%).

3-*Hydroxymethylene-2-oxo-cyclohexanone-phenylhydrazone* (XXII). A mixture of sodium methoxide (from 0·138 g of sodium), ethyl formate (0·5 cc), cyclohexanone-1,2-dione-monophenylhydrazone[12] (0·404 g) and dry benzene (35 cc) was shaken mechanically for 5 hr under nitrogen. The initial pale yellow colour of the solution changed to blood red and a precipitate of the sodium salt of XXII separated out. The mixture was extracted with ether and XXII was removed by shaking with 2% aqueous sodium hydroxide (90 cc) in three lots. Acidification of the extract, gave a product, which on crystallization from aqueous ethanol, gave XXII as purple plates, m.p. 153° (0·25 g) (Found: C, 67·7; H, 6·0; N, 12·1. $C_{13}H_{14}O_2N$ requires: C, 67·8; H, 6·1; N, 12·2%).

9,10-*Dihydrocarbazolo*-(2,1-d)-*isoxazole* (XXIII). Dry finely powdered hydroxylamine hydrochloride (1·675 g) was added to a solution of XXII (2·7 g) in glacial acetic aicd (110 cc) and the mixture was heated under reflux for 30 min at 155–165°. After dilution with hot water (300 cc), the mixture was cooled, extracted with ether and the extract washed with 2% aqueous sodium hydroxide. The. product crystallized from aqueous methanol in dark brown needles, m.p. 196° (0·8 g) (Found: C, 74·5; H, 4·5; N, 13·6. $C_{13}H_{10}ON_2$ requires: C, 74·3; H, 4·8; N, 13·3%).

2-*Cyano*-1-*methoxy*-3,4-*dihydrocarbazole* (XXIV). To a solution of potassium (0·14 g) in t-butanol (15 cc), XXIII (0·8 g) was added and the mixture boiled for 2 hr. After cooling methyl iodide (0·213 cc) was added and the flask stoppered and shaken for 5 hr and kept overnight. The mixture was then refluxed at 120–125° for 4 hr and cooled. t-Butanol was removed under reduced pressure and the residue extracted with ether and the extract washed with 2% aqueous sodium hydroxide. Removal of ether, gave XXIV, which crystallized from aqueous methanol in pale brown needles, m.p. 144° (0·46 g) (Found: C, 74·5; H, 4·9; N, 13·0; OMe, 14·8. $C_{14}H_{12}ON_2$ requires: C, 75·0; H, 5·3; N, 12·5; OMe, 13·8%).

2-*Cyano*-1-*oxo*-1,2,3,4-*tetrahydrocarbazole* (XXVI). To a solution of potassium (0·6 g) in t-butanol (25–30 cc), XXIII (1·1 g) was added and the mixture refluxed at 120–130 for 2 hr. The ether solution of the reaction product was extracted with 2% aqueous sodium of hydroxide. Acidification of the alkaline extract gave a product which crystallized from aqueous methanol in brown needles, m.p. 233° (1·0 g, yield 91%) (Found: C, 73·8; H, 4·4; N, 14·1. $C_{13}H_{10}ON_2$ requires: C, 74·3; H, 4·7; N, 13·3%).

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