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Reactions of indoline (I), 2-methylindoline (II) and hexahydrocarbazole (III) with  $\alpha,\beta$ -unsaturated acids in the presence of polyphosphoric acid have been investigated. Reaction of I with acrylic acid afforded two compounds which were identified as 1,2,4,5-tetrahydro-6H-pyrrolo[3,2,1-*ij*]quinolin-6-one (IV) and 2,3,5,6,9,10-hexahydro-1H-cyclopenta[*f*]pyrrolo[3,2,1-*ij*]quinoline-1,8-dione (VII). The reaction of I with crotonic acid gave compounds V and VIII, analogous to IV and VII. The reaction of II with acrylic acid yielded two compounds VI and IX, whereas with crotonic acid, only X was isolated. With III, acrylic acid afforded 5,6,8,9,10,11,8a,11a-octahydro-4H-pyrido[3,2,1-*jk*]carbazol-4-one (XI) and a compound with a heretofore unknown ring system, viz., 2,3,5,6,7,8,11,12,5a,8a-decahydro-1H-cyclopenta[*h*]pyrido[3,2,1-*jk*]carbazole-1,10-dione. The structures of these compounds were deduced on the basis of their spectral and analytical data.

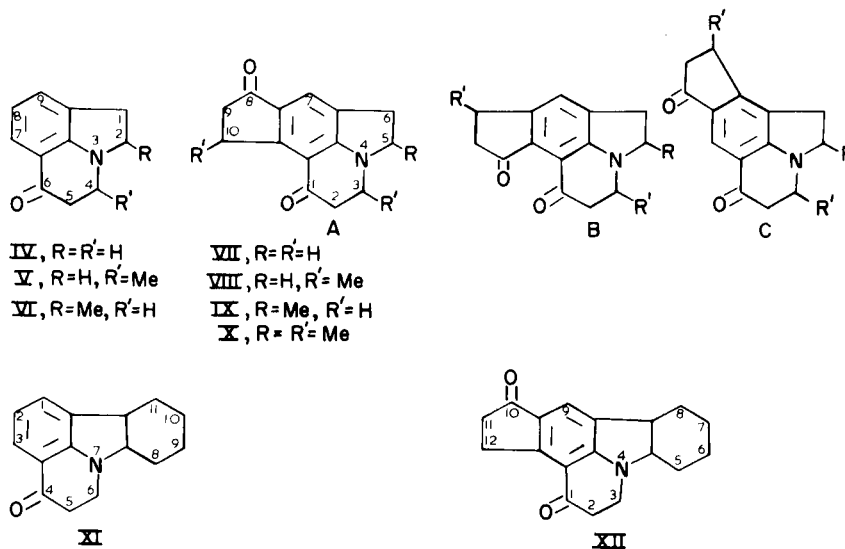
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In the course of our studies on the synthesis of polynuclear heterocyclic compounds, we investigated the reaction of indoline (I), 2-methylindoline (II) and hexahydrocarbazole (III) with  $\alpha,\beta$ -unsaturated acids in the presence of polyphosphoric acid.

Heating I (1 mole) with acrylic acid (2 mole) in the presence of polyphosphoric acid gave two compounds IV (7% yield) and VII (4% yield). Compound IV was eluted with benzene as a yellow semi-solid and crystallized from petroleum ether (40-60°) as yellow plates. It gave a 2,4-dinitrophenylhydrazone. Compound IV was identified as 1,2,4,5-tetrahydro-6H-pyrrolo[3,2,1-*ij*]quinolin-6-one, which has been synthesised by Rapoport and Tretter (1) by the cyanoethylation of I with acrylonitrile followed by hydrolysis and the subsequent cyclization of the resulting propionic acid. Spectral data for IV is described in

Experimental.

Compound VII was eluted with benzene:ether (4:1) and crystallized from benzene as yellow needles, m.p. 210-212°; it had the molecular composition  $C_{14}H_{13}NO_2$  ( $M^+$  227). The uv (methanol) showed maxima at 245, 265, 320, 380 nm ( $\log \epsilon$  4.15, 4.12, 4.13, 3.85) which remained unchanged in the presence of a drop of alkali or acid. The ir (potassium bromide) showed bands at 1690  $cm^{-1}$  ( $>CO$ ) and at 1600, 1580, 1500  $cm^{-1}$  (aromatic). The nmr (deuteriochloroform) integrated for 13 protons and gave the following signals:  $\delta$  2.5-4.0 (12H, m, C<sub>2</sub>, C<sub>3</sub>, C<sub>5</sub>, C<sub>6</sub>, C<sub>9</sub> and C<sub>10</sub>H), 7.41 (1H, s, aromatic C<sub>7</sub>H). Compound VII could not be prepared by heating IV with acrylic acid and polyphosphoric acid, which indicates that VII is formed independently in the reaction. Spectral and analytical data reveal that VII could possess the



structure A or B. However, structure A is more consistent with the nmr data, since in this case the C<sub>7</sub> proton appears downfield at  $\delta$  7.41, due to the neighbouring carbonyl group at C<sub>8</sub>, whereas in compound IV, the C<sub>7</sub> proton appears around  $\delta$  7.12. In structure B the C<sub>7</sub> proton would have given a signal at the same position as in the case of IV. An alternate structure C could be ruled out since the aromatic proton being peri to two carbonyl groups would have been shifted even more downfield than observed. Mechanistically, the formation of VII from I can be explained by a Micheal type of addition on the nitrogen atom followed by ring closure and a Friedel-Craft acylation at position-5 with subsequent cyclization to form the cyclopentane ring, both the named reactions occurring concurrently. It has been reported by Terentev and Pireobrazhenskaya (2) that with indoline and 2-methylindoline having substituents at position-1, the Friedel-Craft acylation takes place at position-5 instead of position-6, which agrees with the mechanism proposed by us for the formation of VII. Theoretically, the electrophilic substitution (Friedel-Craft acylation), could have occurred first but this seems less likely since in the reaction of I with acrylonitrile, only *N*-cyanoethylation takes place and no *C*-cyanoethylation is observed at all. The reaction of I with crotonic acid and polyphosphoric acid afforded V and VIII, analogous to IV and VII, respectively.

A similar reaction of 2-methylindoline (II) with acrylic acid and polyphosphoric acid gave compounds VI and IX. Compound VI was isolated as a yellow oil and IX was obtained as yellow crystalline solid after purification by column chromatography. However, II with crotonic acid yielded only a single compound which was assigned the structure X on the basis of analytical and spectral evidence.

Heating III with acrylic acid and polyphosphoric acid gave compounds XI and XII. The latter has a ring system hitherto unknown and was designated as 2,3,5,6,7,8,11,-12,5a,8a-decahydro-III-cyclopenta[h]pyrido[3,2,1-*jk*]carbazole-1,10-dione.

A comparison of the uv spectra of IV with those of VII, VIII, IX, X and XII favour the structures assigned, since the uv of IV does not show any peak at 320 nm, which is observed in the other compounds, and has been attributed to the presence of the indanone ring (3).

In the above reactions, the yields of the compounds are very low and a considerable amount of tarry material is formed. Also, attempts to isolate intermediate products were unsuccessful.

Compound VII and analogues thereof, as well as compound XII do not appear to have been described thus far and constitute new ring systems.

## EXPERIMENTAL

Melting points were taken in a sulphuric acid bath apparatus and are uncorrected. Elemental analysis were performed in this department by D. S. More and Mrs. J. A. Patanker.

The uv spectra were measured on a Hilger H-700 Spectrophotometer and the ir spectra were recorded with a Perkin-Elmer Spectrophotometer; the nmr spectra were determined with a 60 MHz Varian model in deuteriochloroform with TMS as the internal standard.

2,3,5,6,9,10-Hexahydro-1*H*-cyclopenta[*f*]pyrrolo[3,2,1-*ij*]quino-line-1,8-dione (VII).

Indoline (2.4 g., 0.02 mole) and acrylic acid (2.8 g., 0.04 mole) were added to a mixture of phosphorus pentoxide (45 g.) and phosphoric acid (22 ml.) preheated to 100° for 30 minutes. The reaction mixture was maintained between 125-130° for 6 to 7 hours with occasional shaking. It was then cooled and poured over ice-water and left overnight. The resultant solution was extracted with chloroform. The chloroform extract was washed with aqueous sodium hydrogen carbonate (2-3 times) and then with water. The extract was dried over anhydrous sodium sulphate. Removal of the solvent afforded a brown viscous mass, which was chromatographed over silica gel. Elution with benzene afforded a yellow solid (150 mg.), which was crystallized from petroleum ether (40-60°), m.p. 57-58° (reported (1), m.p. 53°); uv (methanol): 240, 380 nm (log  $\epsilon$  4.1 and 3.49), shoulder 256 nm (log  $\epsilon$  3.65); ir (potassium bromide): 1660, 1600, 1580 and 1500 cm<sup>-1</sup>; nmr (deuteriochloroform):  $\delta$  2.5~3.59 (8H, m, C<sub>1</sub>, C<sub>2</sub>, C<sub>4</sub> and C<sub>5</sub>H), 6.59 (1H, t, J = 7Hz, C<sub>8</sub>H), 7.12 (1H, double doublet J = 7Hz and J = 2Hz, C<sub>9</sub>H), 7.4 (1H, d, J = 7Hz, C<sub>7</sub>H).

Compound IV gave a brownish black 2,4-dinitrophenylhydrazone, m.p. 263-264°.

*Anal.* Calcd. for C<sub>17</sub>H<sub>15</sub>N<sub>5</sub>O<sub>4</sub>: N, 19.8. Found: N, 20.1.

Further elution with benzene-ether (4:1) yielded VII as golden yellow needles (80 mg.) on crystallization from benzene, m.p. 210-212°.

*Anal.* Calcd. for C<sub>14</sub>H<sub>13</sub>NO<sub>2</sub>: C, 73.9; H, 6.1; N, 6.16. Found: C, 73.6; H, 6.2; N, 5.8.

This compound also gave a dark brown 2,4-dinitrophenylhydrazone, m.p. >350°.

*Anal.* Calcd. for C<sub>20</sub>H<sub>17</sub>N<sub>5</sub>O<sub>5</sub>: N, 17.2. Found: N, 17.6.

Reaction of I with Crotonic Acid.

A similar reaction of I with crotonic acid gave compounds V and VIII. After the usual reaction work up and chromatography over silica gel, V was eluted with benzene as a yellow semisolid, m.p. 99-101° on crystallization from petroleum ether (40-60°) (yield 75 mg.); uv (methanol): 240, 380 nm (log  $\epsilon$  4.2, 3.60), shoulder 256 (log  $\epsilon$  3.8); ir (potassium bromide): 1680, 1600, 1500 cm<sup>-1</sup>.

*Anal.* Calcd. for C<sub>12</sub>H<sub>13</sub>NO (M<sup>+</sup> 187): C, 77.02; H, 6.9; N, 7.48. Found: C, 77.4; H, 7.3; N, 7.2.

Compound V afforded a 2,4-dinitrophenylhydrazone derivative, m.p. 270-272°.

*Anal.* Calcd. for C<sub>18</sub>H<sub>17</sub>N<sub>5</sub>O<sub>4</sub>: N, 19.0. Found: N, 19.4.

Further elution with benzene:chloroform (1:3) yielded VIII as yellow solid, m.p. 140-142°, crystallized from petroleum ether (80-100°) (yield 160 mg.); uv (methanol): 240, 265, 320, 380 nm (log  $\epsilon$  4.15, 4.12, 4.32, 3.80, respectively); ir (potassium bromide): 1690, 1600, 1580, 1520 cm<sup>-1</sup>; nmr (deuteriochloroform):  $\delta$  1.2~1.4 (6H, 2d, J = 2 Hz, 2CH<sub>3</sub>), 2~4.16 (10H, m,

C<sub>2</sub>, C<sub>3</sub>, C<sub>5</sub>, C<sub>6</sub>, C<sub>9</sub> and C<sub>10</sub>H), 7.33 (1H, s, Ar. C<sub>7</sub>H).

*Anal.* Calcd. for C<sub>16</sub>H<sub>17</sub>NO<sub>2</sub> (M<sup>+</sup> 255): C, 75.3; H, 6.6; N, 5.44. Found: C, 75.7; H, 6.9; N, 5.6.

Compound VIII gave a 2,4-dinitrophenylhydrazone derivative, m.p. 272-273°.

*Anal.* Calcd. for C<sub>22</sub>H<sub>21</sub>N<sub>5</sub>O<sub>5</sub>: N, 16.1. Found: N, 15.8.

#### Reaction of II with Acrylic Acid.

Similarly, the reaction of II with acrylic acid, after the usual work up and chromatography over silica gel gave VI and IX. Compound VI was eluted with petroleum ether (40-60°): benzene (1:1) as a yellow oil which was distilled under reduced pressure (15 mm) (temperature of oil bath 180-190°) as a bright yellow oil; ir (thin film): 1680, 1600, 1480 cm<sup>-1</sup>; nmr (deuteriochloroform): δ 1.3 (3H, d, J = 6 Hz, CH-CH<sub>3</sub>), 2.33~4.0 (7H, m, C<sub>1</sub>, C<sub>2</sub>, C<sub>4</sub> and C<sub>5</sub>H), 6.54 (1H, t, J = 7 Hz, C<sub>8</sub>H); 7.04 (1H, double doublet J = 7 Hz and J = 2 Hz, C<sub>9</sub>H), 7.39 (1H, d, J = 7 Hz, C<sub>7</sub>H).

*Anal.* Calcd. for C<sub>12</sub>H<sub>13</sub>NO: C, 77.02; H, 6.9; N, 7.28. Found: C, 76.6; H, 7.3; N, 7.3.

Compound VI gave a 2,4-dinitrophenylhydrazone derivative, m.p. 255-257° dec.

*Anal.* Calcd. for C<sub>18</sub>H<sub>17</sub>N<sub>5</sub>O<sub>4</sub>: N, 19.0. Found: 19.4.

Further elution with benzene:chloroform (1:3) yielded IX as a yellow solid, crystallized from petroleum ether (80-100°), m.p. 151-152° (yield 80 mg.). Its uv and ir spectra were similar to those of compound VII; nmr (deuteriochloroform): δ 1.4 (3H, d, J = 7 Hz, CH-CH<sub>3</sub>), 2.4~4.1 (11H, C<sub>2</sub>, C<sub>3</sub>, C<sub>5</sub>, C<sub>6</sub>, C<sub>9</sub> and C<sub>10</sub>H); 7.33 (1H, s, ar. C<sub>7</sub>H).

*Anal.* Calcd. for C<sub>15</sub>H<sub>15</sub>NO<sub>2</sub> (M<sup>+</sup> 241): C, 74.6; H, 6.2; N, 5.8. Found: C, 74.6; H, 6.2; N, 5.7.

Compound IX gave a 2,4-dinitrophenylhydrazone derivative, m.p. > 340°.

*Anal.* Calcd. for C<sub>21</sub>H<sub>19</sub>N<sub>5</sub>O<sub>5</sub>: N, 16.63. Found: N, 17.0.

#### Reaction of II with Crotonic Acid.

The reaction of II with crotonic acid in the presence of polyphosphoric acid, after the usual work up and chromatography over silica gel gave X, but a compound analogous to VI could not be isolated. Compound X was eluted with benzene:ether (9:1) as a yellowish brown semisolid and crystallized from petroleum ether (80-100°) as yellow needles, m.p. 165-167° (yield 150 mg.). The uv and ir for X were similar to those obtained for IX.

*Anal.* Calcd. for C<sub>17</sub>H<sub>19</sub>NO<sub>2</sub>: C, 76.0; H, 6.7; N, 5.2. Found: C, 75.6; H, 6.5; N, 5.1.

Compound X gave a 2,4-dinitrophenylhydrazone derivative, m.p. 268-270° dec.

*Anal.* Calcd. for C<sub>23</sub>H<sub>22</sub>N<sub>5</sub>O<sub>5</sub>: N, 15.6. Found: N, 15.2.

#### Reaction of Hexahydrocarbazole with Acrylic Acid.

A similar reaction of hexahydrocarbazole with acrylic acid in the presence of polyphosphoric acid, after the usual work up and column chromatography over neutral alumina afforded compounds XI and XII. Compound XI was eluted with hexane:benzene (1:4) as a yellow semisolid, crystallized from hexane, m.p. 74° (yield 100 mg.). The uv and ir obtained for XI were similar to those obtained for IV.

*Anal.* Calcd. for C<sub>15</sub>H<sub>17</sub>NO: C, 79.0; H, 7.4; N, 5.9. Found: C, 79.1; H, 7.6; N, 5.8.

Compound XI gave a 2,4-dinitrophenylhydrazone derivative, m.p. 210°-212°.

*Anal.* Calcd. for C<sub>21</sub>H<sub>21</sub>N<sub>5</sub>O<sub>4</sub>: N, 17.2. Found: N, 17.5.

Compound XII was eluted with benzene:ether (4:1) as a yellow solid, crystallized from petroleum ether (80-100°), m.p. 149-150° (yield 100 mg.); nmr (deuteriochloroform): δ 1.1-2.1 (8H, m, C<sub>5</sub>H, C<sub>6</sub>H, C<sub>7</sub>H and C<sub>8</sub>H), 2.5~3.8 (10H, C<sub>2</sub>, C<sub>3</sub>, C<sub>11</sub>, C<sub>12</sub>, C<sub>5a</sub> and C<sub>8a</sub>H), 7.41 (1H, s, ar. C<sub>9</sub>H).

*Anal.* Calcd. for C<sub>18</sub>H<sub>19</sub>NO<sub>2</sub>: C, 76.8; H, 6.7; N, 4.9. Found: C, 76.7; H, 6.8; N, 4.7.

This compound gave a 2,4-dinitrophenylhydrazone derivative, m.p. 273-274°.

*Anal.* Calcd. for C<sub>24</sub>H<sub>23</sub>N<sub>5</sub>O<sub>5</sub>: N, 15.2. Found: N, 15.0.

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