

Synthesis of a New Heterocyclic Ring System
2,3,5,6,7,9,10,11-Octahydro-1*H*-cyclopenta[9,10]benzo[*i,j*]quinolizine-1,9-dione

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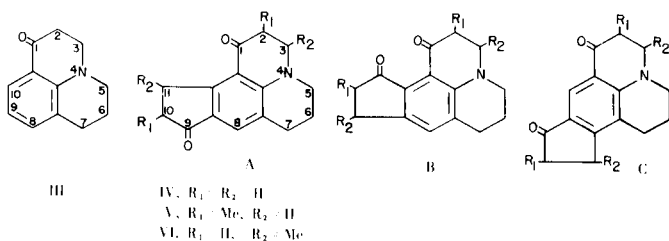
Reaction of 1,2,3,4-tetrahydroquinoline (I) with different α,β -unsaturated acids in the presence of PPA has been investigated. With acrylic acid, I affords two compounds identified as 1-keto-benzo[*i,j*]quinolizine (III) and 2,3,5,6,7,9,10,11-octahydro-1*H*-cyclopenta[9,10]benzo[*i,j*]quinolizine-1,9-dione (IV). A similar reaction of I with α -methyl acrylic and crotonic acids gives compounds V and VI whose structures are analogous to that of IV. These were deduced from their spectral and analytical data.

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In the course of our work on the synthesis of polynuclear heterocyclic compounds we investigated the reaction of 1,2,3,4-tetrahydroquinoline (I) with acrylic acid (II) in the presence of polyphosphoric acid.

Heating the components in molar proportions or with a slight excess of II in polyphosphoric acid afforded two compounds, III (10% yield) and IV (3% yield). The former eluted with hexane:benzene (1:1) as a semi-solid crystallized from cyclohexane in yellow needles, and gave a black 2,4-dinitrophenylhydrazone. The compound III was identified as benzo[*i,j*]quinolizine-1-one previously obtained by Mann and Smith (1) by the cyanoethylation of I followed by hydrolysis and cyclization of the resulting propionic acid. Its spectral data has been reported in the experimental section.

The compound IV (tlc, single spot) obtained by elution with benzene as a yellow solid crystallized from benzene-petroleum ether (40-60°), m.p. 184-185°, and had the molecular composition $C_{15}H_{15}NO_2$ (M^+ 241).



Its uv (methanol) showed maxima at 245, 270, 320, 380 nm $\log \epsilon$ (4.18, 4.13, 4.48, 3.85) which remained unchanged in the presence of a drop of alkali or acid. The ir (Nujol) showed bands at 1680 cm^{-1} ($>CO$) and at

1600, 1580 and 1500 cm^{-1} (aromatic). The nmr (deuteriochloroform) spectrum integrated for 15 protons and gave the following signals: δ 2.1 (2H, m, C_6H), 2.5 (4H, t, $C_7H, C_{11}H$), 2.8 (4H, m, C_3 and C_5H), 3.3 ~ 3.75 (4H, m, $C_2, C_{10}H$), 7.38 (1H, s, ar. C_8H). Further, IV could not be prepared from III by heating it with II in polyphosphoric acid indicating that it was formed independently in the reaction. From the spectral analytical data, IV could possess the structure A or B. However, the structure A is more consistent with the nmr data since in this case the aromatic proton at C_8 appears downfield at δ 7.38 due to the neighbouring carbonyl at C_1 whereas in the compound III, the C_8 proton gives a signal around δ 6.45. In the structure B, the C_8 proton would have given the signal at the same position as in the case of III. An alternate structure such as C could be ruled out since in this case the aromatic proton being peri to two carbonyl groups would have been shifted even more downfield than observed.

Mechanistically, the formation of IV from I can be explained by a Michael type of addition on the nitrogen atom followed by ring closure and a Friedel-Craft acylation at the 9 position and subsequent cyclization to form the cyclopentane ring both the named reactions occurring concurrently. Theoretically, the electrophilic substitution (Friedel-Crafts acylation), as has been observed (2) in the bromination and nitration of I at the position 9, 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.

Heating I with α -methylacrylic acid and crotonic acid in the presence of polyphosphoric acid did not give any

compounds analogous to III but only compounds similar to IV were isolated. The compound V with α -methylacrylic acid (in 3% yield) was isolated as yellow needles, m.p. 140-142°, whereas that VI (in 5% yield) with crotonic acid was obtained as pale yellow prisms, m.p. 171-173° (tlc single spots). Their mass spectra gave M^+ at m/e 269. Their uv (methanol) showed maxima at 240, 270, 320 and 380 nm $\log \epsilon$ (4.09, 4.1, 4.35, 3.85), while their ir (nujol) showed bands at 1690 cm^{-1} ($> \text{CO}$) in addition to the aromatic bands. The nmr (deuteriochloroform) spectra were very similar to that of IV. The signals are recorded in the experimental.

A comparison of the uv spectra of III and IV, V, VI also favours the structures assigned. The uv of III does not show any peak at 320 nm whereas that of IV, V and VI exhibits this peak indicative of the presence of the cyclopentenone ring as observed earlier in this laboratory (3).

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

The above compounds, as far as we know do not appear to have been described so far and constitute a new ring system.

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. Patankar.

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

2,3,5,6,7,9,10,11-Octahydro-1H-cyclopenta[9,10]benzo[*ij*]-quinolizine-1,9-dione (IV).

To a freshly prepared mixture of polyphosphoric acid (from 50 g. of phosphorus pentoxide and 25 ml. of phosphoric acid) preheated to 100° for 30 minutes, 1,2,3,4-tetrahydroquinoline (7 ml.) and acrylic acid (5 ml.) were added and the temperature of the reaction mixture maintained between 120-130° for 7 hours, with occasional shaking. It was then cooled, poured over ice-water and kept overnight. The whole was extracted with chloroform, 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 yielded a dark brown solid which was chromatographed over alumina. Elution with hexane:benzene

(1:1) afforded a yellow semi-solid (500 mg.) which was crystallized from cyclohexane, m.p. 62-63° (reported (1), m.p. 62.5-63.5°); uv (methanol): 245, 265 and 395 nm ($\log \epsilon$ 4.36, 4.02, 3.79 respectively); ir (nujol): 1650, 1608, 1575, 1500 and 820 cm^{-1} ; nmr (deuteriochloroform): δ 2.02 (2H, m, $-\text{C}_6\text{H}$), 2.64 (4H, m, C_2H ; C_7H), 3.19 (4H, m, C_3H and C_5H), 6.45 (1H, double doublet, $J = 7$ Hz and $J = 2$ Hz, $-\text{C}_8\text{H}$), 6.98 (1H, t, $J = 7$ Hz, C_9H), 7.55 (1H, double doublet, $J = 7$ Hz and 2 Hz, C_{10}H).

This compound gave a black 2,4-dinitrophenylhydrazone, m.p. 245-246°.

Anal. Calcd. for $\text{C}_{18}\text{H}_{17}\text{N}_5\text{O}_4$: N, 19.07. Found: N, 19.10.

Further elution with benzene yielded IV as a yellow solid (300 mg.) crystallized from benzene-petroleum ether (40-60°), m.p. 184-185°.

Anal. Calcd. for $\text{C}_{15}\text{H}_{15}\text{NO}_2$: C, 74.7; H, 6.2; N, 5.9. Found: C, 75.0; H, 6.5; N, 5.7.

This compound gave a reddish brown 2,4-dinitrophenylhydrazone, m.p. $> 330^\circ$.

Anal. Calcd. for $\text{C}_{21}\text{H}_{19}\text{N}_5\text{O}_5$: N, 16.6. Found: N, 16.5.

Similarly, reaction of I with α -methylacrylic acid and crotonic acids gave compounds V and VI, respectively. After the usual reaction work up and chromatography over alumina V was eluted with benzene as yellow needles, m.p. 140-142°, crystallized from benzene-petroleum ether (40-60°), yield 250 mg.; nmr (deuteriochloroform): δ 1.2 (6H, 2d, 2CH_3), 2.1 (2H, m, $-\text{C}_6\text{H}$), 2.5 (4H, t, C_7 and C_{11}H), 2.8 (4H, m, C_3 and C_5H), δ 3.3 ~ 3.75 (2H, m, C_2 and C_{10}H), 7.4 (1H, s, ar. C_8H).

Anal. Calcd. for $\text{C}_{17}\text{H}_{19}\text{NO}_2$: C, 75.8; H, 7.0; N, 5.2. Found: C, 75.7; H, 7.1; N, 5.5.

This compound gave a 2,4-dinitrophenylhydrazone, m.p. 238-240°.

Anal. Calcd. for $\text{C}_{23}\text{H}_{23}\text{N}_5\text{O}_5$: N, 15.5. Found: N, 15.4.

Compound VI was eluted from benzene:ether (1:1) as pale yellow needles, m.p. 171-173° crystallized from petroleum ether (100-200°), yield 200 mg. The nmr spectrum (deuteriochloroform) was very similar to V.

Anal. Calcd. for $\text{C}_{17}\text{H}_{19}\text{NO}_2$: C, 75.8; H, 7.0; N, 5.2. Found: C, 76.0; H, 7.3; N, 5.2.

This compound gave a 2,4-dinitrophenylhydrazone, m.p. 272-274°.

Anal. Calcd. for $\text{C}_{23}\text{H}_{23}\text{N}_5\text{O}_5$: N, 15.5. Found: N, 15.6.

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REFERENCES AND NOTES

- (1) F. G. Mann and B. B. Smith, *J. Chem. Soc.*, 1898 (1951).
- (2) L. Hoffmann and K. Koenigs, *Ber.*, **16**, 727 (1883).
- (3) M. S. Kamath and J. R. Merchant, *Indian J. Chem.*, **13**, 861 (1975).