

1H,7H-Pyrano[3,2-e]-v-benzotriazol-7-one. A New Ring System

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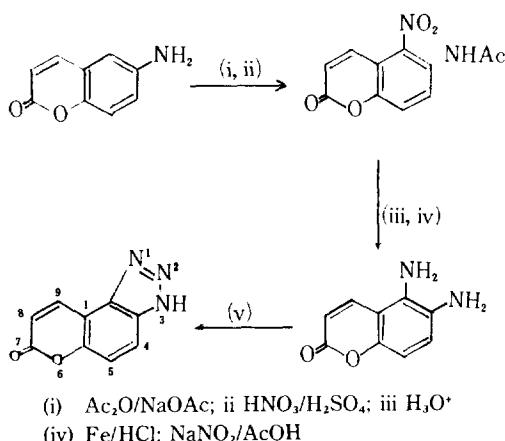
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Heterocyclic ring systems arising from the condensation of a coumarin ring to other heterocyclic rings have been reported in the literature. Some of these contain a pyrrole or a pyridine ring fused to the benzene ring of the coumarin molecule¹ while in some others heterocyclic rings are fused to the pyran ring of the coumarin system.²⁻⁴ Benzopyrans containing a fused five membered system have been also found to possess pharmacological properties. Angalecin a furobenzopyran has spasmolytic activity⁵ while another benzopyran containing a v-triazole ring is also of interest as a potential antiasthmatic agent.⁶ In the present communication we would like to report the synthesis of a new ring system-1H,7H-pyrano[3,2-e]-v-benzotriazol-7-one (I) in which a v-triazole ring has been fused to the benzene ring of coumarin.

The synthesis of the ring system is presented in Scheme 1. 6-Aminocoumarin (II)⁷, after acylation,⁸ was nitrated with mixed acids (H_2SO_4 - HNO_3) at 0°C-5°C for 24 h to afford



6-acetylamino-5-nitrocoumarin (III) in 70% yield.⁹ The substitution of the nitro group has been occurred at the 5 position of the coumarin ring, which is borne out by the ¹HNMR spectrum of III, displaying four doublets due to the protons at 3, 4, 7 and 8 position of III. Hydrolysis of III in refluxing 10% aqueous H_2SO_4 for 2 h in 80% yield¹⁰ followed by the reduction with iron powder and hydrochloric acid gave the key intermediate 5,6-diaminocoumarin (IV) in 53% yield,¹¹ which on diazotization with sodium nitrite in aqueous acetic acid at room temperature furnished 1H,7H-pyrano[3,2-e]-v-benzotriazol-7-one (I).¹² The new heterocyclic compound (I) was thoroughly characterized through its elemental analysis, IR, and ¹HNMR spectra.

Further work on this and related systems is in progress. **Acknowledgement.** We wish to thank Conselho Nacional de

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References

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8. Dictionary of Organic Compounds, Chapman and Hall, New York, N.Y., 5th Ed., 1982, vol. 1, p. 150.
9. m.p. 215-216°C; ¹HNMR (CF_3COOH) δ 2.49 (s, 3H, CH_3), 6.90 (d, $J=10$ Hz, 1H, H-3), 7.78 (d, $J=9$ Hz, 1H, H-8), 8.25 (d, $J=10$ Hz, 1H, H-4), 8.26 (d, $J=9$ Hz, 1H, H-7), 9.15 (s, 1H, NH); IR(KBr) 3100-3000, 1752, 1748, 1525, 1355 cm⁻¹. Anal. Calcd for $\text{C}_{11}\text{H}_8\text{N}_2\text{O}_2$: C, 53.23; H, 3.25; N, 11.29. Found: C, 52.98; H, 3.21; N, 11.09.
10. m.p. 225-227°C; IR(KBr) 3450, 3320, 1520, 1380 cm⁻¹. Anal. Calcd for $\text{C}_8\text{H}_8\text{N}_2\text{O}_2$: C, 52.43; H, 2.93; N, 13.59. Found: C, 52.34; H, 2.88; N, 13.30.
11. m.p. 195-196°C; ¹HNMR(DMSO- d_6) δ 6.18 (d, $J=10$ Hz, 1H, H-3), 6.39 (d, $J=8$ Hz, 1H, H-8), 6.82 (d, $J=8$ Hz, 1H, H-7), 8.25 (d, $J=10$ Hz, 1H, H-4), 5.00 (m, 4H, NH_2); IR(KBr) 3450-3200, 1700 cm⁻¹. Anal. Calcd for $\text{C}_8\text{H}_8\text{N}_2\text{O}_2$: C, 61.36; H, 4.58; N, 15.90. Found: C, 61.23; H, 4.36; N, 15.70.
12. m.p. 259-260°C; ¹HNMR(DMSO- d_6) δ 6.60 (d, $J=10$ Hz, 1H, H-8), 7.36 (d, $J=10$ Hz, 1H, H-5), 8.04 (d, $J=10$ Hz, 1H, H-4), 8.34 (d, $J=10$ Hz, 1H, H-9); IR(KBr) 3450, 1760 cm⁻¹. Anal. Calcd for $\text{C}_8\text{H}_8\text{N}_2\text{O}_2$: C, 57.76; H, 2.69; N, 22.45. Found: C, 58.00; H, 2.89; N, 22.34.