Synthesis of Novel Oxazolo(4,5-a)carbazoles

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1-Hydroxyimino-1,2,3,4-tetrahydrocarbazoles, α-Acetoxy Imine, Oxazolo(4,5-a)carbazole

1-Hydroxyimino-1,2,3,4-tetrahydrocarbazoles, 1a–e on treatment with acetyl chloride at room temperature afforded the corresponding novel oxazolo(4,5-a)carbazole derivatives 2a–e respectively.

Carbazole derivatives [1–6] have been reported to exhibit pharmacological properties like anti-tumour, anticonvulsant, psychotropic, antiinflammatory, antihistamine and antibiotic properties. Oxazole derivatives [7–15] have been used as optical whitening agents, sensitizing dyes, photoreducing pigments, muscle relaxant and effective against wide range of enteric infections, appetite depressants. In the above contest our present investigation was aimed at to prepare hitherto unknown oxazolo(4,5-a)carbazole derivatives 2a–e from the corresponding 1-hydroxyimino-1,2,3,4-tetrahydrocarbazoles 1a–e [6] in a single step with acetyl chloride at room temperature.

1-Hydroxyimino-8-methyl-1,2,3,4-tetrahydrocarbazole 1a was reacted with acetyl chloride at room temperature for 24 h to afford a single product 2a in 65% yield. In its IR spectrum two bands at 3300 cm⁻¹ and 1640 cm⁻¹ were assigned to a NH stretching and a nitrogen carbon double bond stretching. Its ¹H NMR spectrum showed the presence of two singlets for two methyl protons. The methyl proton in the benzene ring, C₈–CH₃, appeared substantially downfield at δ 2.60, the other methyl proton in the oxazole ring, C₂–CH₃, appeared at δ 2.28. The aromatic region showed a multiplet between δ 6.96–7.92, assigned of C₄–H, C₅–H, C₆–H and C₇–H and a broad singlet at δ 9.72 due to a NH proton, which is D₂O-exchangeable. The molecular ion peak (M⁺) at m/e 236 in its mass spectrum and elemental analysis: C 76.12, H 5.04 and N 11.42 are agreed to the molecular formula C₁₅H₁₂N₂O. Based on all these details the compound was assigned the structure 2,9-dimethyloxazolo(4,5-a)carbazole (2a).

Similarly oxazolo(4,5-a)carbazole derivatives 2b–e were prepared and their structures confirmed by spectral and elemental analysis (Scheme 1 and Table I).
A mechanism for the conversion of 1-hydroxyimino-1,2,3,4-tetrahydrocarbazoles 1 to oxazolo(4,5-a)carbazoles 2 is shown in Scheme 2. In the first step 1 is O-acylated after tautomerization the enamine undergoes a [3,3]-sigmatropic rearrangement [16, 17]. After another prototropic shift ring closure of the enamine affords 2.

Experimental

General procedure

Acetyl chloride (3 ml excess) was added slowly under ice cooling to 1-hydroxyimino-tetrahydrocarbazole (1, 1 mmol) and stirred at room temperature for 24 h. The contents were poured into cold water and extracted with chloroform (3×15 ml). The combined organic extracts were washed with water and concentrated to a brown viscous liquid. This was purified by passing through a silica gel column and eluting with petroleum ether–ethyl acetate mixture (2:1) to afford 2 as colourless prism (Table I).

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