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SYNTHESES WITH HETEROCYCLIC ENAMINES. I. A FACILE ROUTE TO AZA-CHROMONES

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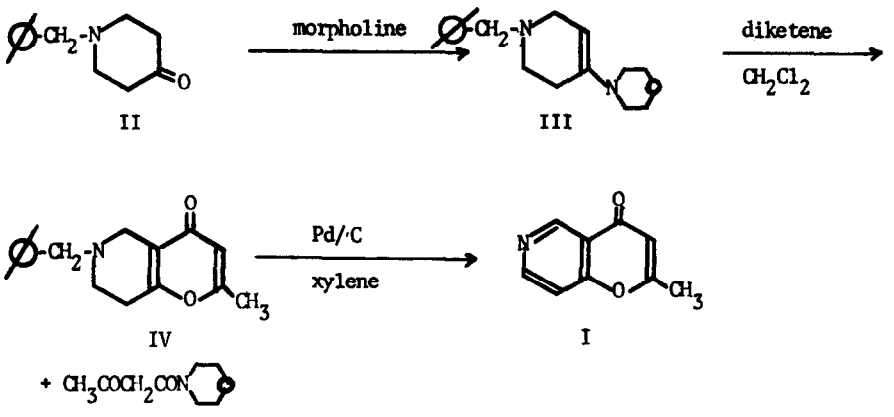
Although numerous syntheses of carbocyclic and hetrocyclic systems by the enamine method are now known[1], only a few syntheses of hetrocyclic systems, utilizing heterocyclic enamines have been reported[2,3].

We wish to report a simple synthesis of 6-aza-2-methylchromone (I), by the use of an heterocyclic enamine[4].

I was prepared in 3 steps, starting from 1-benzyl-4-piperidone (II), in overall yield of 35% (see Scheme 1).

Scheme 1



Treatment of II with morpholine, in the usual manner[5], afforded the enamine III in 75% yield[6]; b.p. 146-150° (0.1 mm); ms, M^+ 258. Reaction of I equivalent of III with 2 equivalents of diketene[7] in CH_2Cl_2 yielded IV as viscous yellow oil; 65%, b.p. 180-184° (0.05 mm); ms, M^+ 255. Acetoacetmorpholide is a byproduct in this reaction.

When IV was refluxed for 48 hrs in xylene in the presence of 10% Pd/C, dehydrogenation and debenzylation occurred, and I was obtained in 72% yield; m.p. 150°; ir (CCl_4), 1660 cm^{-1}, 1600 cm^{-1}, 1455 cm^{-1}, 1350 cm^{-1}, 1170 cm^{-1}, 950 cm^{-1}; u.v., $\lambda_{max.}^{MeOH}$ (ε), 216 mm

(16400), 241 nm (6100), 268 nm (6500), 278 nm (6400); n.m.r. (δ), 2.39 (3H,s), 6.22 (1H,s), 7.30 (1H,d,J=6cps), 8.76 (1H,d,J=6cps), 9.38 (1H,s); ms, M^{+} 161.

Syntheses and properties of other aza-chromones will be reported elsewhere.

Footnotes and references

1. Enamines: synthesis, structure and reactions, Ed. A.G. Cook, Dekker, New York, 1969.

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4. The preparation of 8-azaflavone from pyridine derivatives has been reported recently: H. Sliwa, Bull. Soc. Chim. Fr. (2) 631 (1970).

5. G. Stork, A. Brizzolara, H. Landesman, J. Szmuszkovicz and R. Terrel, J. Am. Chem. Soc. 85, 207 (1963).

6. All compounds reported herein have ir, n.m.r and mass spectra fully in accord with proposed structures. New compounds gave satisfactory elemental analyses.

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