

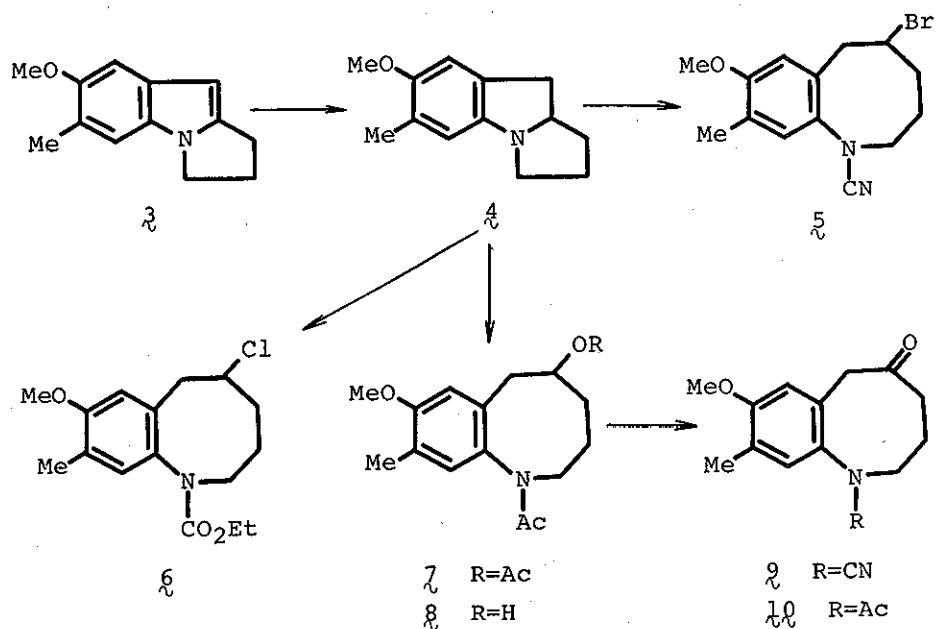
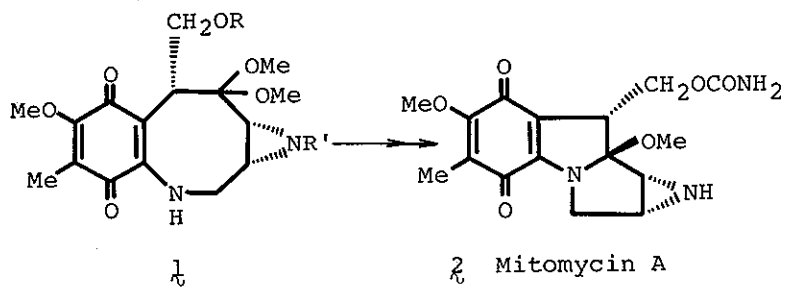
ALTERNATIVE SYNTHESSES OF
2,3-BENZAZOCIN-5-ONE DERIVATIVES VIA PYRROLO[1,2-a]INDOLES

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Transformations of 2,3,9,9a-tetrahydro-1H-pyrrolo-
[1,2-a]indole (4) into hexahydro-2,3-benzazocine deriva-
tives (6 and 7) using ethyl chloroformate or acetic
anhydride were described.

The 2,3-benzazocin-5-one derivative 1 has been shown as a key
intermediate in the total synthesis of mitomycins.¹ We have
recently reported the transformation of the pyrrolo[1,2-a]indole
3 into the 2,3-benzazocin-5-one 9 through 5.² In this communi-
cation, we wish to report the alternative transformations of the
pyrrolo[1,2-a]indole 3 to the 2,3-benzazocine derivatives (6, 7
and 10).

The reaction of the indoline 4, prepared from 3 with sodium
borohydride reduction in acetic acid,² with ethyl chloroformate
in chloroform in the presence of sodium carbonate at room tempe-
rature for 8 hr gave 6 as a syrup [ir $\nu_{\text{max}}^{\text{CHCl}_3}$ 1690 cm^{-1} ; nmr δ



(CCl₄) 1.16 (3H, t, $J = 7$ Hz, CH₂-CH₃), 2.16 (3H, s, ArCH₃), 3.84 (3H, s, OCH₃), 6.66 and 6.80 (each 1H, each s, ArH x 2); m/e 313, 311 (M⁺), 276 (M⁺-Cl), 202 (base peak) in a moderate yield.

On the other hand, heating the indoline **4** in acetic acid in the presence of acetic anhydride under reflux afforded, in a reasonable yield, the diacetate **7**,³ mp 126 - 128°; ir $\nu_{\max}^{\text{CHCl}_3}$ 1725, 1640 cm⁻¹; nmr δ (CCl₄) 1.64 and 1.66 (each 1.5H, each s, NCOCH₃), 2.00 (3H, s, OCOCH₃), 2.18 (3H, s, ArCH₃), 3.86 (3H, s, OCH₃), 6.60 and 6.80 (each 0.5H, each s, ArH), 6.90 (1H, s, ArH), m/e 305 (M⁺), 202 (base peak).

Hydrolysis of the O-acetyl group of this compound **7** with potassium carbonate in aqueous methanol afforded the alcohol **8**,³ mp 167 - 168°; ir $\nu_{\max}^{\text{CHCl}_3}$ 1630 cm⁻¹; nmr δ (CCl₄) 1.64 and 1.66 (each 1.5H, each s, NCOCH₃), 2.14 (3H, s, ArCH₃), 3.80 (3H, s, OCH₃), 6.70 and 6.76 (each 0.5H, each s, ArH), 6.82 (1H, s, ArH); m/e 263 (M⁺).

The above nmr spectra of **7** and **8** would indicate the presence of two rotamers about the amide linkage in a ratio of ca 1 : 1.⁴

The oxidation of **8** was carried out with chromium trioxide-pyridine complex in methylene chloride at room temperature to give the objective benzazocin-4-one **10**³ in a good yield, mp 148 - 149°; $\nu_{\max}^{\text{CHCl}_3}$ 1705 (C=O), 1650 cm⁻¹ (>NC=O); nmr δ (CDCl₃) 1.68 (3H, s, COCH₃), 2.18 (3H, s, ArCH₃), 3.66 (2H, s, ArCH₂CO), 3.84 (3H, s, OCH₃), 6.68 and 6.92 (each 1H, each s, ArH x 2); m/e 261 (M⁺).

Thus, two alternative routes to the benzazocin-4-one derivatives from 2,3-dihydro[1,2-a]indole have been developed.

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3. All new crystalline compounds gave satisfactory microanalyses and reasonable spectroscopic data.
4. C.f. M. Shamma and L. Töke, J. C. S. Chem. Comm., 1973, 740.

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