SYNTHESIS OF 1-BENZAZOCIN-5-ONE DERIVATIVE HAVING AZIRIDINE RING

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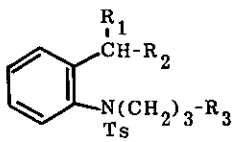
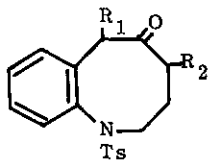
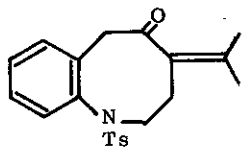
The title compound is an efficient intermediate for the synthesis of mitomycin analogs. We have now found that 1-benzazocin-5-one derivatves (4, 5, 6, and 7) were obtained from 1, 2, and 3 in considarably good yield by Dieckmann reaction (sodium-potassium alloy in toluene), on an examination of its various conditions. The α,β-unsaturated ketone (8) was derived by the coupling reaction of 2-bromo-2-nitropropane with the anion of the β-keto-ester (4) and then deethoxycarbonylation and elimination. The synthesis of the aziridine compound (9) was achieved by addition of bromine azide, followed by treatment of lithium aluminum hydride and chromium trioxide-pyridine oxidation. Also, an alternate and direct synthesis of the aziridine compound (9) was performed by the reaction of 8 with sodium azide in polyphosphoric acid. Other α,β-unsaturated ketones (10, and 11) were prepared from the ketones (5, and 6) *via* sulfenylation and dehydrosulfenylation. The transformation of 10, and 11 into the aziridine compound (12) was unsuccessful at the reactions as mentioned above and is now under investigation. Furthermore, *the removal of tosyl group and transannular cyclization of 7, 9, and 11 was examined.*



1, R_1=H, R_2=COOEt, R_3=COOEt
2, R_1=Me, R_2=COOMe, R_3=COOEt
3, R_1=Me, R_2=COOMe, R_3=CN



4, R_1=H, R_2=COOEt
5, R_1=COOEt, R_2=H
6, R_1=Me, R_2=COOEt
7, R_1=Me, R_2=CN



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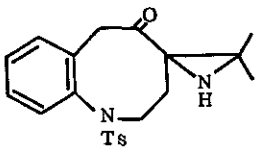

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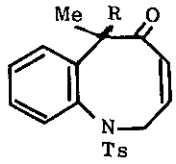
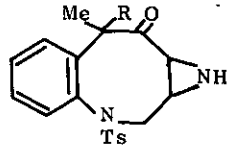


10, R=H
11, R=Me



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