

ON THE SYNTHESIS OF AJMALINE

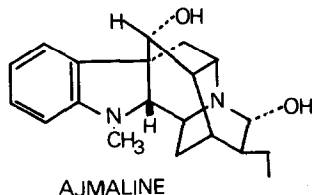
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(Received in Japan 26 December 1968; received in UK for publication 4 February 1969)

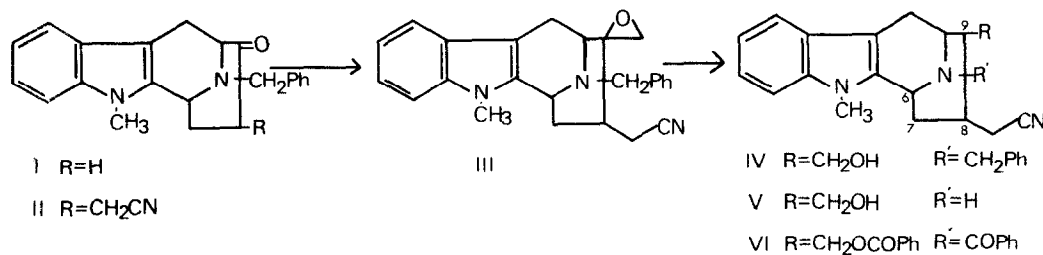
Success of the synthesis of isoajmaline reported in the foregoing communication tempted us to exploit a new route to reach ajmaline, whose first synthesis was already described in the brilliant work of S.Masamune et al¹⁾ in 1967.



In their synthesis the nitrile (VI ; 8a in their paper) formed the key intermediate, which we could prepare in a few steps starting from the ketone (I), which also was the starting material in our isoajmaline synthesis. Yield in each steps were from fair to good.

Thus pyrrolidine-enamine of (I) prepared as usual was treated with chloroacetonitrile in dioxane solution to give (II) (IR* 2250cm⁻¹(CN), 1720cm⁻¹(C=O), yield 50%, picrate mp. 203-205°). Reaction with dimethyloxosulfonium methylide²⁾ in DMSO converted the latter to the corresponding oxirane obtained as a hard syrup, which was covered with benzene to separate crystalline (III) in 70% yield on standing (mp. 165-166°, IR 2250cm⁻¹(CN), 905cm⁻¹(oxirane)), the oxirane ring

*The IR spectra were taken in CHCl₃ unless stated otherwise.



of which was reductively cleaved by the agency of HAlCl_2 or AlH_3 ³⁾ to afford the carbinol (IV) (IR $3250\text{cm}^{-1}(\text{OH})$, $2250\text{cm}^{-1}(\text{CN})$, yield 80%, O-benzoyl derivative mp. 198-201°). Reductive debenzoylation with H_2 over 10%Pd-C furnished the secondary base (V) (mp. 191-193° (dec.), IR $3300\text{-}3200\text{cm}^{-1}(\text{OH}, \text{NH})$, $2250\text{cm}^{-1}(\text{CN})$, yield 80%), which was dibenzoylated with an excess of benzoyl chloride and pyridine. The resultant compound (VI)* (mp. 140-145°, IR $2250\text{cm}^{-1}(\text{CN})$, $1720\text{cm}^{-1}(\text{O-CO-C}_6\text{H}_5)$, $1630\text{cm}^{-1}(\text{N-CO-C}_6\text{H}_5)$) was proved to be identical with the Masamune's intermediate (8a in his report) through direct comparison. (IR and NMR data).

Acknowledgement

We are grateful to Prof. S. Masamune for providing us with IR and NMR charts of his compound.

References

- 1) S.Masamune, S.K.Ang, C.Egli, N.Nakatsuka, S.K.Sarkar, Y.Yasunari, J. Am. Chem. Soc., **89**, 2506(1967).
- 2) E.J.Crey, M.Chaykovsky, J. Am. Chem. Soc., **87**, 1353(1965).
- 3) M.N.Rerick, E.L.Eliel, J. Am. Chem. Soc., **84**, 2356(1962).

*Dimorphism of this compound will be discussed in the full paper.