

THE SYNTHESIS OF d1-OCTAHYDRO-4H-INDOLIZINO[1,8-a,b]CARBAZOLES

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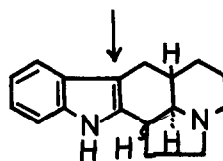
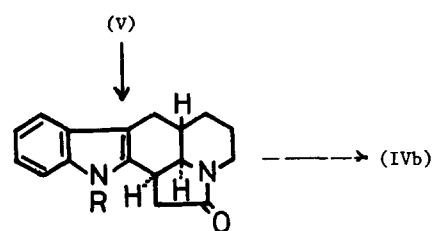
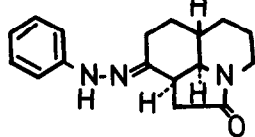
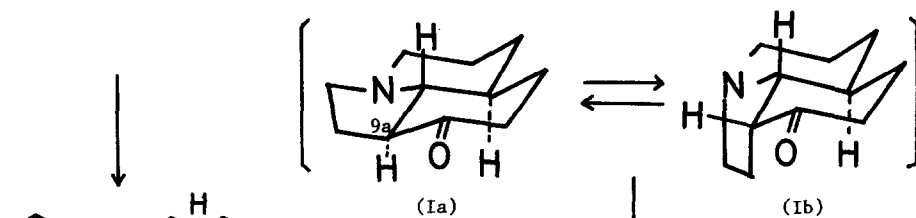
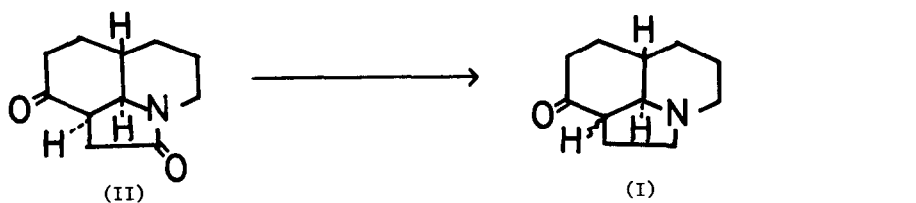
(Received in Japan 10 March 1969; received in UK for publication 29 April 1969)

The stereochemistry of octahydro-4H-pyrrolo[3,2,1-i,j]quinolin-9(2H)-one(I) and the tricyclic lactam(II) was discussed in the preceding paper(1). The phenylhydrazones of these ketones were submitted to the Fischer indole synthesis with anhydrous(98-100%) formic acid which is not only effective as a catalyst and sometimes as a simultaneous reducing agent, but also interesting in respect of direction of cyclization (2).

The phenylhydrazone(III) of the amino-ketone(I) indicating two spots on TLC due to an equilibrium mixture of Ia and Ib, was refluxed at 135-140° with anhydrous formic acid for 35 min. The reaction product was purified by chromatography on alumina to afford two substances in totally 67% yield; the one(IVa) showed m.p. 149-150°, the other(IVb) indicating m.p. 239-240° in the production ratio of IVa:IVb = 1:1.3, each of which proved to be pure by indicating only one spot on TLC. Although both compounds gave the same molecular ion peaks(M^+ = 252) and the identical ultraviolet spectra being characteristic of the indole, the Bohlmann's bands (3) were observed with the former(IVa) and not with the latter(IVb).

In the meantime, the phenylhydrazone(V), m.p. 219-221°, derived from the tricyclic lactam-ketone(II) was heated at 140° with formic acid for 4 hrs. affording the N-formylindole(VI), m.p. 263-264°, in 79% yield as a sole isolable product. The compound(VI) was hydrolyzed with alkali to afford the indole(VII), m.p. 296-298°, which in turn, was reduced with lithium aluminum hydride in tetrahydrofuran to give only one product(IVb), m.p. 239-240°, in 93% yield, being identified with one(IVb) of the previously obtained products from the compound(I).

Thus, the stereochemical formulas, (A) and (B), should be given to the indole derivatives, (IVa) and (IVb), respectively, which are able to well explain the above results, particularly the positive Bohlmann's absorptions for IVa and the negative for IVb (3). The reason is not clear at present why neither indolenine nor indoline was detected in this case, although the similar tricyclic ketones(VIII, $R=C_2H_5$, $CH_2CH_2OC_6H_5$; $X=H_2$, O) involving the larger substituents(R) at C-6a afforded the indoline derivatives in addition to indoles under the similar

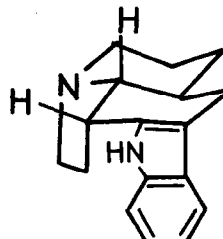
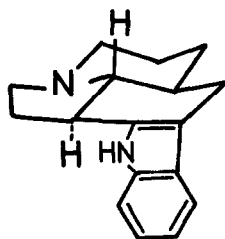
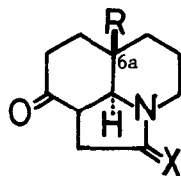


(VI) R = CHO

(VII) R = H

(IVa) M.p. 149-150°, B.b. +

(IVb) M.p. 239-240° B.b. -



condition (4). However, the present results that two diastereomeric indoles were isolated as IVa and IVb on the Fischer cyclization of I, confirms the previous proposal claiming that the ketone(I) should exist as a conformational equilibrium mixture of Ia and Ib through the ready epimerization of C(9a)-H adjacent to the carbonyl function.

Acknowledgements: The support of the United States Public Health Service, National Institutes of Health, Grant (5 ROI MH-08187) for this research project is gratefully acknowledged.

REFERENCES

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2. Y. Ban, T. Oishi, Y. Kishio and I. Iijima, Chem. Pharm. Bull. Japan, 15, 531 (1967).
3. F. Bohlmann, Chem. Ber., 91, 2157 (1958).
4. See the following communication.