The Rearrangement of 2,3-Dimethyl-1-(3-oxobut-1-enyl)indole

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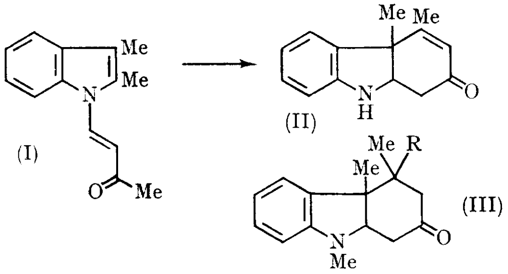
THE rearrangement of 2,3-dimethyl-1-(3-oxobut-1-enyl)indole (I) to 1,2,4a,9a-tetrahydro-4,4a-dimethyl-2-oxocarbazole (II) in the presence of methanolic hydrogen chloride has been reported in brief by Teuber *et al.*[1] Although some convincing evidence was presented in favour of the structure (II) for the product of this remarkable rearrangement, we felt that it was desirable to substantiate it by the unambiguous synthesis of (II) or a close relative.

The compound (II) was prepared by the method outlined by Teuber *et al.*,[1] and subsequently hydrogenated (Pd–C) to its 3,4-dihydro-derivative, m.p. 104–105°, ν_{max} 3345, 1710 cm.$^{-1}$. Methylation of this product (Me_2SO_4) gave 1,2,3,4,4a,9a-hexahydro-4,4a,9-trimethyl-2-oxocarbazole (III; R = H) as two stereoisomers: A, m.p. 64—65°, and B, m.p. 69°.

The acid-catalysed condensation of 1,3-dimethylindole with pent-3-en-2-one gave the ketone (III; R = H) as two stereoisomers; B, m.p. 69°, and C, 85°. The two isomers B prepared by these two independent routes exhibit completely superposable i.r. spectra and give identical R_F values on thin-layer chromatograms, and are clearly identical compounds. Isomers, A, B, and C exhibit very similar i.r. spectra, but there are some significant differences consistent with their formulation as stereoisomers. That A (which was not obtained in sufficient quantity to allow extensive investigation), B, and C are stereoisomers is confirmed by their behaviour on electron impact; the mass spectra of A, B, and C are virtually identical, and show only very minor differences in relative peak intensities.* Interestingly, these mass spectra are very closely similar to the mass spectrum of the amino-ketone (III; R = Me),[2] the structure of which has been independently established.[2,3]



(I) (II) (III)

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[1] H. J. Teuber, U. Reinehr, and D. Cornelius, *Tetrahedron Letters*, 1965, 1703.

[2] D. A. Cockerill, Sir Robert Robinson, and J. E. Saxton, *J. Chem. Soc.*, 1955, 4369.

[3] B. Robinson and G. F. Smith, *J. Chem. Soc.*, 1960, 4574.