The Reaction of Skatole with 3-Chloro-3-methylbut-1-yne: a Novel Ring Expansion involving an Allenic Carbene

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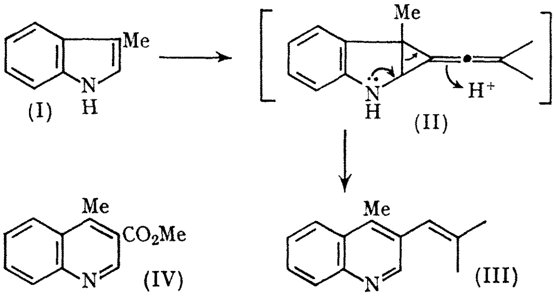
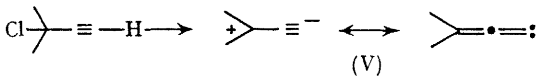
OUR interest in the β-substitution of indoles with C_5 units led us to investigate the reaction of skatole (I) with 3-chloro-3-methylbut-1-yne. A similar reaction affording the expected indolenine in good yield has been described.[1] When the above reaction was carried out in acetone over anhydrous potassium carbonate, the basic fraction afforded in 30% yield a yellow oil, b.p. 110—120° (air bath temp.)/0·1 mm. which gave a crystalline perchlorate m.p. 185—186°. The mass spectrum of the free base exhibited a molecular ion at *m/e* 197 and analytical data indicated a molecular formula of $C_{14}H_{15}N$. The spectral properties, λ_{max} (EtOH), 228 (ϵ 22,000), 278 (3600) and 318 nm. (1650); n.m.r. ($CDCl_3$): τ 1·18 (s, 1H, Ar·N:C*H*·), 1·6—2·6 (m, 4H, aromatic), 3·5 (broad s, 1H, ·C*H*:C<) 7·27 (s, 3H, Ar·CH_2), 7·83 [d, 3H, *J* ~ 1Hz., ·CH:C·(CH_3)·], 8·12 [d, 3H, *J* 1 Hz., ·CH:C(CH_3)·], were clearly not in accord with the expected indolenine. Hydrogenation of the base gave a product (not isolated) which exhibited a characteristic quinoline u.v. spectrum. Ozonolysis afforded acetone, identified as its 2,4-dinitrophenylhydrazone, and an unstable aldehyde which was immediately oxidised by the method of Corey[2] to an ester, m.p. 121—123°, λ_{max} (EtOH), 215 (ϵ 22,300), 235 (51,600), and 284 nm. (5500). This proved to be identical (i.r., u.v., n.m.r., and t.l.c.) with the ester (IV) prepared from lepidine-3-carboxylic acid[3] (kindly provided by Dr. Manske). The above spectral and chemical evidence is completely consistent with the structure (III) for the free base.

We suggest that the reaction proceeds through the intermediate (II), formed by the addition of the resonance-stabilised carbene (V) to skatole. The addition of (V), generated by the action of strong base on 3-chloro-3-methylbut-1-yne, to alkenes has been shown to give cyclopropane derivatives.[4] It is surprising that under the mild conditions used in the above reaction that carbene addition is preferred to nucleophilic substitution.





Initial observations with pyrrole suggest that a similar ring expansion occurs in this case.

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