Ring-expansion of Cyclic Ketones *via* Reaction of Enamines with Carbenes. Synthesis of A-Homo-steroids

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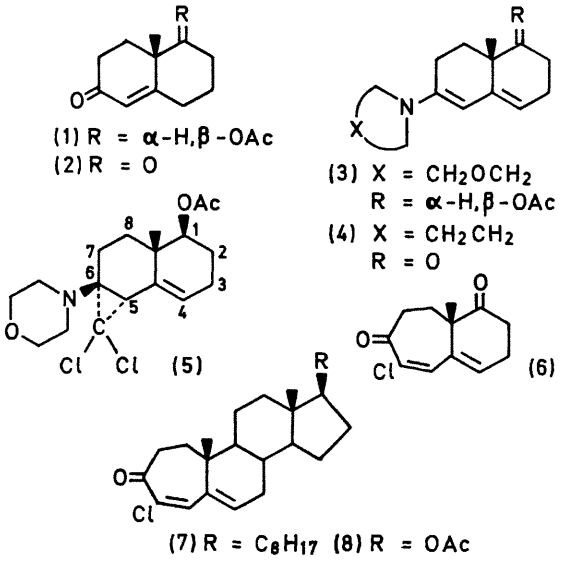
Summary Reaction of dichlorocarbene, generated from thermal decomposition of sodium trichloroacetate, with pyrrolidine enamines derived from αβ-unsaturated cyclic ketones leads to the formation of ring-expansion products.

WHILE the dichlorocarbene adduct of cyclopentanone enamine has been thermally converted into 2-chlorocyclohex-2-enone,[1] attempts to achieve ring expansion of cyclohexanone, *via* analogous adducts, have so far proved unsuccessful.[2,3]

In connection with our current interest in the reactivity patterns of "functionalized enamines," we have examined the reaction of dichlorocarbene with the enamines derived from cyclic αβ-unsaturated ketones (1) and (2). When the morpholine enamine (3) was heated under reflux in dimethoxyethane (DME) with a four-fold excess of sodium trichloroacetate for 10 hr., the crystalline adduct (5), m.p. 158—159°, was obtained in 35% yield. While the site of addition in (5) is evidenced by a distorted triplet ($CDCl_3$ δ 5·75, 1H) for the 4-H vinyl proton; the stereochemical assignment of the cyclopropane ring (5α,6α) rests on the lack of any unusual displacement of the 8a-methyl signal ($CDCl_3$ δ 1·04, 3H)—which might be expected for the 5β,6β-product. The α-addition pattern conforms to the configuration of certain Δ^4-steroid–carbene adducts.[4]

In contrast to the behaviour of (3), reaction of enamine (4) with sodium trichloroacetate, in DME, gave chloroketone (6), m.p. 104—106°, in good yield. The structure of (6) followed from its spectroscopic data† [$C_{12}H_{13}O_2Cl$; i.r. (KBr) 1700, 1650, and 1565 cm^{-1}; n.m.r. ($CDCl_3$) δ 1·25 s (CH_3) 6·35 t (=C*H*), and 7·27 s (CCl=C*H*); u.v. (EtOH) 294·5 nm (13,750)]. That the course of the reaction is solely determined by the nature of the base and not by the substituent at the 1-position, was shown by the parallel behaviour of the morpholine and pyrrolidine enamines derived from (1) and (2), respectively.

The enamine ring-expansion reaction was utilized for a two-step conversion of Δ^4-cholestenone and testosterone acetate—*via* their pyrrolidine dienamines—into the corresponding A-homo-steroids (7) (m.p. 137·5—140°; 31%) and (8) (m.p. 158—161°; 34%).



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† Spectroscopic and analytical data support the structural assignments of all new compounds described.

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