The Stereochemistry of the Addition of Hydrogen Chloride to Endocyclic αβ-Unsaturated Ketones

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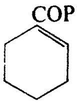
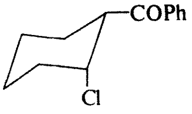
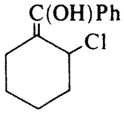
CONSIDERABLE attention has been given to the addition of hydrogen halides to endocyclic *αβ*-unsaturated carboxylic acids, the mechanism of the addition, and the stereochemistry of the resulting products,[1] but apart from one reference[2] no attention has been paid to the corresponding reactions with *αβ*-unsaturated ketones.

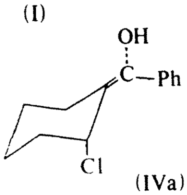
Hydrogen chloride gas when passed into an ethereal solution of 1-benzoylcyclohexene (I) gave an almost immediate precipitate of white solid which from light petroleum (60—80°) gave pure 1-benzoyl-2-chlorocyclohexane[2] (90% yield; m.p. 99—100°; i.r. (KBr disc.), 1690 (s) (C=O of satd. ketone), 675 cm.$^{-1}$ s (C—Cl stretch); M^+ 222·081).

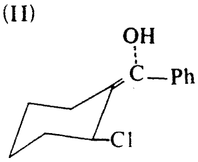
The n.m.r. spectrum of 1-benzoyl-2-chlorocyclohexane at 60 Mc./sec. and 100 Mc/sec. ($CDCl_3$) showed peaks τ *ca.* 2·3 (m, 5H, ArH) 5·35 (distorted q, 1H), 6·45 (dt, triplets, 1H) and 8·1 (8H, methylene protons). The reaction of 1-benzoylcyclohexene with deuterium chloride gave the deuteriated compound, which showed multiplet peaks at τ 2·45, 5·35 (now a distorted triplet) and 8·1, the peak at 6·45 having disappeared. The signal at τ 6·45 was therefore that of the methine proton adjacent to the carbonyl group. Calculations with the Karplus equation [4] showed that the hydrogen atom adjacent to the carbonyl group is in the axial conformation and that the hydrogen atom adjacent to the chlorine atom is in the equatorial conformation and that (II) is the predominant conformation in solution.

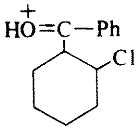

(I)

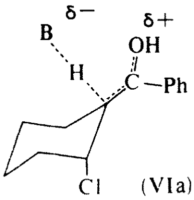

(II)

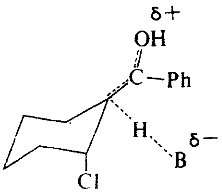

(III)


(IVa)


(IVb)


(V)


(VIa)


(VIb)

The configuration was also identified from the i.r. spectrum (KBr disc). Calculations with empirical data[5] gave the position of the C–Cl stretch for (II) as 685 ± 10 cm.$^{-1}$ and values of 742 and 650 cm.$^{-1}$ for the other possible conformations and configuration. The observed C–Cl stretch at 675 cm.$^{-1}$ again establishes the configuration as the *cis*-isomer with the chlorine axial and the benzoyl group equatorial.

The probable reaction mechanism is *via* the formation of the enol (III), formed by overall 1,4-addition of HCl to (I). This enol can exist in two conformations (each with a corresponding geometrical isomer) (IVa) and (IVb) of which (IVb) will be destabilised with respect to (IVa) because of the $A_{1,3}$ interaction between the equatorial chlorine and the phenyl group.[6] Attack by an acid species BH on the enol (IVa) to give (V) can occur at the carbon atom in a line at right angles to the plane formed by the double-bond, the hydroxy-group and the phenyl group to give transition states (VIa) and (VIb). The steric compression should be greater in the transition state with the attacking BH species on the same side as the chlorine atom and therefore the transition state (VIa) should be favoured. This would give the observed product *cis*-1-benzoyl-2-chlorocyclohexane (III).

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