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Reaction of Acetyl Cation with Cyclohexane

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Recently, spectroscopic investigation of carbonium ions were carried out successfully[1] in which intermolecular hydride shift even from a simple saturated hydrocarbon to lead to an alkyl cation was observed.[2]

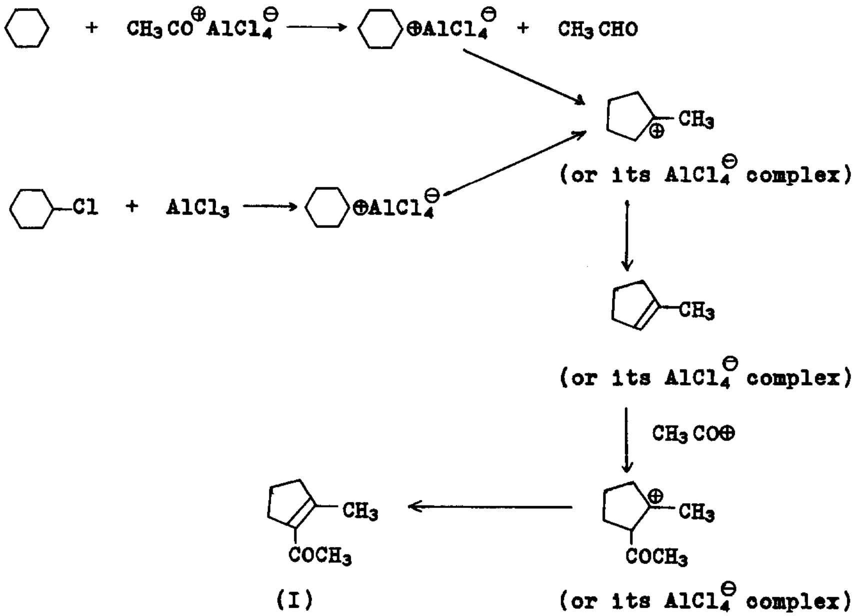
We now wish to report a reaction of cyclohexane with acetyl chloride in the presence of the equimolecular amount of aluminum chloride. The reaction gave only a rearranged acetyl derivative.[3] The reaction will give an useful preparation of ketones from very readily available hydrocarbons.[4] The investigation of the reaction will afford some information about the fate of a carbonium ion in solution.

Thus acetyl chloride (4.0 g) was added to aluminum chloride (6.7 g) in chloroform (20 ml) at room temperature. When the mixture became homogeneous, cyclohexane (4.2 g) was added and resultant solution was refluxed for two hours and then kept at room temperature overnight. The mixture was poured onto ice-HCl and distillation after usual work up gave the fraction A (b.p. 83-85° at 35 mmHg ; 2.2 g, 36% based on cyclohexane used) and B (up to 84° at 7 mmHg; 0.77 g). The latter consisted of several compounds and their structural determinations are now under way. Fraction A consisted of single product (single peak in using several columns) and showed α,β-unsaturated carbonyl in IR spectrum (1685 and 1620 cm^{-1}).[5] It was readily converted to semicarbazone, melted at 220-221° after recrystallization from aq. methanol (221° as a semicarbazone of I[6]). Nmr spectrum was also consistent with I ; singlet at 7.89τ (3 protons) two singlets at 7.97 and 8.00τ (3 protons) and other alicyclic protons (6 protons). Result of the bromoform reaction (Br_2 and NaOH) which gave bromoform and a carboxylic acid as principal products also supports the structural assignment in that acetyl function is present. Hydrogenation of the unsaturated ketone on Pd-C proceeded quantitatively, giving saturated ketone

(IR, 1705 cm^{-1}). This is an additional evidence for C=C-C=O function. Thus I was determined as 2-methyl-Δ^1-cyclopentenyl methyl ketone. Cyclohexyl chloride also gave the same product, I, in a comparative yield on treatment with acetyl chloride and aluminum chloride.

A probable mechanism may be written as shown in Scheme I. Skeletal rearrangement of cyclohexyl cation was observed elsewhere[2] and attack of an acetyl cation moiety on an alicyclic double bond was sometimes observed.[7] But usually cationic addition to cyclohexene gave a mixture of unrearranged products, acetyl cyclohexene-1 and cyclohexyl acetate.[7c]

Scheme I



So that the strikingly simple product obtained in our reaction seems very interesting in the sense that it would afford the convenient preparative route to (I) and also that it would allow us to gain further insight into the nature of carbonium ion derived from hydride shift. Reactions of a series of saturated hydrocarbon and saturated compounds of various functional groups are now investigating.

References

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