CHAPTER -II

Reactions of Ketenes

A. Scope of the present study

In recent years, extensive studies on ketene reactions have been reported in the literature. In almost all the cases, the ketenes have been prepared *in situ* and reacted with the substrates. A large variety of ketenes have been generated mainly via two methods viz. by dehydrohalogenation of corresponding acid halides and zinc dehalogenation of α-haloacyl halides. Substrates are mainly olefins, cyclic or acyclic, other compounds containing between carbon-carbon or carbon and other heteroatom and the carbonyl compounds.

In present study our principal aim was to prepare some ketene derivatives and study their reactions with some other substrates having olefinic linkage or carbonyl grouping. We attempted to prepare pentamethylene ketene and dichloro-ketene for these studies. Pentamethylene ketene was prepared *in situ* by dehydrohalogenation of cyclohexane carbonyl chloride[21] with triethylamine. Dichloroketene was prepared from both dichloroacetyl chloride and trichloroacetyl chloride. The substrates used were dihydronaphthalene, 1-methyl-3-4-dihydronaphthalene and aromatic ring substituted cinnamic esters. Improved method of Hassner[15] was also used for the reaction of dichloroketene with dihydronaphthalene.

Unfortunately, all attempts virtually failed to yield expected product and instead of yielded ketene dimer or inconclusive results.

B. Results and Discussions

In reactions of pentamethylene ketene with dihydronaphthalenes and substituted cinnamic esters the main product isolated was the dimer, the other products were so little that they could not be isolated and characterised.

Similarly, reactions of dichloroketene and the olefins could not be studied, the products had not been isolated and characterised fully.

The reason for the failure has been thought to be that the olefinic double bond in dihydronaphthalene and 1-methyldihydronaphthalene is fairly inactive and on the other hand ketenes generated by dehydrohalogenation method tends to polymeric readily due to the catalytic activity of triethylamine present. Later, these reactions were attempted according to the reported procedure of Hassner for the reactions of ketenes with hindered olefins. In this procedure dichloroketene was generated by dehalogenation method and both the reactants and substrate are maintained at very large dilution with solvent ether so that dimerisation of ketene occurs less. But in this method also no adduct with the added olefin could be isolated.

Methyl cinnamate, o-methoxymethyl cinnamate and p-methoxy methyl cinnamate are by far more active (as found in a separate work) olefins but failure of addition of pentamethylene ketene and dichloroketene was observed.

Zinc dehalogenation method of obtaining dichloroketene was employed for the reactions with α-tetralone in presence of anhydrous zinc chloride as catalyst but bimolecular addition with the enol form could not be effect.

E. Experimental

1. Preparation of cyclohexane carboxylic acid[68]

270 ml of 96% sulphuric acid was poured into a 3-necked flask equipped with a magnetic stirrer, a dropping funnel with a gas by pass, and a thermometer that dip into

the acid. The reaction mixture was stirred moderately and maintained at 15-20° by means of cooling bath as 3 ml of 98-100% formic acid was added dropwise. Under the same condition a solution of 25 g of cyclohexanol in 46g of 98-100% formic acid was added in the course of 1 hr. The reaction mixture foams during additions. The mixture which is a very light cream colour was stirred for 1 hour at 15-20° and then poured with stirring onto 1 kg of crushed ice in a 4L beaker. The carboxylic acid was separated as oil.

The acid was taken up in 200 ml of hexane, the hexane layer was separated, and the aquous layer was extracted with two 150 ml portions of hexane. The combined hexane solution were extracted with a mixture of 175 ml of 1.4 N potassium hydroxide solution and 50g of crushed ice. The two alkaline solutions were combined and extracted with 100 ml of hexane to remove traces of neutral oil, and then acidified to pH 2 with 12N hydrochloric acid (about 35 ml). The liberated acid was taken up in 150 ml hexane. The aquous layer was extracted with 100 ml of hexane and the combined hexane layer washed with 75 ml of water and dried over 3g of anhydrous magnesium sulphate. The hexane was evaporated by washing the solution at 30°-60° at 15-30 mm pressure overnight. The residue was a colourless viscous liquid, distillation at 110°/5 mm affords a colourless syrapy liquid, solidifies at 30°; yield 21g.

2. Cyclohexane carbonyl chloride[69]

A reflux consenser with a calcium chloride guard tube was fitted up with the centre neck of a 3-necked flask, one side neck was closed and the other side neck was attached with a dropping funnel. 14g (redistilled) thionyl chloride was placed in the flask and 10g of cyclohexane carboxylic acid was taken in the dropping funnel. The flask was heated gently on a water bath and the acid was added during one hour. The evolved hydrochloric acid was absorbed in water. After addition of total amount of acid the mixture was heated on water bath for further 30 minutes and then distilled into a second distilling flask. The distillate further was distilled and acid chloride boiling at 179° and yield 6g was obtained.

3. Dichloroacetyl Chloride.

This was prepared in the same manner as above from 14g redistilled thionyl chloride and 13g dichloroacetic acid. Distilled at 109 yield 4g.

4. Trichloroacetyl chloride[15]

To a stirred mixture of 9.7 g of trichloroacetic acid and 0.3 ml of dimethyl formamide at 85°C was added 5.1 ml redistilled thionyl chloride dropwise, when addition was over, heating at this temperature was continued for 2 hours. The bath temperature was lowered to 60-65°C and the product was distilled (40-45° at 20-25 mm) and collected in an ice-cold receiver. The first few ml were discarded. The product was distilled once more at reduced pressure and finally at atmospheric pressure to yield 7.4g of trichloroacetyl chloride b.p. 119-120°C.

5. Activated zinc[15]

Brady's method was modified to some extent. A stirred suspension of 10.0g of zinc dust in 40 ml of water was degassed by bubbling nitrogen gas through it for 2 hrs. Then 750 mg of copper sulphate was added at once. The black suspension was stirred while nitrogen gas was bubbled through it for an additional 45 minutes. The Zn-Cu couple was collected on a sintered glass funnel under a stream of nitrogen and washed successively with 100 ml of degassed water and acetone. The Zn-Cu couple was transferred to a small flask under a stream of nitrogen and dried at reduced pressure (0.2 mm) for 2 hours. Nitrogen was admitted to the system when the vacuum was broken and the Zn-Cu couple stored under nitrogen atmosphere in a tightly stoppered flask.

6. Reaction of cyclohexane carbonyl chloride and dichloroacetyl chloride with different olefin[21]

General method - A solution of 0.1 mol of acid chloride in 50 ml dry benzene was added dropwise to a refluxing solution of 0.15 mol of triethylamine and 0.2 - 0.3 mole of an unsaturated compound in 150 ml dry benzene. After completion of the addition refluxing was continued for about 20 hours. The amine salt was removed by filtration and washed with benzene. Benzene solution was concentrated and the residue was worked up according to common procedures.

7. Reactions of dichloroacetyl chloride with α-tetralone[14]

To a 500 ml 3-necked flask equipped with an addition funnel charged with 15.0 ml (10.89g) dry triethyl amine diluted to 50 ml with dry ether, a mechanical stirrer, and a claisen adapter fitted with a thermometer and n upright condenser whose reflux end was connected to a nitrogen bubbler was added 0.100 mol of 2-tetralone 100 ml ether 0.1 g fused zinc chloride, 100 ml dry ether 10.0 ml of dichloroacetyl chloride, and 20 ml dry ether. The temperature of the reaction mixture was maintained at 22-24°C. With vigorous stirring under nitrogen atmosphere. The triethylamine solution was added dropwise over 1 hour. When addition was complete the mixture was stirred for an additional 1 hr. period. Then the residue was filtered and washed with ether and the ether solution was washed with water and dried over anhydrous sodium sulphate and concentrated on a rotary evaporator to provide the crude residue.

8. Reactions of trichloroacetyl chloride with dihydronaphthalene[15]

A 1 L 3-necked flask equipped with a condenser, addition funnel, magnetic stirrer and a nitrogen inlet tube was flame dried while purged with nitrogen. When cool the flask was charged with 7.48g of dihydronaphthalene, 3.7g of activated zinc and 500 ml of anhydrous ether. The suspension was stirred under nitrogen and a solution of 9.8g trichloroacetyl chloride and 8.3g of phosphorus oxychloride in 25 ml anhydrous ether was added dropwise over a 1 hr. period. After addition was over, the mixture was refluxed with stirring for 2 hrs. Then the reaction mixture was filtered to remove unreacted zinc. The ether solution concentrated to about 25%, an equal volume of pentane was added and the solution stirred for a few minutes to precipitate the zinc salts. The solution was decanted from the residue, washed successively with water, a cold saturated solution of sodium bicarbonate and brine , and dried over anhydrous sodium sulphate, solvent was removed. Residue analysed but no desired adduct could be characterized.