Halogenated Ketenes. XXVII. The Mechanism of the Dehydrohalogenation of α-Halo Acid Halides[1]

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The triethylamine dehydrohalogenation of α-chloropropionyl chloride produces an enolate salt which has been suggested as being an intermediate in the formation of methylchloroketene.[2] Isobutyryl chloride reacts with triethylamine to yield an acylammonium salt which is apparently the precursor to dimethylketene.[2-5] However, in the synthesis of *tert*-butylhaloketenes, we have discovered some new evidence which has prompted us to further examine the dehydrohalogenation of α-halo acid halides.

The reaction of 2-bromo-3,3-dimethylbutanoyl chloride or 2-chloro-3,3-dimethylbutanoyl chloride with triethylamine in chloroform at room temperature did not yield any detectable amount of vinyl ester, but does produce *tert*-butylbromo- and *tert*-butylchloroketenes which are stable in the reaction solution as evidenced by infrared bands at 2121 and 2110 cm^{-1}, respectively. Efforts to trap an enolate with the more effective acylating agent, trichloroacetyl chloride, were also unsuccessful. Attempts to observe either the enolate or acylammonium salt at −78° by infrared absorption were also unsuccessful. Triethylamine reacted with 2-chloro-3,3-dimethylbutanoyl chloride at −78° to produce a strong ketene absorption. This data suggest that as the steric bulk increases about the α carbon, the α proton becomes less accessible and the ketene is formed from the acylammonium salt.

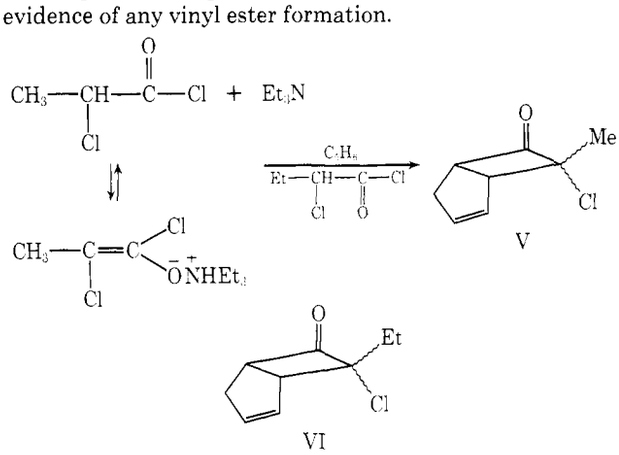
The reaction of α-chloropropionyl chloride in chloroform at −78° with triethylamine yields the enolate salt.[2] Treatment of this salt with an equimolar amount of α-chlorobutyryl chloride produced four products (Scheme I) as evidenced by vpc and confirmed by nmr. The vinyl esters were produced in a ratio of 1:1:0.7:0.6 respectively.

Vinyl esters I and II are expected to be produced by acylation of the enolate by either of the two acid halides. However, the formation of III and IV indicates that the enolate derived from α-chlorobutyryl chloride has been formed which dictates that enolate formation is reversible.

To ensure that enolate formation from α-chloropropionyl chloride and triethylamine had gone to completion, the enolate salt was isolated and washed with hexane as had previously been reported.[2] The addition of an equimolar amount of α-chlorobutyryl chloride in chloroform again produced all four vinyl esters in the same ratio as before.

When the enolate salt of α-chlorobutyryl chloride was formed at −78° and treated with an equimolar amount of α-chloropropionyl chloride, the same four vinyl esters, I–IV, were also produced but in a ratio of 1:6:5:3. This difference in vinyl ester ratios on reversing the order of addition dictates that equilibration is not the most rapid reaction and indicates that a reaction other than enolate formation is occurring at low temperature prior to equilibration. This reaction is probably ketene formation through the acylammonium salt.

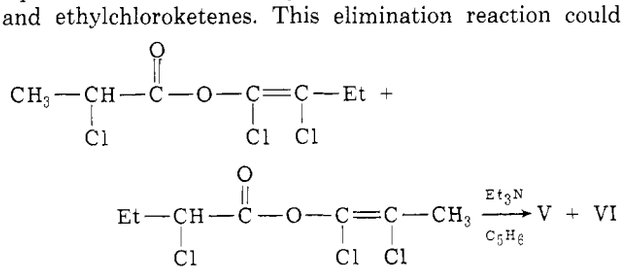
The addition of equimolar amounts of α-chlorobutyryl chloride and cyclopentadiene to the enolate salt derived from α-chloropropionyl chloride and triethylamine at −78° produced approximately equal amounts of the methylchloro- and ethylchloroketene cycloadducts with cyclopentadiene upon warming to room temperature.[6,7] There was no evidence of any vinyl ester formation.



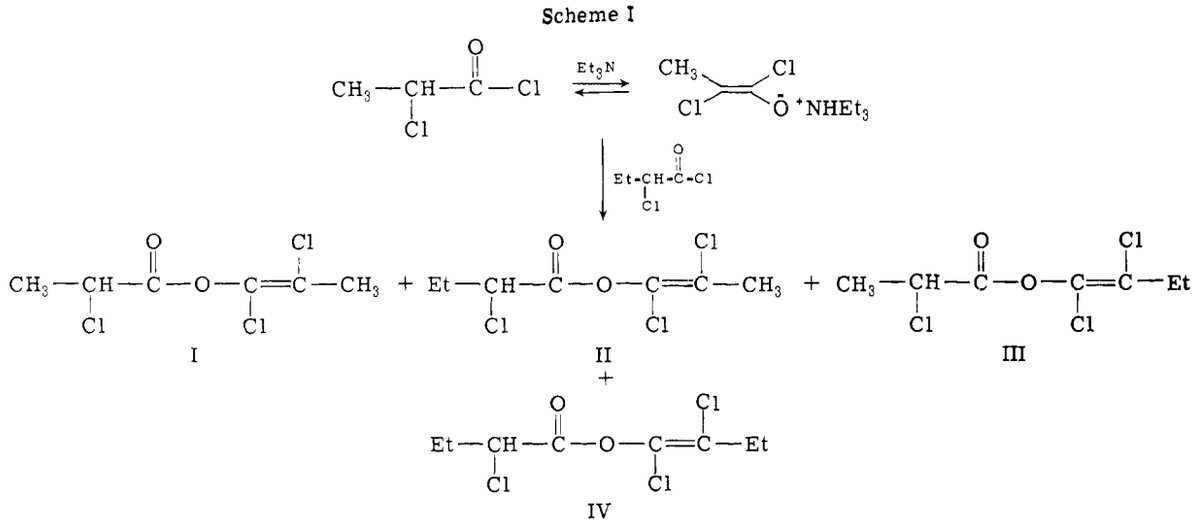
V

VI

Also, it has been found that a synthetic mixture of vinyl esters II and III in a 2:1 ratio, respectively, react with triethylamine in the presence of cyclopentadiene to yield equal mixtures of the two cycloadducts from methylchloro- and ethylchloroketenes. This elimination reaction could



Scheme I

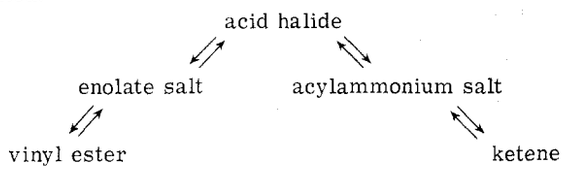


I II III IV

also take place either by nucleophilic attack on the ester carbonyl, or by formation of the vinyl ester enolate and loss of carboxylate. In either case an equal mixture of the two cycloadducts would be expected.

These results clearly demonstrate to us that the enolate forming step in the triethylamine reaction with α-halo acid halides is reversible and furthermore suggests the precursor to halogenated ketenes is the acylammonium salt.

Consequently, it has become clear that a complex series of equilibria are involved in the dehydrohalogenation of α-halo acid halides. The data are consistent with a single pathway to ketene through the acylammonium salt as illustrated.



Experimental Section

Proton nmr spectra were recorded on a Jeolco Minimar 60-Mhz and a Jeolco PS-100 nmr spectrometers employing tetramethylsilane as an internal standard and CCl_4 as a solvent. Solvents and triethylamine were distilled from sodium and stored over Linde type 4-A molecular sieve. Vpc was performed on an F & M Scientific Model 700 gas chromatograph with a 10 ft × 0.25 in. column packed with 10% SE-30 on acid washed chromosorb W (80/100).

***tert*-Butylbromo- and *tert*-Butylchloroketenes.** To a stirred solution of 0.1 mol of triethylamine in 90 ml of chloroform was added dropwise 0.1 mol of 2-bromo-3,3-dimethylbutanoyl chloride or 2-chloro-3,3-dimethylbutanoyl chloride in 10 ml of chloroform at room temperature. The ketene was observed by ir: *tert*-butylbromoketene, 2121 cm^{-1}, and *tert*-butylchloroketene, 2110 cm^{-1}. *tert*-Butylbromoketene persisted in the reaction mixture for 3 days while *tert*-butylchloroketene was observable for only 4 hr. Numerous attempts to isolate the *tert*-butylbromoketene were unsuccessful.

Attempts to trap an enolate from 2-halo-3,3-dimethylbutanoyl chloride with the starting acid halide as previously described were unsuccessful.[8] Efforts to trap an enolate with the more effective acylating agent, trichloroacetyl chloride, are described.

To a stirred solution of 0.05 mol of triethylamine in 40 ml of chloroform was added dropwise 0.05 mol of 2-chloro-3,3-dimethylbutanoyl chloride in 10 ml of chloroform at room temperature. After the addition was complete, 0.05 mol of trichloroacetyl chloride was added and the reaction mixture stirred overnight. No evidence of the mixed vinyl ester, 1,2-dichloro-3,3-dimethyl-1-butenyl trichloroethanoate, was found, only nonvolatile polymeric products.

Vinyl Ester from α-Chlorobutyryl Chloride and the Enolate of α-Chloropropionyl Chloride, I, II, III, and IV. A solution 0.05 mol of α-chloropropionyl chloride in 10 ml of chloroform was added dropwise to a stirred solution of 0.05 mol of triethylamine in 75 ml of chloroform at −78°. Stirring was continued for 0.5 hr after the addition was complete and then 0.05 mol of α-chlorobutyryl chloride in 10 ml of chloroform was added dropwise. The reaction mixture was then allowed to warm to room temperature and stirred overnight. A 100-ml portion of hexane was then added to precipitate the amine salt. Filtration, concentration on a rotatory evaporator, and distillation afforded 6 ml, 49–73° at 0.25 mm, of the four vinyl esters in a ratio of 1:1:0.7:0.6 for I, II, III and IV, respectively, as evidenced by vpc and nmr. Geometrical isomers of the four vinyl esters were not separated under these vpc conditions. The simple vinyl esters, I and IV, have been previously described.[8] The two mixed vinyl esters, II and III, could not be separated by distillation nmr, δ (for the mixture), 1.0 (m, 3 H), 1.65 (d, 1.4 H), 2.0 (s, 0.9 H), 2.15 (s, 0.7 H), 2.10 (m, 2 H), and 4.25 (m, 1 H).

Anal. Calcd for $C_7H_9Cl_3O_2$: C, 36.28; H, 3.98. Found: C, 36.52; H, 3.91.

Generation of Methylchloro- and Ethylchloroketenes from α-Chlorobutyryl Chloride and the Enolate of α-Chloropropionyl Chloride. The enolate salt of α-chloropropionyl chloride was prepared at −78° as described above. To this solution were added with stirring 0.05 mol of α-chlorobutyryl chloride and 0.05 mol of freshly cracked cyclopentadiene. The reaction solution was allowed to warm to room temperature and stirring continued overnight. The amine salt was precipitated by the addition of 100 ml of hexane and removed by filtration. Concentration on a rotatory evaporator and vacuum distillation afforded 3.2 g (40%) of an equal mixture of 7-chloro-7-methylbicyclo[3.2.0]hept-2-en-6-one and 7-chloro-7-ethylbicyclo[3.2.0]hept-2-en-6-one as determined by vpc and comparison with known samples of the two cycloadducts.

Generation of Methylchloro- and Ethylchloroketenes from 1,2-Dichloro-1-butenyl 2-Chloropropanoate and 1,2-Dichloropropenyl 2-Chlorobutanoate. The mixed vinyl esters, II and III, were collected in a 2:1 ratio respectively by preparative vpc. A 50-μl portion of this mixture was added to 0.5 ml of chloroform and 150 μl of freshly cracked cyclopentadiene and 100 μmol of triethylamine. The mixture was stirred at room temperature overnight. Both 7-chloro-7-methylbicyclo[3.2.0]hept-2-en-6-one and 7-chloro-7-ethylbicyclo[3.2.0]hept-2-en-6-one were formed in equal amounts as determined by vpc and comparison with known samples of the cycloadduct.

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Registry No.—I, 52920-13-5; II, 52920-14-6; III, 52920-15-7; IV, 23649-91-4; V, 33471-78-2; VI, 52920-16-8; *tert*-butylbromoketene, 29264-48-0; *tert*-butylchloroketene, 52920-17-9; 2-bromo-3,3-dimethylbutanoyl chloride, 29336-30-9; 2-chloro-3,3-dimethylbutanoyl chloride, 52920-18-0; α-chloropropionyl chloride, 7623-09-8; triethylamine, 121-44-8; α-chlorobutyryl chloride, 7623-11-2; α-chloropropionyl chloride enolate salt with triethylamine, 50635-68-2.

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Synthesis of 5-Ethynyl-2,2′-bithienyl and Related Compounds[1]

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Because of the potential importance of certain 5-substituted-2,2′-bithienyls in the study of nematode control,[3] we were prompted to synthesize 5-(3-buten-1-ynyl)-2,2′-bithienyl (**1**), a highly potent naturally occurring nematicide. Even though **1** has been previously synthesized,[4] we desired an economical synthesis which would provide a better supply of **1** and related compounds for physiological testing. Also, we required a synthesis of 5-(3-penten-1-ynyl)-2,2′-bithienyl (**2**) for comparison of its ultraviolet spectrum with that of **1**.

The synthesis of **1** was accomplished as shown in Scheme I. A key step in this synthesis is the high yield preparation of 5-ethynyl-2,2′-bithienyl (**5**) using the Corey and Fuchs method.[5] Vapor phase dehydration of 5-(3-hydroxy-1-butynl)-2,2′-bithienyl (**6**) over alumina at 540° (0.18 mm) produced a mixture containing **5**, **6**, and **1**. The low yield of **1** (30%) in this step may partially be due to the competitive retro aldol reaction which produces **5**. Attempted dehydra-