Halogenated Ketenes. XXIII. Studies on the Mechanism of the Dehydrohalogenation of Acid Halides[1]

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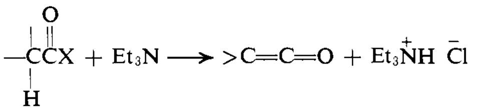
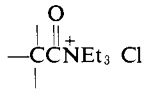
Abstract: The reaction of triethylamine and α-chloropropionyl chloride at $-78°$ produces an enolate salt which has been detected spectroscopically. As the temperature is raised from $-78°$ this salt decays to methylchloroketene. The triethylamine dehydrochlorination of isobutyryl chloride occurs through an acylammonium salt which has also been detected spectroscopically. Molecular orbital calculations using the CNDO/2 approximations on the two acid halides reveal that the charge densities on the two α carbons are responsible for the two different mechanisms.

The dehydrohalogenation of acyl halides with triethylamine is an old and very commonly employed method for the preparation of ketenes.



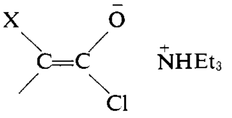
$$\mathrm{-\underset{H}{\underset{|}{C}}\overset{O}{\overset{\|}{C}}X + Et_3N \longrightarrow >C{=}C{=}O + Et_3\overset{+}{N}H\ \overset{-}{Cl}}$$

There is good evidence that the initial step of the reaction involves the formation of an acyl ammonium halide (I) as a precursor to the ketene.[2-4] However, more recently the isolation of α-halovinyl esters (III) from the reaction of α-haloacyl halides and triethylamine have suggested the enolate salt (II) as a precursor to these halogenated ketenes.[5-8]

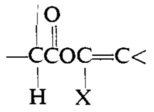


$$\mathrm{-\underset{|}{C}\overset{O}{\overset{\|}{C}}\overset{+}{N}Et_3\ Cl}$$

I



II



$$\mathrm{-\underset{H}{\underset{|}{C}}\overset{O}{\overset{\|}{C}}O\underset{X}{\underset{|}{C}}{=}C<}$$

III

The purpose of the present study was to spectroscopically detect the suspected enolate intermediate and to show unequivocally that two different mechanistic pathways occur for the triethylamine dehydrohalogenation of acid halides. Also, we performed molecular orbital calculations using the CNDO/2 approximation on two acid halides which undergo dehydrohalogenation by the two different pathways in an effort to better understand the determining factors in the mechanistic pathway a particular acid halide follows.

Isobutyryl chloride and α-chloropropionyl chloride appear to represent two mechanistic extremes in the triethylamine dehydrohalogenation of acid halides to form ketenes. Consequently, these two acid halides were chosen for comparison purposes in this study. However, it should be realized that while dimethylketene is a stable isolable ketene, methylchloroketene has never been detected, only trapped as a (2 + 2) cycloadduct.

The reaction of α-chloropropionyl halide with triethylamine in hexane in the presence of cyclopentadiene at room temperature produced the $({}_{\pi}2_s + {}_{\pi}2_a)$ cycloadduct of methylchloroketene and cyclopentadiene in 77% yield.[9] Many cycloadducts of methylchloroketene have been made in this manner.[10-12] The addition of an equimolar amount of triethylamine to α-chloropropionyl chloride in hexane at $-78°$ produces an insoluble salt. This salt was separated from the reaction solution. The salt was slurried in fresh hexane and an excess of cyclopentadiene was added to both the salt slurry and the original reaction solution after the salt had been removed. Both were allowed to warm to room temperature. The methylchloroketene cycloadduct was obtained only from the salt. Consequently, the insoluble salt produced at $-78°$ must be a precursor to the ketene.

The addition of trichloroacetyl chloride to an equimolar amount of α-chloropropionyl chloride and triethylamine in hexane at $-78°$ produces 1,2-dichloropropenyl trichloroacetate in 67% yield. Therefore, the insoluble salt must be the enolate (II).[7,8]

The reaction of α-chloropropionyl chloride and triethylamine in chloroform does not produce an insoluble salt as the salt is soluble in this solvent. When this reaction is effected in an nmr tube at $-60°$, a singlet is observed at δ 1.8 (relative to TMS) and a broad singlet at δ 10.68 (relative to TMS). These two peaks are in a ratio of 3:1, respectively. That the resonance at δ 10.68 is due to the proton on nitrogen in the triethylammonium enolate (II) is supported by the fact that this proton in triethylammonium chloride appears at δ 10.40 and this same proton in triethylammonium acetate at δ 10.49. As the temperature of the nmr tube was allowed to warm to room temperature, the α-halovinyl ester was produced.

An infrared spectrum of α-chloropropionyl chloride in chloroform in the cold reveals three bands in the carbonyl region, 1840 w, 1770–1780 s, and 1725 w cm^{-1}. A spectrum of α-chloropropionyl chloride, triethylamine, and chloroform at $-50°$ reveals a new strong band at 1730 cm^{-1} which upon warming grew

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[1] Paper XXII: W. T. Brady and J. P. Hieble, *J. Amer. Chem. Soc.*, **94**, 4278 (1972).

[2] H. Adkins and Q. E. Thompson, *ibid.*, **71**, 2242 (1949).

[3] H. M. Walborsky, *ibid.*, **74**, 4962 (1952).

[4] D. Cook, *Can. J. Chem.*, **40**, 2362 (1962).

[5] R. Giger, M. Rey, and A. S. Dreiding, *Helv. Chim. Acta*, **51**, 1466 (1968).

[6] J. M. Lavanish, *Tetrahedron Lett.*, 6003 (1968).

[7] R. Giger, R. Allain, M. Rey, and A. S. Dreiding, *Helv. Chim. Acta*, **53**, 120 (1970).

[8] W. T. Brady, F. H. Parry, III, R. Roe, Jr., E. F. Hoff, Jr., and L. Smith, *J. Org. Chem.*, **35**, 1515 (1970).

[9] W. T. Brady and B. M. Holifield, *Tetrahedron Lett.*, 5511 (1966).

[10] W. T. Brady and B. M. Holifield, *Tetrahedron*, **23**, 4251 (1967).

[11] W. T. Brady, R. Roe, Jr., E. F. Hoff, Jr., and F. H. Parry, III, *J. Amer. Chem. Soc.*, **92**, 146 (1970).

[12] W. T. Brady and R. Roe, Jr., *ibid.*, **93**, 1662 (1971).

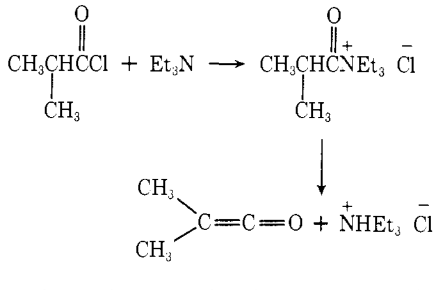
at the expense of the acid halide peaks. As the reaction continued to warm from 0° to room temperature, the formation of triethylammonium chloride could be observed by the formation of a broad peak at 1600–1630 cm^{-1}. This peak forming at 1730 cm^{-1} is not due to the carbonyl stretch of I because it is established that the carbon stretch for acylammonium salts occurs in the region of 1800 cm^{-1}.[4]

In contrast to this result, the low temperature nmr study of the reaction of isobutyryl chloride and triethylamine in chloroform reveals a quartet at δ 2.78 (relative to TMS) and a triplet at δ 1.01 (relative to TMS) due to the triethylamine moiety, a doublet within the triplet at δ 1.02 (relative to TMS) due to the methyl groups in the α carbon being split by the α hydrogen. A singlet increasing in intensity at δ 1.4 (relative to TMS) is attributed to the formation of dimethylketene.

These low temperature infrared spectra of isobutyryl chloride and triethylamine in chloroform show the development of a peak at 1810 cm^{-1} due to the acylammonium salt at the expense of the carbonyl peaks of the acid halide. These spectroscopic data for isobutyryl chloride complement previous work suggesting acylammonium salt as the ketene precursor.[4]

The mechanism of the triethylamine dehydrohalogenation of isobutyryl chloride is illustrated in Scheme I.

Scheme I



The reaction of an equimolar amount of α-chloropropionyl chloride and triethylamine in chloroform at −78° upon warming to room temperature yields the α-halovinyl ester (1,2-dichloropropenyl 2-chloropropanoate). Similar experiments have been previously reported but we feel it is most significant.[5,8] These data suggest to us that the enolate salt decays to methylchloroketene upon warming from −78° and the ketene produced either reacts with the enolate to yield the α-halovinyl ester or polymerizes. Trapping methylchloroketene with cyclopentadiene at room temperature produces the corresponding cycloadduct (77%) and no α-halovinyl ester but trapping the ketene with cyclohexene produces a very low yield of cycloadduct but a significant amount of the α-halovinyl ester. Consequently, the enolate very successfully competes with the unreactive cyclohexene for the ketene but is very unsuccessful in competition with the reactive cyclopentadiene.

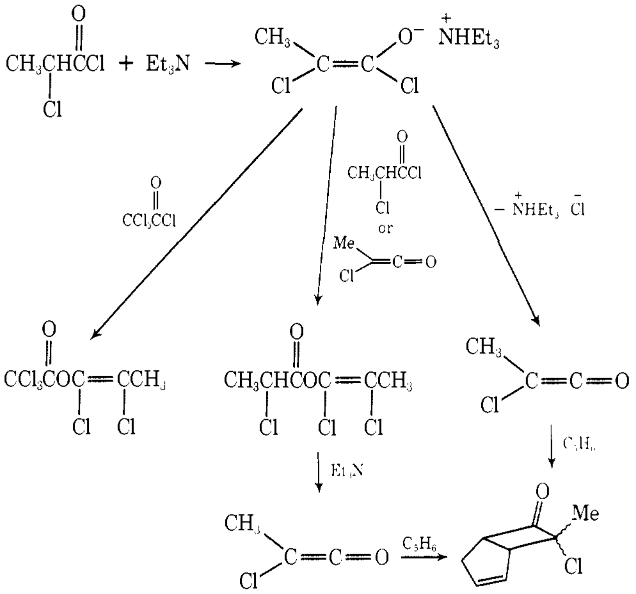
A study of methylchloroketene and the enolate salt is complicated by the fact that the α-halovinyl ester and the triethylamine produce methylchloroketene. This has been demonstrated by trapping the ketene with cyclopentadiene.[5]

α-Chloropropionyl chloride was allowed to react with triethylamine in hexane at 0–5° in the presence of cyclopentadiene to trap the methylchloroketene as it formed. At various times, aliquots were withdrawn from the reaction mixture and quenched with water and the hexane layer was assayed for cycloadduct by vpc. The time required for half the ultimate amount of cycloadduct to be formed was 4 min. Simple first- or second-order kinetics were not observed for the course of the reaction. However, second-order kinetics were observed for the first 4 min of the reaction. This is suggestive that after a certain amount of cyclopentadiene is consumed a competing polymerization and/or vinyl ester formation occur, thus complicating the kinetics.

Numerous efforts to directly observe methylchloroketene formed in an nmr tube and an infrared cell have been unsuccessful. It is concluded that this ketene is not directly observed because the ketene will react with its precursor and polymerize unless a more reactive reactant is available, thus having a very short lifetime.

The mechanism of formation and the fate of methylchloroketene as described above are illustrated in Scheme II.

Scheme II



A consideration of the two different mechanistic pathways for the triethylamine dehydrochlorination of α-chloropropionyl chloride and isobutyryl chloride led to a consideration of the acidities of the α hydrogens. The α hydrogen of α-chloropropionyl chloride would be expected to be more acidic and thus more susceptible to the E1cb pathway which is what has been presented experimentally. However, it was felt that these two acid halides are particularly suitable for a CNDO/2 calculation to determine electron densities on the atoms involved in the dehydrohalogenation.[13] The results of the calculations should provide information as to the associated electron densities for the two acid halides and a better understanding of the two different mechanistic pathways under consideration.

The bond lengths (Å) used for each acid halide were as follows: C=O, 1.22; C—H, 1.09; C(O)—Cl, 1.77; C—CH$_3$, 1.54; C—CO, 1.50. The C—Cl bond length

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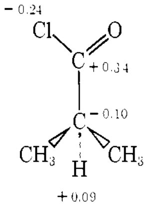
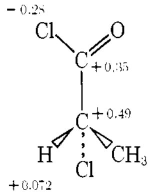
(13) J. A. Pople and D. L. Beveridge, "Approximate Molecular Orbital Theory," McGraw-Hill, New York, N. Y., 1970.

for α-chloropropionyl chloride was taken as 1.76 Å. Bond angles (deg) used were: H—C—H, 109.5; O=C—Cl, 123; C—C—CH_3, 109.5; C—C—Cl, 110.

The conformations selected of the two acid halides are shown below along with the electron densities of the atoms directly involved in the dehydrohalogenation.





It is interesting to note that the acidities of the α hydrogens of the two acid halides are relatively similar. However, the most important factor based on the CNDO/2 calculations appears to be the charge density on the α carbon. In the case of isobutyryl chloride, the α carbon possesses a partial negative charge which would be expected to poorly accommodate a negative charge buildup by formation of the enolate. However, in the case of α-chloropropionyl chloride the α carbon has a fairly high positive charge and can easily accommodate the negative charge of the enolate.

Consequently, the CNDO/2 calculations are very compatible with what has been observed experimentally and indicate it is not the acidity of the α hydrogens of the acid halides that is the mechanistic determining factor but rather the charge densities on the α carbons of the acid halides.

Experimental Section

Proton nmr spectra were recorded on a Jeolco PS-100 nmr spectrometer equipped with a variable-temperature controller employing tetramethylsilane as an internal standard and chloroform as the solvent. The infrared spectra were recorded on a Perkin-Elmer 620 infrared spectrometer equipped with a variable-temperature cell CRYO-TIP Model AC-1 by Air Products and Chemicals, Inc. Vpc was performed on an F&M Scientific Model 700 gas chromatograph with a 10 ft × 0.25 in. column packed with a 10% SE-30 on acid-washed Chromosorb W (60–80 mesh).

Hexane and triethylamine were distilled from sodium and stored over Linde Type 4A molecular sieve. Chloroform was dried over phosphorus pentoxide and distilled prior to use as a solvent.

Cycloadduct from Enolate Salt. To a solution of 0.1 mol of triethylamine in 200 ml of hexane at −78° was added dropwise 0.1 mol of α-chloropropionyl chloride in 10 ml of hexane. After the addition was complete, the white salt, which precipitated during the addition, was quickly separated from the reaction solution by filtration. After filtration, the salt was washed with precooled hexane. The cold salt was suspended in 100 ml of hexane containing 0.3 mol of cyclopentadiene and stirred overnight. The mixture was filtered and the filtrate concentrated on a rotatory evaporator. Distillation afforded 6 g (40%) of the cycloadduct (7-chloro-7-methylbicyclo[3.2.0]hept-2-en-6-one)[9] and some α-halovinyl ester (1,2-dichloropropenyl 2-chloropropanoate).[5]

Nmr Spectra. Equal volumes of 0.1 *M* triethylamine in chloroform and 0.1 *M* acid halide in chloroform were mixed at −78°. An aliquot of the resulting solution was placed with a hypodermic syringe in a precooled nmr tube. Spectra were recorded at −60° and various higher temperatures as the probe warmed to room temperature.

Infrared Spectra. Equal volumes of 0.05 *M* triethylamine in chloroform and 0.05 *M* acid halide in chloroform were mixed at −78° and the resulting solution was injected with a precooled syringe into the cold low temperature infrared cell. Spectra were recorded as the temperature was increased.

Kinetic Runs. α-Chloropropionyl chloride (0.1 mol) in 10 ml of chloroform was added dropwise with vigorous stirring to a solution of 0.1 mol of triethylamine in 90 ml of chloroform at −78°. After the addition was complete, the reaction mixture was allowed to warm for 30 min at which time 0.3 mol of freshly distilled cyclopentadiene was added. Aliquots were withdrawn at various times and quenched in water. The hexane layer was separated, dried, and analyzed by vpc.

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Halonium Ion Rearrangements. Temperature-Dependent ^{13}C Chemical Shifts as Indicators of Equilibria between Cyclic Halonium Ions and Open Carbonium Ions[1a]

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Abstract: A marked temperature dependence of the ^{13}C chemical shifts of a number of substituted tetramethylenehalonium ions, particularly 1,1-dimethyltetramethylenechloronium ion, has been observed. The dependence has been explained in terms of shifts in an equilibrium between the halonium ions and appropriate carbonium ions. The observed chemical shifts were used to calculate equilibrium constants. Additional studies have been made of the rearrangement reactions leading to 1,1-dimethyltetramethylenechloronium ion from 1,6-dichlorohexane in SbF_5–SO_2 solution. The first observed ionization product for 1,6-dihalohexanes was 1-ethyltetramethylenehalonium ion.

Averaged ^1H and ^{13}C chemical shifts of species which interconvert rapidly on the nmr time scale have been used[2,3] in calculation of equilibrium constants. It is known from the work of Olah and coworkers[4] that in carbonium ions the cationic carbon is highly de-

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(1) (a) Support by the National Science Foundation (Grant GP 30683) is gratefully acknowledged. (b) Postdoctoral investigator.

(2) A. F. Casy, "PMR Spectroscopy in Medicinal and Biological Chemistry," Academic Press, New York, N. Y., 1971, pp 123–132.

(3) J. B. Stothers, "Carbon-13 NMR Spectroscopy," Academic Press, New York, N. Y., 1972, p 163.

(4) See, for example, (a) G. A. Olah and A. M. White, *J. Amer. Chem. Soc.*, 91, 5801 (1969); (b) G. A. Olah, A. M. White, J. R. DeMember, A. Commeyras, and C. Y. Lui, *ibid.*, 92, 4627 (1970).