

86-9; 6, 23736-87-0; 7, 23736-88-1; 7 3,5-dinitrobenzoate, 23809-49-6; 7a, 23736-89-2; 8, 23736-90-5; 8a, 23736-91-6; 9, 4870-61-5; 11, 23809-50-9; 11a, 23736-93-8; 13, 23736-94-9; 14, 23736-95-0; 14a, 23736-96-1; 15, 23736-97-2; 16, 23809-51-0; 16a, 23809-52-1; 18, 23809-53-2; 19, 23736-98-3; 19 3,5-dinitrobenzoate, 23736-99-4; 19a, 23737-00-0; 20, 23809-54-3; 20a, 23737-01-1; 22, 23737-02-2; 24, 23737-03-3; 24a, 23809-55-4; 25, 23809-56-5; 26,

23737-04-4; 26a, 23737-05-5; 27, 23737-06-6; 28, 23737-07-7; 28a, 23737-08-8.

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Halogenated Ketenes. XII. The Reaction of Some Acid Halides with Triethylamine. α -Halovinyl Esters^{1,2}

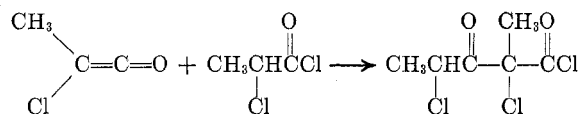
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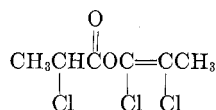
The reaction of triethylamine with an excess of some acid halides to produce α -halovinyl esters (enol esters of acid halides) has been investigated. The α -halovinyl esters produced are considered to be the result of acylation of an intermediate enolate ion. The reaction is most appropriate for disubstituted acetyl halides where at least one of the substituents is halogen. Some of the implications of the enolate ion intermediate are discussed and the synthesis of several representative examples of this new class of compounds is described.

It has recently been reported from this laboratory that in an attempted preparation of the dimer of methylchloroketene by the dehydrochlorination of α -chloropropionyl chloride, a novel compound was isolated.⁴ This material was assigned the structure of a β -keto acid halide and was assumed to be the result of a reaction of methylchloroketene and the acid halide, since conducting the reaction in the presence of cyclopentadiene produced a good yield of cycloadduct. This type of reaction was described by



Staudinger, and by others since that time, and more recently by us.⁵⁻⁹ Nevertheless, upon investigation of this situation further it has become apparent to us and others that the material produced is not a β -keto acid halide.

Dreiding and coworkers have recently confirmed and supplemented our initial report on the α -chloropropionyl chloride system, but have assigned the material the following structure.¹⁰

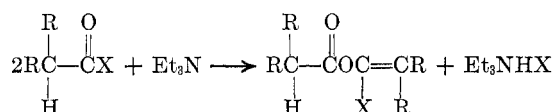


Lavanish has reported that similar results are obtained with dichloroacetyl chloride and triethylamine and assigns the structure as trichlorovinyl dichloroacetate.¹¹

The purpose of this report is to correct our previous structure assignment and to reveal the results of a more extensive and comprehensive study of this reaction, which we believe involves the synthesis of a new class of compounds.

Results

In addition to the two systems that have already been reported, we have examined the reaction of triethylamine with a number of other acid halides in an effort to produce other α -halovinyl esters. This reaction may be represented as indicated.



It becomes immediately apparent that this is not a general reaction of acid halides. Table I lists the acid halides which we found will react with a deficiency of triethylamine to produce the α -halovinyl esters.

Attempts to prepare α -halovinyl esters from several other acid halides were unsuccessful; e.g., acetyl chloride, chloroacetyl chloride, propionyl chloride, isobutyryl chloride, α -phenylbutyryl chloride, and diphenylacetyl chloride did not produce α -halovinyl esters.

A different type of α -halovinyl ester was also prepared from α -chloropropionyl chloride. After the treatment of α -chloropropionyl chloride with a stoichiometric amount of triethylamine, a stoichiometric

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(2) Support of this investigation by the Robert A. Welch Foundation and a National Science Foundation Grant (GP-7386) is gratefully acknowledged.

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(8) H. D. Stachel, *Arch. Pharm. (Weinheim)*, **294**, 775 (1961).

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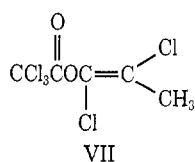
(10) R. Giger, M. Rey, and A. S. Dreiding, *Helv. Chim. Acta*, **51**, 1466 (1968).

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TABLE I
 α-HALOVINYL ESTERS

Acid halide	Compd	α-Halovinyl ester
α-Bromopropionyl chloride	I	$\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3\text{CH}(\text{Br})\text{COC}=\text{CCH}_3 \\ \quad \quad \\ \text{Br} \quad \text{Cl} \quad \text{Br} \end{array}$
α-Chlorobutyryl chloride	II	$\begin{array}{c} \text{O} \\ \parallel \\ \text{C}_2\text{H}_5\text{CH}(\text{Cl})\text{COC}=\text{CC}_2\text{H}_5 \\ \quad \quad \\ \text{Cl} \quad \text{Cl} \quad \text{Cl} \end{array}$
α-Chlorobutyryl bromide	III	$\begin{array}{c} \text{O} \\ \parallel \\ \text{C}_2\text{H}_5\text{CH}(\text{Cl})\text{COC}=\text{CC}_2\text{H}_5 \\ \quad \quad \\ \text{Cl} \quad \text{Br} \quad \text{Cl} \end{array}$
α-Chloro-α-phenylacetyl chloride	IV	$\begin{array}{c} \text{O} \\ \parallel \\ \text{C}_6\text{H}_5\text{CH}(\text{Cl})\text{COC}=\text{CC}_6\text{H}_5 \\ \quad \quad \\ \text{Cl} \quad \text{Cl} \quad \text{Cl} \end{array}$
α-Chloropropionyl bromide	V	$\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3\text{CH}(\text{Cl})\text{COC}=\text{CCH}_3 \\ \quad \quad \\ \text{Cl} \quad \text{Br} \quad \text{Cl} \end{array}$
Dibromoacetyl chloride	VI	$\begin{array}{c} \text{O} \\ \parallel \\ \text{CHBr}_2\text{COC}=\text{CBr}_2 \\ \\ \text{Cl} \end{array}$

amount of trichloroacetyl chloride was added. This resulted in the formation of both isomers of VII.

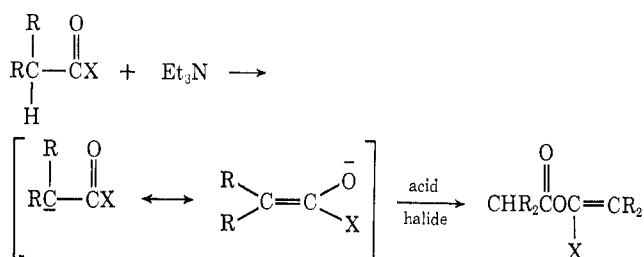


However, efforts to synthesize a similar material from propionyl chloride and chloroacetyl chloride with trichloroacetyl chloride were unsuccessful.

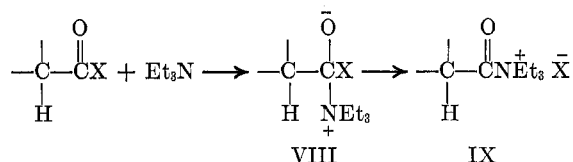
The α-halovinyl esters appear to more closely resemble acid halides in physical properties than esters. These compounds usually possess a disagreeable odor and are susceptible to hydrolysis (some fume in air), and the carbonyl absorptions in the infrared are shifted out of the ester region into the acid halide region.

Discussion

It has already been proposed that the formation of α-halovinyl esters (enol esters of acid halides) is the result of an initial proton abstraction by triethylamine

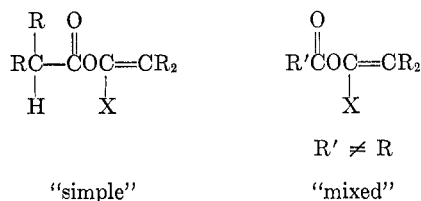


and subsequent acylation of the resulting enolate ion.^{10,11} However, this seems inconsistent with several reports in the literature. There is strong evidence that the reaction of acid halides with triethylamine initially involves a quaternary ammonium intermediate.¹²⁻¹⁴



Perhaps VIII undergoes an elimination which produces the enolate ion rather than the obvious initial proton abstraction.

The α-halovinyl esters may be of two distinct types,



"simple" and "mixed." If the enolate ion is acylated by the acid halide from which it was derived, a "simple" α-halovinyl ester results. If the enolate ion is acylated by a foreign acid halide, such as trichloroacetyl chloride, a "mixed" α-halovinyl ester is produced.

The lack of formation of "simple" α-halovinyl esters from acetyl chloride, chloroacetyl chloride, propionyl chloride, isobutyryl chloride, α-phenylbutyryl chloride, and diphenylacetyl chloride suggests that an enolate ion is not produced and another mechanistic pathway to ketene is operative. The inability of chloroacetyl chloride to form a "simple" α-halovinyl ester indicates that the acidity of the α hydrogen of the acid halide is not the only factor involved in formation of the enolate ion, since the α hydrogen of α-chloropropionyl chloride is even less acidic.

A comparison of acid chlorides to acid bromides reveals that the former are more desirable for this reaction, as the yields are better and the work-up is easier. Apparently, the better leaving group promotes the second step (the ketene-forming step) and more polymer is obtained.

Truce and Bailey have recently reported on the mechanism of alcoholysis of some acid halides in the presence of triethylamine.¹⁴ The reaction of acid halides and triethylamine was performed in the presence of methanol-*d*. It was stated that the formation of monodeuterated ester is ample evidence for the ketene intermediate. We would like to submit that monodeuterated ester may also be produced from the enolate ion, and perhaps this is the case in some of the systems investigated by Truce and Bailey.

Experimental Section

Proton nmr spectra were recorded on a Varian A-60 instrument employing tetramethylsilane as an internal standard. Vapor phase chromatography was accomplished on an F & M Model 700 chromatograph. Hexane was used after being dried over

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Linde type 4-A Molecular Sieve. α -Chloro- α -phenylacetyl chloride was prepared according to the method of Walden.¹⁵ All of the other acid halides were prepared from the corresponding acids and an appropriate reagent according to standard procedures.

1-Chloro-2-bromopropenyl 2-Bromopropanoate (I).—To a stirred solution of 47.8 g (0.28 mol) of α -bromopropionyl chloride in 200 ml of hexane at room temperature was added dropwise 14.2 g (0.14 mol) of triethylamine in 50 ml of hexane. After stirring overnight, filtration afforded a theoretical amount of amine salt. Evaporation of the solvent and distillation of the residue yielded 19.4 g (45%) of I: bp 60° (0.15 mm); ir 1788 (C=O) and 1661 cm^{-1} (C=C); nmr (CCl_4) δ 1.90 (doublet, 3 H) 2.27 and 2.40 (singlets, 3 H total, two isomers), and 4.45 (quartet, 1 H).

Anal. Calcd for $\text{C}_6\text{H}_7\text{Br}_2\text{ClO}_2$: C, 23.5; H, 2.28. Found: C, 24.0; H, 2.23.

1,2-Dichloro-1-butenyl 2-Chlorobutanoate (II).—An 8.9-g (0.088 mol) portion of triethylamine in 50 ml of hexane was added dropwise to a stirred solution of 25 g (0.18 mol) of α -chlorobutyryl chloride in 200 ml of hexane at room temperature. After the solution had been stirred for 4 hr, a theoretical amount of amine salt was filtered. The filtrate was evaporated and vacuum distilled at 59° (0.45 mm) to yield 8.8 g (41%) of II: ir 1788 (C=O) and 1653 cm^{-1} (C=C); nmr (CCl_4) δ 1.16 (multiplet, 6 H), 2.30 (multiplet, 4 H), and 4.28 (triplet, 1 H).

Anal. Calcd for $\text{C}_8\text{H}_{11}\text{Cl}_3\text{O}_2$: C, 39.1; H, 4.47. Found: C, 39.2; H, 4.40.

1-Bromo-2-chloro-1-butenyl 2-Chlorobutanoate (III).—To a stirred solution of 14.25 g (0.077 mol) of α -chlorobutyryl bromide in 200 ml of hexane was added dropwise at room temperature 3.87 g (0.04 mol) of triethylamine in 50 ml of hexane. After the solution had been stirred for an additional 2 hr, the salt was removed by filtration and 3.5 g (31%) of III was obtained by distillation of the filtrate at 69° (0.1 mm): ir 1780 (C=O) and 1648 cm^{-1} (C=C); nmr (CCl_4) δ 1.20 (multiplet, 6 H), 2.22 (multiplet, 4 H), and 4.30 (triplet, 1 H). Treatment of III with methanol gave a compound which was chromatographically identical with and had an ir spectrum identical with that of an authentic sample of methyl α -chlorobutyrate.

1,2-Dichloro-2-phenylvinyl 2-Chloro-2-phenylacetate (IV).—To a well stirred solution of 36.2 g (0.19 mol) of α -chloro- α -phenylacetyl chloride in 200 ml of hexane was added dropwise a solution of 9.7 g (0.096 mol) of triethylamine in 25 ml of hexane at room temperature. Stirring was continued for 2 days and the salt was filtered and washed with two 100-ml portions of dry ether. The hexane filtrate was combined with the ether washings

and evaporated. The resulting oil was recrystallized from ether to yield 18.7 g (54%) of IV: mp 59–60°; ir 1792 (C=O) and 1626 cm^{-1} (C=C); nmr (CCl_4) δ 5.19 (singlet, 1 H), 7.18 (singlet, 5 H), and 7.25 (singlet, 5 H).

Anal. Calcd for $\text{C}_{16}\text{H}_{11}\text{Cl}_2\text{O}_2$: C, 56.2; H, 3.22. Found: C, 56.2; H, 3.34.

1-Bromo-2-chloropropenyl 2-Chloropropanoate (V).—To a stirred solution of 46 g (0.27 mol) of α -chloropropionyl bromide in 200 ml of hexane was added dropwise 13.5 g (0.13 mol) of triethylamine in 50 ml of hexane. Stirring was continued at room temperature overnight. The salt was filtered and the solution was distilled to yield 15 g (43%) of V: bp 52° (0.17 mm); ir 1786 (C=O) and 1653 cm^{-1} (C=C); nmr (CCl_4) δ 1.75 (doublet, 3 H), 2.09 and 2.25 (singlets, 3 H total, two isomers) and 4.51 (quartet, 1 H). Treatment of V with methanol gave a compound which was chromatographically identical with and had an ir spectrum identical with that of an authentic sample of methyl α -chloropropionate.

1-Chloro-2,2-dibromovinyl Dibromoacetate (VI).—A solution of 9.0 g (0.09 mol) of triethylamine in 25 ml of hexane was added dropwise to a solution of 42.3 g (0.18 mol) of dibromoacetyl chloride in 200 ml of hexane at -78° . After the solution had been warmed to room temperature overnight, the salt was filtered and the hexane solution was evaporated and distilled to yield 4.1 g (11%) of VI: bp 100° (0.15 mm); ir 1786 (C=O) and 1600 cm^{-1} (C=C); nmr (CCl_4) δ 5.92 (singlet).

Anal. Calcd for $\text{C}_4\text{HBr}_4\text{ClO}_2$: C, 10.99; H, 0.229. Found: C, 10.64; H, 0.376. A sample weighing 0.00766 g produced 0.01557 g of silver halide by the Carius method. The theoretical weight of silver halide for that weight of sample is 0.01569 g.

1,2-Dichloropropenyl Trichloroacetate (VII).—To a stirred solution of 31 g (0.24 mol) of α -chloropropionyl chloride in 200 ml of hexane at -78° was added dropwise a solution of 23.2 g (0.23 mol) of triethylamine in 50 ml of hexane. Stirring was continued for 1 hr at this temperature. A 45.5-g (0.25 mol) portion of trichloroacetyl chloride was added to the reaction mixture and stirring was continued as the mixture warmed to room temperature overnight. The salt was filtered and the filtrate was concentrated and vacuum distilled at 50° (0.1 mm) to yield 42 g (67%) of VII: ir 1799 (C=O) and 1661 cm^{-1} (C=C); nmr (CCl_4) δ 2.16 (singlet) and 2.29 (singlet), the relative areas indicate an isomer distribution of 1.85.

Anal. Calcd for $\text{C}_5\text{H}_3\text{Cl}_5\text{O}_2$: C, 22.0; H, 1.10; Cl, 65.14. Found: C, 21.7; H, 1.30; Cl, 64.93.

Registry No.—I, 23649-90-3; II, 23649-91-4; III, 23649-92-5; IV, 23649-93-6; V, 23649-94-7; VI, 23649-95-8; VII, 23649-96-9; triethylamine, 121-44-8.

(15) P. Walden, *Chem. Ber.*, **28**, 1287 (1895).