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THE REACTION OF DICHLOROACETYL CHLORIDE WITH TRIETHYLAMINE: TRICHLOROVINYL DICHLOROACETATE[1]

J. M. Lavanish

PPG Industries
Chemical Division
P. O. Box 31
Barberton, Ohio 44203

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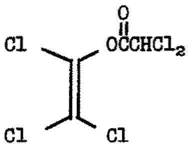
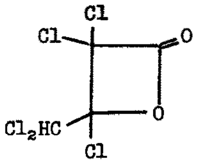
The dehydrohalogenation of acid halides is a convenient method for the generation of a variety of ketenes. Dichloroketene (I) was first prepared by the dehydrochlorination of dichloroacetyl chloride with triethylamine.[2] Good yields of cycloadducts have been obtained from I and a number of olefins,[3,4] conjugated olefins,[2,5,6] aldehydes[7,8] and dicyclohexylcarbodiimide.[9] Attempts to isolate I have been unsuccessful, presumably due to its facile polymerization in the absence of a trapping agent.[2]

As part of an attempt to determine the effects of varying experimental conditions on the generation of I the following reaction was performed. A solution of 0.10 mole (10.1 g.) of triethylamine in 50 ml. of dry ether was added over 30 minutes to a stirred solution of 0.22 mole (32.4 g.) of dichloroacetyl chloride in 100 ml. of dry ether under a nitrogen atmosphere. After stirring at room temperature for three hours the tan slurry was filtered and the filtrate was concentrated under vacuum to give 23.2 g. of an amber colored liquid. Vacuum distillation gave 8.1 g. of water-white distillate (II), b.p. 67°C at 0.9 Torr. The tarry distillation residue appeared to consist mostly of polymeric I /found: C, 20.8; Cl, 63.9; (C_2Cl_2O) requires C, 21.6; Cl, 64.0/. Distillate II fumed on exposure to the atmosphere, emitting a strong odor of HCl, and yellowed on standing in a sealed vial at room temperature. The neat infrared spectrum of II showed signals at 3007 (m), 1790 (s) and 1620 cm^{-1} (m) with no other signals above 1300 cm^{-1} and the nmr spectrum consisted of a single sharp line at 6.15 ppm.

The presence of hydrogen, as evidenced by the spectral data, clearly ruled out the possibility that II might be an oligomer of I. Structure III, which can be derived by



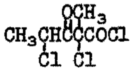
II



III

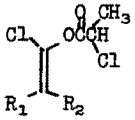
addition of I to the carbonyl group of dichloroacetyl chloride (analogous to the β-lactone obtained from I and chloral) would be expected to have a carbonyl frequency of ca. 1875 cm^{-1} and to show no olefinic infrared band.[7,8] However, the spectral data are entirely consistent with the assignment of II as trichlorovinyl dichloroacetate. Dissolution of II in ethanol gave ethyl dichloroacetate as the only detectable product. The identity of II was further confirmed by satisfactory elemental analysis. The yield was 43% based on triethylamine.

Brady and Roe[10] have recently reported on the reaction of α-chloropropionyl chloride with triethylamine. Under reaction conditions similar to those used by us they isolated a compound with infrared bands at 5.6 and 6.04μ (1786 and 1655 cm^{-1}) and nmr signals at 5.5 ppm (quartet, 1H), 7.8 ppm (singlet, 1.5H) and 8.25 ppm (doublet, 3H) to which they assigned structure IV. We feel that the spectral data are better accommodated by the



$CH_3\underset{Cl}{C}H\overset{O}{\overset{\|}{C}}\underset{Cl}{\overset{CH_3}{C}}COCl$

IV

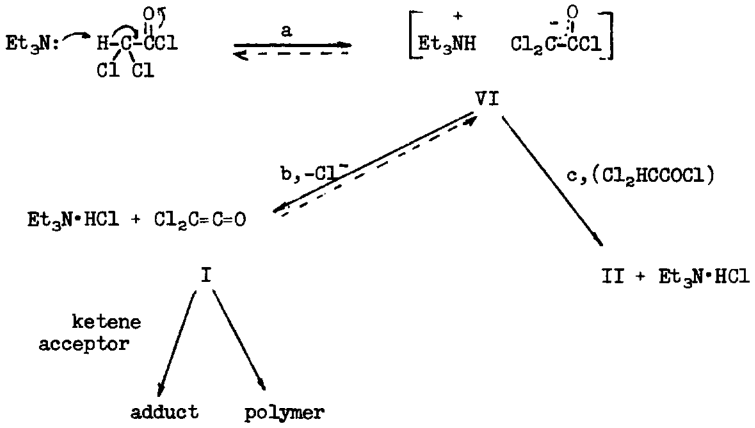


V

Va R_1=CH_3, R_2=Cl
Vb R_1=Cl, R_2=CH_3

mixture of vinyl esters V. Brady and Roe further stated that reactions of their compound with nucleophiles yielded only derivatives of α-chloropropionic acid, in accord with V but difficult to rationalize on the basis of IV. The conditions which Brady and Roe describe for the preparation of V suggest that V is more tolerant to triethylamine than is II, since we have found that II is rapidly decomposed by triethylamine. Attempts by us to produce the analogous vinyl esters from acetyl chloride or chloroacetyl chloride with triethylamine did not lead to isolable amounts of products.

The generation of I from dichloroacetyl chloride and triethylamine must involve proton abstraction somewhere along the reaction profile. The question to be resolved is whether the loss of chloride ion is concerted with or subsequent to the proton abstraction step. We believe that the formation of II provides tentative evidence for a consecutive rather than a concerted process.



Proton abstraction would yield the enolate complex VI (path a). Transfer of chloride (path b), forming triethylamine hydrochloride, would give I, which in the presence of a suitable acceptor would give an adduct or in the absence of an acceptor would polymerize. If, however, the concentration of dichloroacetyl chloride is sufficiently high, trapping of VI prior to chloride transfer becomes competitive and significant amounts of II are obtained (path c). The existence of equilibrium processes is suspected, but at present no information on this point is available. The concentration of acid chloride in the experiment described is 2 to 4 times greater than that usually used in these Laboratories for the in situ generation of I. Therefore, in experiments designed to trap I as an adduct, that is, when the concentration of dichloroacetyl chloride is 1/2 to 1/4 of that described and only a slight excess of acid chloride over triethylamine is used, insignificant amounts of II would be expected. In fact, II has been detected in small quantities in the infrared spectra of the crude reaction mixtures in some of these cases.

Although we feel that II is formed via the described reaction of the acid chloride with its enolate, we have not overlooked the fact that a different sequence of reactions, possibly involving adduct III as an intermediate, may be responsible for the formation of II. In experiments currently in progress we hope to provide firmer evidence for the mechanism and also to delineate the scope of the reaction relative to other acid halides.

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[1] Presented in Part at the Central Regional Meeting of the American Chemical Society, Akron, Ohio, May, 1968.

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