tion was extracted twice with chloroform, and the organic portions were combined, washed with 5% hydrochloric acid, water, and dried. Removal of the solvent at reduced pressure gave 0.360 g. of red oil. Chromatography on acid-washed alumina afforded 0.140 g. (41%) of ketone as a clear orange oil which crystallized upon standing at room temperature from the hexane–benzene (1:1) fraction. The ketone was purified by recrystallization from hexane to give red leaflets, m.p. 120–121°, infrared maximum at 6.00 μ, ultraviolet maxima at 272 mμ (ε 3140) and 337 mμ (ε 1012).

Anal. Calcd. for $C_{15}H_{16}FeO$: C, 67.19; H, 6.02; mol. wt., 268. Found: C, 67.02; H, 6.06; mol. wt., 275.

Acknowledgment.—This work was supported in part by a Frederick Gardner Cottrell Grant from the Research Corporation.

Preparation of Vinyl Chloroformate by the Gas Phase Decomposition of Ethylene Glycol Bis(chloroformate)[1]

Lieng-Huang Lee

Polymer and Chemicals Research Laboratory,
The Dow Chemical Company, Midland, Michigan

Received July 2, 1965

The decomposition of simple alkyl chloroformates has been studied. Lewis and Herndon[2–4] have further established the decomposition to be one example of the SNi mechanism. The SNi mechanism was defined as a one-step unimolecular mechanism passing through a cyclic transition state.

The decomposition of ethylene glycol bis(chloroformate) has not been studied. Küng[5] discovered that by pyrolyzing ethylene glycol bis(chloroformate), vinyl chloroformate ($CH_2{=}CHOCOCl$) was obtained together with other products. These products generally contained 2-chloroethyl chloroformate, 1-chloroethyl chloroformate, 1,2-dichloroethane, 1,1-dichloroethane, and vinyl chloride. The yield of the desired product, vinyl chloroformate, was generally low. Vinyl chloroformate could be an important starting material for the synthesis of other vinyl monomers[6] if this compound can be made in better yield. The purposes of this study were, therefore, to understand the mechanism of the thermal degradation of ethylene glycol bis(chloroformate) and improve the yield of vinyl chloroformate. The decomposition products were analyzed with vapor phase chromatography. The relationship between the primary and the secondary decomposition products is discussed.

Experimental Section

Decomposition of Ethylene Glycol Bis(chloroformate).—The pyrolysis apparatus was similar to those used for the ester pyrolysis described elsewhere.[7] The vertical pyrolysis tube was made of Vycor (18.5 × 1 in.) and placed in the center of a cylindrical heater. The dropping funnel (500 ml.) was equipped with a side arm and a Teflon adjustable stopcock. The funnel was connected to the top portion of the vertical tube with a ball joint. The bottom of the vertical tube was connected to a receiver (250 ml.) placed in a dewar flask containing an acetone Dry Ice mixture. The side-arm outlet of the receiver was connected to a second receiver. The gases were scrubbed using two gas-scrubbing bottles containing 10% NaOH solution. It should be noted that the temperature was measured on the thermocouple inserted in the heater. The temperature on the wall of the tube was 10–20° higher than the heater temperature.

Prior to the addition of ethylene glycol bis(chloroformate) [Columbia Southern Chemical Corp., b.p. 188° (725 mm.)], the system was flushed with nitrogen through the side arm of the dropping funnel. During the pyrolysis, the nitrogen stream was kept at a rate of 6–8 cc./min. After the pyrolysis was completed, the pyrolysate mixture was distilled or analyzed with the Perkin-Elmer vapor phase chromatography unit. The v.p.c. analyses results are shown in Table I. The low boilers were run at 50° with a helium flow rate of 40 cc./min. The retention times of various compounds are as follows: vinyl chloride, 2.6 min.; 1,1-dichloroethane, 9.3 min.; vinyl chloroformate, 10.2 min.; and 1,2-dichloroethane, 15.9 min. The high and low boilers were run at 100° with a helium flow rate of 150 cc./min. The retention times of various compounds are as follows: vinyl chloride, 0.6 min.; vinyl chloroformate and 1,1-dichloroethane, 1.5 min.; 1,2-dichloroethane, 2.1 min.; an unidentified compound, presumably 1-chloroethyl chloroformate, 3.9 min.; 2-chloroethyl chloroformate, 7.3 min.; and ethylene glycol bis(chloroformate), 26.5 min. Except for 1-chloroethyl chloroformate, the positions of these peaks were checked with those of the known compounds. It should be noted that, owing to some unknown factors in the pyrolysis, the reproducibility of the results was not satisfactory.

The distillation of the pyrolysate was conducted in two steps. The first step was to fractionate the low-boiling fractions under atmospheric pressure with a Todd distillation column, Model A (approximately 60 plates). 1,1-Dichloroethane, b.p. 57–58° (lit.[8] b.p. 57.3°), was separated first. Vinyl chloroformate, $n^{25}D$ 1.4090, d^{25} 1.1597, b.p. 67–69° [lit.[5] b.p. 68–69° (735 mm.)], was then obtained. Without the use of the fractionating column, the first two compounds and 1,2-dichloroethane, b.p. 83–84° (lit.[8] b.p. 83.4–83.7°), were extremely difficult to separate. The identity of both 1,1-dichloroethane and 1,2-dichloroethane was checked by comparing them with the authentic samples. The structure of vinyl chloroformate was confirmed by infrared analysis. The spectrum (Figure 1) shows the C–H stretching band at 3100 cm.$^{-1}$, the CH_2 stretching band at 2960 and 2870 cm.$^{-1}$, and the C=O stretching at 1780 cm.$^{-1}$. The presence of the vinyl group is demonstrated by the C=C stretching band at 1640 cm.$^{-1}$ and the out-of-plane CH deformation at 940 (CH_2 twisting) and 910 cm.$^{-1}$ (CH_2 wagging).

It should be noted that the spectrum is considerably different from that of the starting material, ethylene glycol bis(chloroformate). The CH_2 stretching band is at 2970 cm.$^{-1}$, and the CH_2 deformation band is at 1460 cm.$^{-1}$. Since there are two symmetric C–O–C bonds in ethylene glycol bis(chloroformate), the C–O–C absorption yields a doublet: 1220 and 1188 cm.$^{-1}$. In the case of vinyl chloroformate, only one C–O–C band was found at 1150 cm.$^{-1}$.

The second step of distillation was conducted under vacuum. Most of the distillate was 2-chloroethyl chloroformate, b.p. 89–90° (76 mm.) [lit.[5] b.p. 89–90° (76 mm.), 61–63° (21 mm.)]. The infrared spectrum of this compound is shown in Figure 2. It should be noted that, in this case, the C–O–C is at 1180 cm.$^{-1}$. The spectrum of this compound is identical with that of the pure compound obtained from Eastman Kodak. It was reported originally by the inventor that there was a considerable amount of 1-chloroethyl chloroformate, b.p. 57–59° (76 mm.). We did not obtain a sufficient quantity of this compound, therefore, there was no spectrum made for this compound.

In order to study the source of vinyl chloroformate, we conducted two separate studies. The first study was to pyrolyze 2-chloroethyl chloroformate in the same apparatus. We did not obtain vinyl chloroformate. The decomposition products were 1,2 dichloroethane and vinyl chloride. When we pyrolyzed

---

[1] This paper was presented before the Division of Polymer Chemistry, 148th National Meeting of the American Chemical Society, Chicago, Ill., Sept. 1964.

[2] E. S. Lewis and W. C. Herndon, *J. Am. Chem. Soc.*, **83**, 1955 (1961).

[3] E. S. Lewis, W. C. Herndon, and D. C. Duffey, *ibid.*, **83**, 1959 (1961).

[4] E. S. Lewis and W. C. Herndon, *ibid.*, **83**, 1961 (1961).

[5] F. E. Küng, U. S. Patent 2,377,085 (1945).

[6] F. Strain and F. E. Küng, U. S. Patent 2,384,143 (1945).

[7] W. J. Bailey and H. R. Golden, *J. Am. Chem. Soc.*, **75**, 4780 (1953).

[8] "Handbook of Chemistry and Physics," The Chemical Rubber Publishing Co., Cleveland, Ohio.

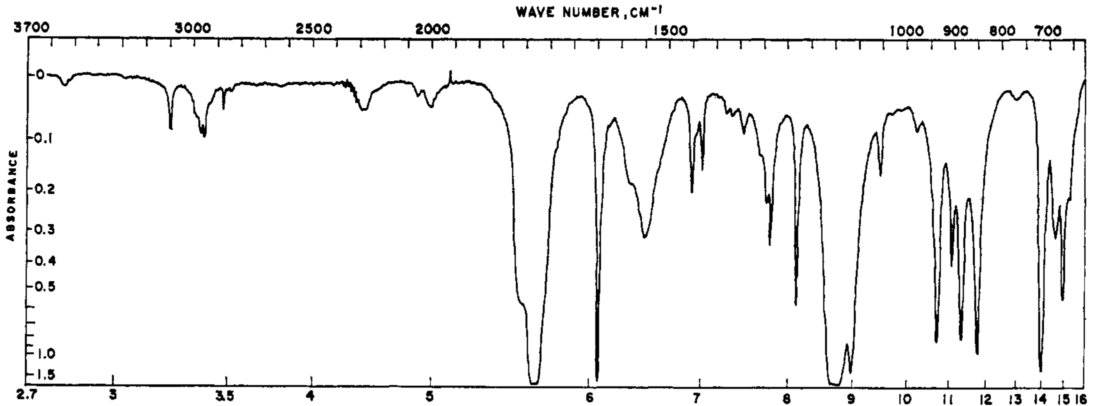


Figure 1.—The infrared spectrum of vinyl chloroformate: of a 10% CCl_4 solution between 2.5 and 7.5 μ (cell thickness, 0.117 mm.); and of a 10% CS_2 solution between 7.5 and 16 μ (cell thickness, 0.114 mm.).

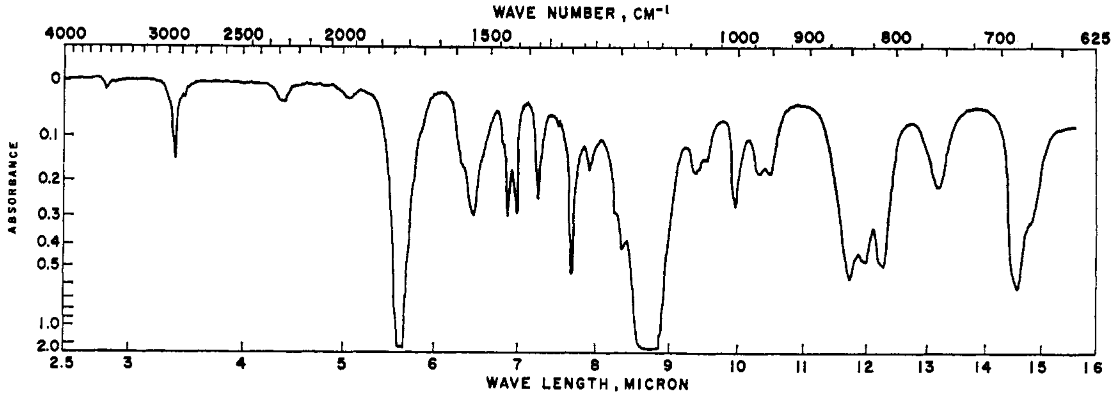


Figure 2.—The infrared spectrum of 2-chloroethyl chloroformate: of a 10% CCl_4 solution between 2.5 and 7.5 μ (cell thickness, 0.106 mm.); and of a 10% CS_2 solution between 7.5 and 16 μ (cell thickness, 0.104 mm.).

Table I

Decomposition Products of Ethylene Glycol Bis(chloroformate)

Expt. no.	Temp., °C.	Feed rate, (cc./min.)	Vinyl chloride, %	Unknown, %	1,1-Dichloroethane, %	Vinyl chloroformate, %	1,2-Dichloroethane, %	1-Chloroethyl chloroformate, %	2-Chloroethyl chloroformate, %	Unreacted bis(chloroformate, %
1	460	5	1.3	0.2	0	10	1	0	10	77
2	480	5	9.1	0.8	0	40	7	0	15	28
3	465	5	7.6	0.4	0	44	8	0	16	24
4	460	1.5	3.2	0.2	7.1	22	20	0.7	10	37
5	460	1.1	0.2	0.0	0.2	15	17	0.9	14	51

vinyl chloroformate in the same apparatus, we obtained the unreacted vinyl chloroformate and vinyl chloride.

The second study made use of an indirect method. We found this method effective in supporting the decomposition study. The method involved the use of the mass spectrometer. The sample was injected at the inlet and maintained at 200° for approximately 10 min. The pressure of the inlet system was 0.1 mm. The ionization was conducted using an electron energy of 75 e.v. and an ion-source pressure of 10–9 mm. The ion fragments of ethylene glycol bis(chloroformate) contained vinyl chloroformate ion, vinyl chloride ion, and a small amount of chloroethyl chloroformates ions and dichloroethanes ions, but the ion fragments of the decomposition products of 2-chloroethyl chloroformate did not contain vinyl chloroformate ion (*m/e* 106 and 108). The absence of vinyl chloroformate ion confirmed the above finding that vinyl chloroformate was formed as a result of the pyrolysis of ethylene glycol bis(chloroformate) but not as a result of the pyrolysis of 2-chloroethyl chloroformate. Furthermore, we also established that the main decomposition product of vinyl chloroformate was vinyl chloride. Most of the vinyl chloroformate did not decompose in the mass spectrometer under the experimental conditions. This indicates that vinyl chloroformate appeared to be more stable than 2-chloroethyl chloroformate as shown by the amount of the undecomposed vinyl chloroformate ion present in the spectrum.

This indirect method served to confirm the above pyrolysis results and to help the following discussion regarding the primary and the secondary products obtained from the thermal decomposition of ethylene glycol bis(chloroformate).

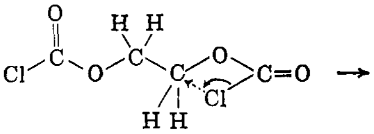
Results and Discussion

The decomposition products were quantitatively analyzed with vapor phase chromatography. In Table I, the first three experiments were conducted at high feed rates. The products contained vinyl chloroformate, 2-chloroethyl chloroformate, 1,2-dichloroethane, and vinyl chloride. The last two experiments were made with slower feed rates. Two additional products were obtained: 1,1-dichloroethane and a trace amount of an unidentified compound which is presumably 1-chloroethyl chloroformate reported by Küng.

The results of the thermal decomposition of ethylene glycol bis(chloroformate) indicate that at 460–480° there were at least two types of simultaneous reactions:

substitution and elimination. There were possibly three major primary products: vinyl chloroformate, 2-chloroethyl chloroformate, and 1,2-dichloroethane. The elimination reaction became important only at higher temperatures (above 460°). These results agree with Lewis and Herndon's findings on other chloroformates.

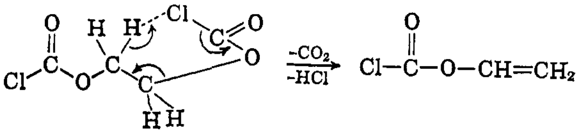
According to Lewis and Herndon, the substitution reaction of chloroformates is presumably a one-step reaction through a cyclic transition state of ROCOCl to RCl. The mechanism was supported by a large negative entropy of activation, the relative reactivities of different alkyl chloroformates, retention of configuration, and absence of rearranged alkyl chlorides.



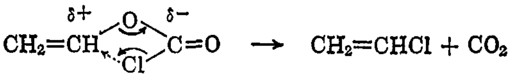
$$CO_2 + ClOCOCH_2CH_2Cl \rightarrow ClCH_2CH_2Cl$$

The decomposition results (Table I) show that with a high feed rate 2-chloroethyl chloroformate was present in an amount (weight) at least twice that of 1,2-dichloroethane. As the feed rate decreased, the amount of 1,2-dichloroethane increased.

The elimination reaction[2] for other chloroformates was shown by Lewis and Herndon to proceed *via* a more polar transition state. In the case of ethylene glycol bis(chloroformate), the six-membered cyclic transition state may be shown as follows.



Vinyl chloride may be formed *via* the transition state given below. This substitution is one of the best examples for an S_Ni mechanism, because the existence of the ion-pair intermediate is highly questionable as a result of the unfavorable structure of a vinyl cation.



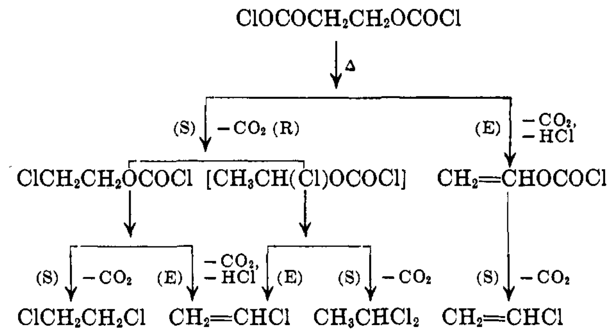
One of the products obtained with a slow feed rate was 1,1-dichloroethane. We assume that the logical source of this compound was 1-chloroethyl chloroformate as reported by Küng. The possible involvement of 1-chloroethyl chloroformate needs further investigation.

Conclusion

The preceding discussion on mechanism and the experimental results suggest that the yield of vinyl chloroformate can be increased by the following three methods: (1) by raising the temperature slightly above 460° (It should be noted that the minimum temperatures were found to be different in different apparatus.); (2) by using a high feed rate (With a high feed rate, the formation of 1-chloroethyl chloroformate and 1,1-dichloroethane could be prevented. Also, with a high feed rate, the further decomposition of vinyl chloroformate into vinyl chloride could be minimized.); and (3) by using a diluent such as nitrogen (The use of a diluent could minimize the formation of secondary products, perhaps simply because of better heat transfer.).

The relationship between the primary and the secondary decomposition products may be summarized by Scheme I.

Scheme I



S = substitution, E = elimination, R = rearrangement

Acknowledgment.—The author gratefully acknowledges Professor Martin Stiles of the University of Michigan and Professor J. C. Martin of the University of Illinois for discussions, Mr. L. Hart of the Analytical Laboratory for the vapor phase chromatographic analysis, Mr. R. W. Miller for technical assistance, Mr. R. S. Gohlke for the mass spectrometer analyses, and Mr. R. Nyquist for the infrared analyses.

Reduction of Polyfluoroalkyl Nitriles with Sodium Borohydride

S. E. Ellzey, Jr., J. S. Wittman, III,
and W. J. Connick, Jr.

Southern Regional Research Laboratory,[1]
New Orleans, Louisiana 70119

Received June 14, 1965

During a study of the effects of various highly fluorinated molecules on the properties of cotton textiles, it was necessary to prepare certain representative primary polyfluoroalkylamines.

A compilation[2] of methods for preparing primary fluorinated alkylamines reveals that the reduction of the corresponding carboxamides with lithium aluminum hydride[3a,b] is of general utility. Side reactions[3b] leading to aldehyde formation lower the yields somewhat and certain precautions which appear necessary in this procedure[3b] because of the reactive nature of the hydride or because of the nature of the reaction intermediates[4a,b] may prove troublesome. A recent report[5] which appeared near the completion of our work indicates that high yields of 1,1-dihydroperfluoro-

---

[1] One of the laboratories of the Southern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture.

[2] A. M. Lovelace, D. A. Rausch, and W. Postelnek, "Aliphatic Fluorine Compounds," Reinhold Publishing Corp., New York, N. Y., 1958, pp. 285–288.

[3] (a) J. E. Carnahan and H. J. Sampson, U. S. Patent 2,646,449 (1953); (b) D. R. Husted and A. H. Ahlbrecht, U. S. Patent 2,691,043 (1954).

[4] (a) T. S. Reid and G. H. Smith, *Chem. Eng. News*, **29**, 3042 (1951); (b) W. Karo, *ibid.*, **33**, 1368 (1955).

[5] M. Sander, *Monatsh. Chem.*, **95**, 608 (1964).