The Reactions of Vinyl Chloroformate and Oxime Chloroformates with Silver Salts

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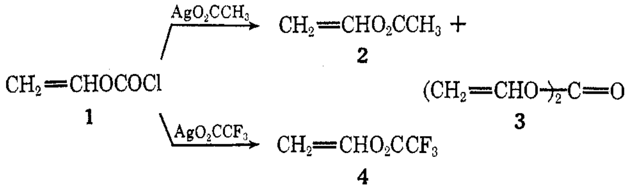
Vinyl chloroformate (**1**) reacts with silver acetate in chlorobenzene at 60° to give 17% vinyl acetate (**2**) and 65% divinyl carbonate (**3**). Under the same conditions **1** reacts with silver trifluoroacetate to give 77% vinyl trifluoroacetate (**4**). The latter reaction is shown on the basis of ^{18}O labeling to proceed with retention of the carbon–oxygen bond and is considered to involve a carbonate intermediate. In the presence of tetramethylurea, vinyl chloroformate reacts with silver hexafluoroantimonate in chlorobenzene to give *O*-(carboxyvinyl)tetramethyluronium hexafluoroantimonate (**7**) in 80% yield. The reaction of phenyl chloroformate with silver hexafluoroantimonate in chlorobenzene at 100° in the presence of tetramethylurea to give phenyl *N*,*N*-dimethyl carbamate is suggested to involve a uronium salt **9** similar to **7**. The oxime chloroformates of benzophenone, fluorenone, and *syn*- and *anti*-4-methylbenzophenone react with silver tetrafluoroborate to give amides by the normal Beckmann rearrangement. Cationic intermediates with sp–sp²-hybridized carbon and nitrogen do not appear to be involved in these reactions.

The generation of species exhibiting carbonium ion reactivity from silver ion and primary and bridgehead bicyclo[2.2.1]chloroformates for which the corresponding chlorides are unreactive has been taken to indicate that the loss of carbon dioxide provides a substantial driving force for reaction, analogous perhaps to the loss of nitrogen from a diazonium ion.[1-4] As a probe into the structural limits on the formation of cationic intermediates by this process, we have investigated the reactions of vinyl and oxime chloroformates with silver salts. Our results show that possible high-energy cationic intermediates with a positive charge on a formally sp–sp² hybridized unsubstituted carbon[5,6] or nitrogen[7] are avoided and alternative pathways are followed.

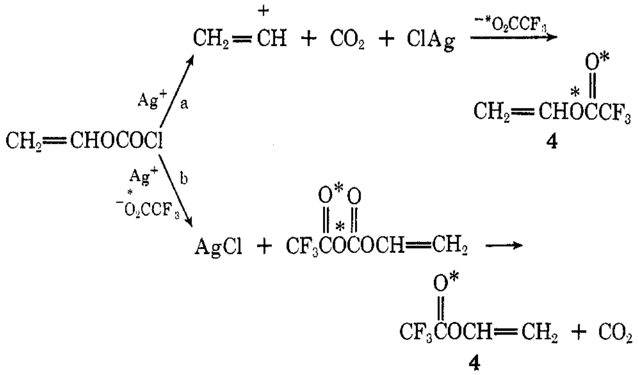
Results and Discussion

Vinyl Chloroformate.—The reaction of vinyl chloroformate (**1**) with silver acetate in chlorobenzene for 34 hr at 60° gives 17% vinyl acetate (**2**) and 65% divinyl carbonate[8] (**3**). When silver trifluoroacetate is used, 77% vinyl trifluoroacetate (**4**) is formed after 24 hr. The reactions give yields of 78 and 87% silver chloride, respectively.



While vinyl acetates **2** and **4** could be formed by cleavage of the oxygen–vinyl carbon bond (path a) and reaction of the resulting vinyl carbonium ion with acetate, an alternative process, formation of an intermediate carbonate by reaction of **1** with acetate (path b) followed by rearrangement to **4** without cleavage of the oxygen–vinyl carbon bond, can also be envisioned. These processes are outlined in Scheme I for reaction of **1** with ^{18}O-labeled silver trifluoroacetate. This scheme shows that the amount of ^{18}O in the trifluoroacetate **4** can be used to distinguish between these two possible processes.[9-11] If path a is followed, all of the oxygen-18 label in the silver trifluoroacetate will appear in **4**; on the other hand, if path b is followed, **4** will

SCHEME I



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[1] P. Beak, R. J. Trancik, and D. Simpson, *J. Amer. Chem. Soc.*, **91**, 5073 (1969), and references cited therein.

[2] For an excellent review see D. N. Kevill, "The Chemistry of Acyl Halides," S. Patai, Ed., Wiley-Interscience, New York, N. Y., 1972, p 381.

[3] D. N. Kevill, W. A. Reis, and J. B. Kevill, *Tetrahedron Lett.*, 957 (1972), and references cited therein.

[4] For closely related reactions see G. A. Olah and P. Schilling, *Justus Liebigs Ann. Chem.*, **761**, 77 (1972), and references cited therein; W. E. Dupy, H. R. Hudson, and D. A. Karam, *Tetrahedron Lett.*, 3193 (1972).

[5] For recent reviews of vinyl carbonium ions see H. G. Richey and J. M. Richey, "Carbonium Ions," Vol. II, G. A. Olah and P. v. R. Schleyer, Ed., Wiley-Interscience, New York, N. Y., 1970, (a) pp 900–922, (b) p 901; M. Hanack, *Accounts Chem. Res.*, **3**, 209 (1970); R. C. Fahey, *Top. Stereochem.*, **3**, 237 (1968); G. Modena and U. Tonellato, *Advan. Phys. Org. Chem.*, **9**, 185 (1971); C. A. Grob, *Chimia*, **25**, 87 (1971).

[6] For cases in which vinyl diazonium ions are considered to be precursors of vinyl cations, see M. S. Newman and A. E. Weinberg, *J. Amer. Chem. Soc.*, **73**, 4199 (1951); M. S. Newman and A. Kuther, *ibid.*, **73**, 4199 (1951); D. Y. Curtin, J. A. Kampmeier, and B. R. O'Connor, *ibid.*, **87**, 863 (1965); D. Y. Curtin, J. A. Kampmeier, and M. L. Farmer, *ibid.*, **87**, 874 (1965); W. M. Jones and F. W. Miller, *ibid.*, **89**, 1960 (1967); A. C. Day and M. C. Whiting, *J. Chem. Soc. B*, 991 (1967); M. S. Newman and C. D. Beard, *J. Amer. Chem. Soc.*, **92**, 7564 (1970), and references cited therein.

[7] Although iminium ions are not usually considered intermediates in the Beckmann rearrangement, they have been postulated in special cases: P. T. Lansbury, "Nitrenes," W. Lwowski, Ed., Interscience, New York, N. Y., 1970, pp 405–419; R. M. Pinder, *J. Chem. Soc. C*, 1690 (1969), and references cited therein.

[8] The formation of **3** from reaction of **1** and triethylammonium or pyridium benzoate has been independently observed by Professor R. A. Olofson, private communication, Sept 1971. For an elegant use of the vinyloxycarbonyl function as a protecting group for amines in peptide synthesis, see R. A. Olofson and Y. S. Yamamoto, Abstracts of Papers, Division of Organic Chemistry, 156th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1968, p 23.

[9] A critical assumption in Scheme I is that rearrangement of **5** to **4** proceeds with acyl oxygen cleavage, a pathway which has been established for other carbonates,[10] unless an alkyl group especially capable of stabilizing a carbonium ion is bonded to oxygen.[11]

[10] D. B. Denney and D. Z. Denney, *J. Amer. Chem. Soc.*, **84**, 2455 (1962); C. J. Michejda, D. S. Tarbell, and W. H. Saunders, Jr., *ibid.*, **84**, 4113 (1962).

[11] C. J. Michejda and D. S. Tarbell, *J. Org. Chem.*, **29**, 1168 (1964); R. C. L. Chow and D. S. Tarbell, *ibid.*, **32**, 2188 (1967); T. Kashiwazi and S. Oae, *Tetrahedron*, **26**, 3631 (1970); C. J. Michejda and D. Von Riesen, *J. Org. Chem.*, **37**, 3021 (1972).

be formed with only one half of the label originally in the silver trifluoroacetate. The results summarized in Table I show that, with silver trifluoroacetate-^{18}O containing 5.63% isotopic excess, the vinyl trifluoroacetate produced contains 2.87% excess ^{18}O, thereby eliminating a as the path for formation of **4** and suggesting the carbonate, trifluoroacetic carbonic vinyl anhydride, as a reaction intermediate. If **4** and, by implication, **2** are produced according to path b *via* the corresponding carbonates, the conversion of these intermediates to ester can be considered to proceed either intra- or intermolecularly. Both processes have precedent,[10-13] although the latter, involving vinylate **6**, the enolate anion of acetaldehyde, as well as acetate in an ionic chain process analogous to that proposed by Tarbell,[12] is consistent with the formation of divinyl carbonate.

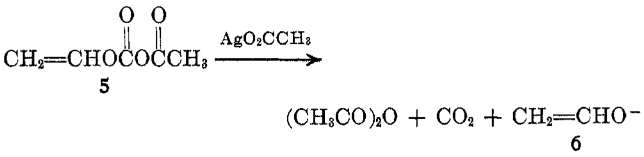
TABLE I

OXYGEN-18 LABELING OF VINYL TRIFLUOROACETATE (4) FROM THE REACTION OF VINYL CHLOROFORMATE (1) WITH OXYGEN-18 LABELED SILVER TRIFLUOROACETATE IN CHLOROBENZENE AT 60°

Compd	f (^{18}O)^a	f (^{18}O) excess	Relative % enrichment
Unlabeled silver trifluoroacetate^b	0.24 ± 0.01^c	0	0
^{18}O-labeled silver trifluoroacetate^b	5.87 ± 0.01	5.63 ± 0.05	100
Vinyl trifluoroacetate from the reaction of **1** with unlabeled silver trifluoroacetate	0.27 ± 0.01	0	0
Vinyl trifluoroacetate from the reaction of **1** with labeled silver trifluoroacetate	3.14 ± 0.03	2.87 ± 0.04	51.0 ± 0.8

[a] Calculated from f (^{18}O) = $(b + 2c)/2$, where a, b, and c are intensity values for I, I + 2, and I + 4 normalized so that $a + b + c = 100$. [b] Values for silver trifluoroacetate were determined after conversion to methyl trifluoroacetate. [c] Errors are standard deviations of the average of three scans from an isotope ratio mass spectrum.

In an intermolecular scheme, attack of acetate on acetic vinyl carbonic anhydride (**5**) to give acetic anhydride, carbon dioxide, and **6**, probably in a series of steps, would be followed by reaction of **6** with **5** to give **3** or **2**. However, a competing intramolecular rearrangement of **5** to **2** cannot be ruled out by the data. In view of the probable role of vinylate in these reactions, it is pertinent that the same reactants in acetic acid give acetaldehyde, identified as its 2,4-dinitrophenylhydrazone, the product expected from protonation of **6**. Control experiments did establish that the acetaldehyde is a primary reaction product and does not result solely from hydrolysis of vinyl acetate or vinyl chloroformate, which might be swept into the 2,4-dinitrophenylhydrazine solution.



$$\underset{\mathbf{5}}{CH_2{=}CHO\overset{O}{\overset{\|}{C}}O\overset{O}{\overset{\|}{C}}CH_3} \xrightarrow{AgO_2CCH_3} (CH_3CO)_2O + CO_2 + \underset{\mathbf{6}}{CH_2{=}CHO^-}$$

$$\mathbf{5} + \mathbf{6} \longrightarrow \underset{\mathbf{3}}{(CH_2{=}CHO\text{)}_2C{=}O} + CH_3CO_2^-$$

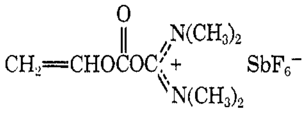
$$\mathbf{5} + \mathbf{6} \longrightarrow \mathbf{2} + CH_2{=}CHO^- + CO_2$$

The nucleophiles, acetate, vinylate, and trifluoroacetate, clearly play a critical role in the formation of **2**, **3**, and **4** from vinyl chloroformate. In an effort to eliminate the influence of such nucleophiles, reactions of **1** with silver tetrafluoroborate and silver hexafluoroantimonate were carried out. The product of the reaction of vinyl chloroformate and silver tetrafluoroborate in chlorobenzene at 60° is vinyl fluoroformate in 36% yield. The yield of the fluoroformate was determined indirectly by conversion to ethyl vinyl carbonate. This reaction is analogous to the conversion of phenyl chloroformate to phenyl fluoroformate previously reported.[1]

$$\underset{\mathbf{1}}{CH_2{=}CHOCOCl} \xrightarrow[C_6H_5Cl]{AgBF_4} CH_2{=}CHOCOF + BF_3$$

The reaction of vinyl chloroformate with silver hexafluoroantimonate in chlorobenzene at 40° is uneventful for *ca.* 10 min but then a violent exothermic reaction occurs.[14] No volatile products could be detected and *p*-chlorostyrene, a possible reaction product, was not stable under these conditions. In contrast, *p*-chlorostyrene was stable under these reaction conditions in the presence of 2 equiv of tetramethylurea. However, the product of the reaction of **1** and silver hexafluoroantimonate in the presence of tetramethylurea is *O*-(carboxyvinyl)tetramethyluronium hexafluoroantimonate (**7**) in 80% yield. The structure of **7** rests on ir, nmr, and analytical data as well as conversion to ethyl vinyl carbonate on reaction with ethanol. A similar species has been proposed as a reaction intermediate in the reaction of aryl chloroformates with dimethylformamide to give aryloxy immonium salts,[15] and related structures have been suggested as intermediates in the dehydration of carboxylic acids by carbodiimides[16] and in dicyclohexylcarbodiimide mediated sulfuration reactions.[17] The reaction of **7** with ethanol at the carbonyl carbon provides an analogy for the product-forming steps in the latter two cases.

$$\underset{\mathbf{1}}{CH_2{=}CHOCOCl} + [(CH_3)_2N]_2C{=}O \xrightarrow{AgSbF_6}$$



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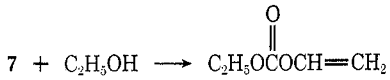

$$\mathbf{7} + C_2H_5OH \longrightarrow C_2H_5O\overset{O}{\overset{\|}{C}}OCH{=}CH_2$$

The reaction of phenyl chloroformate with silver hexafluoroantimonate and tetramethylurea in chloro-

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[12] E. J. Longosz and D. S. Tarbell, *J. Org. Chem.*, **26**, 2161 (1961); D. S. Tarbell, *Accounts Chem. Res.*, **2**, 296 (1969).

[13] R. Bochan, *J. Amer. Chem. Soc.*, **81**, 3341 (1959).

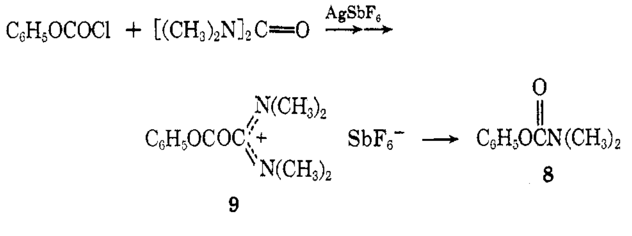
(14) A plausible rationalization for this observation is that small amounts of acid initially produced start a rapid polymerization of **1**.

(15) V. A. Pattison, J. G. Colson, and R. L. K. Carr, *J. Org. Chem.*, **33**, 1084 (1968).

(16) H. G. Khorana, *Chem. Rev.*, **53**, 145 (1953).

(17) C. P. Hoiberg and R. O. Mumma, *J. Amer. Chem. Soc.*, **91**, 4273 (1971).

benzene at 100° gives an 82% yield of phenyl *N*,*N*-dimethylcarbamate (**8**).[1,15] In the absence of the urea, the same reaction gave only black, intractable precipitates. The similarity of the reactions of phenyl and vinyl chloroformate prompted a reinvestigation of the reaction of phenyl chloroformate in the presence of tetramethylurea to determine if carbamate formation might proceed *via* a uronium salt **9** similar to **7**. When this reaction is run at 80° for 20 hr, an 84.5% yield of the carbamate **8** is observed, along with 99% of silver chloride. Lowering the reaction temperature to 40° gives only 40% of **8** but 97% of silver chloride after 20 hr. The observed temperature dependence of the yield of **8** suggests that it may be formed *via* a thermally unstable intermediate. At ambient temperature phenyl chloroformate gives only 10% of **8** and an acetone-soluble oil in addition to silver chloride. The ir and nmr spectra of this material are very similar to those of **7**. Although a sample pure enough for elemental analysis could not be obtained, it seems likely that this material is *O*-(carboxyphenyl)tetramethyluronium hexafluoroantimonate (**9**) and that **9** is a reaction intermediate in the formation of **8**.

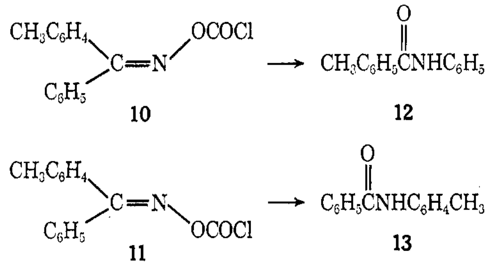


$C_6H_5OCOCl + [(CH_3)_2N]_2C{=}O \xrightarrow{AgSbF_6}$

Comparison of the chloroformate–silver ion leaving group to other groups which have been reported to be effective in producing vinyl carbonium ions requires correlation of the present wholly unsubstituted vinyl system with substituted cases for the other functions. In the cases of the diazonium ions, however, the systems are β substituted, and, if those reactions are correctly formulated as involving primary vinyl carbonium ions, nitrogen appears to be a better leaving group than the combination of silver chloride and carbon dioxide offered in the present system.[6] A comparison with the sulfonates[5] is less indicative, however, since the cases which most clearly involve vinyl carbonium ions from sulfonates are α substituted by groups which would be expected to stabilize the transition state for carbonium ion formation.

Oxime Chloroformates.—Although iminium ions have been reported as reaction intermediates on reaction of oximes with polyphosphoric acid at 130–170°, for systems[7] with geometric requirements which discourage rearrangement concerted with nitrogen–oxygen bond cleavage, the silver ion induced Beckmann rearrangements of para-substituted *N*-chlorobenzophenone imines[18] and deamination of benzophenone hydrazones[19] have provided no evidence for such species. Both previous studies involved attempts to obviate internal assistance for ionization of the nitrogen–oxygen bond by loss of a very stable leaving group.[18,19] The reaction of oxime chloroformates with silver salts appears to provide another opportunity for formation of an iminium ion in an unhindered system.

Reaction of benzophenone oxime chloroformate with silver tetrafluoroborate in chlorobenzene at ambient temperature followed by exposure to aqueous acid gives the expected high yields of carbon dioxide and silver chloride as well as 75% benzanilide. A similar reaction of 9-fluoreneone oxime chloroformate and silver tetrafluoroborate requires heating to 55° to give yields of silver chloride and carbon dioxide of 88 and 84%, respectively, and, after hydrolysis, 87% phenanthridione. Since fluorenone oxime itself requires heating to 175–180° in polyphosphoric acid for Beckmann rearrangement,[20] this result suggests that some driving force is provided by silver chloride and carbon dioxide as leaving groups. Information about the intermediacy of iminium ions is provided by the stereoselectivity of the rearrangement.[7,18,19] Samples enriched in the syn and anti chloroformates of 4-methylbenzophenone oxime were prepared and treated with silver fluoroborate at ambient temperature. From the sample containing 15 ± 3% syn chloroformate **10** and 85 ± 3% anti chloroformate **11** are obtained 15 ± 3% *N*-phenyl-*p*-toluamide (**12**) and 85 ± 3% *N*-(*p*-tolyl)benzamide (**13**), while the sample which is 95 ± 3% **10** and 5 ± 3% **11** gives a product mixture of 88 ± 3% **12** and 12 ± 3% **13**. The apparent slight decrease in stereoselectivity in the latter case could be attributed to a small amount of isomerization of the chloroformate prior to reaction. Thus, the lack of stereospecificity expected for an iminium intermediate[7,18,19] is not observed and the reaction of oxime chloroformates, while perhaps a convenient procedure for the Beckmann rearrangement, is stereospecific and similar to that previously reported for other leaving groups.



Experimental Section[21]

Gas–Liquid Partition Chromatography (Glpc).—Glpc was performed on Aerograph Models A-90-P or A-90-P3. Product yields are reported in mole per cent based on starting chloroformate and were determined using internal standard with corrections for differences in detector responses between products and internal standards, unless otherwise noted, and planimetric measurement of peak areas. The glpc columns referred to are column A, 12 ft × 0.25 in. 15% XF-1150 on HMDS Chromosorb P; column B, 12 ft × 0.375 in. 20% XF-1150 on HMDS Chromosorb P; column C, 7 ft × 0.375 in. 16% SE-30 on Chromosorb P;

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(18) R. N. Leoppky and M. Rotman, *J. Org. Chem.*, **32**, 4010 (1967).

(19) D. L. Fishel and B. L. Hawbecker, Abstracts of Papers, Division of Organic Chemistry, 156th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1968, p 170.

(20) E. C. Horning, V. C. Stromberg, and H. A. Lloyd, *J. Amer. Chem. Soc.*, **74**, 5153 (1952).

(21) Melting points were determined on a Thomas-Hoover capillary melting point apparatus and are uncorrected. Nmr spectra were obtained on Varian Models A-60A, A-56/60, HA-100, or T-60 spectrometers by Mr. Robert Thirft and his associates or by J. B. Chemical shifts are reported in δ (parts per million) relative to the internal standard tetramethylsilane unless otherwise noted. Ir spectra were obtained on Perkin-Elmer Models 137 or 521 spectrometers. Mass spectra were recorded by Mr. J. Wrona or Mr. P. Matejek on an Atlas CH-5 medium-resolution spectrometer. Elemental analyses were carried out by Mr. J. Nemeth and his associates.

column D, 8 ft × 0.25 in. 20% XF-1150 on AW-DMCS Chromosorb P; column E, 15 ft × 0.25 in. 20% XF-1150 on AW-DMCS Chromosorb P; column F, 6 ft × 0.25 in. 16% SE-30 on Chromosorb P; column G, 7 ft × 0.25 in. 30% UCON LB550x on firebrick; and column H, 2 ft × 0.25 in. 20% XF-1150 on AW-DMCS Chromosorb P. All solid supports were 60/80 mesh.

Materials.—Chlorobenzene (Fischer) and benzene (Baker and Adamson) were distilled from calcium hydride at atmospheric pressure under dry nitrogen. Glacial acetic acid (Du Pont) was refluxed with 1–2% acetic anhydride and distilled at atmospheric pressure under dry nitrogen. 1,1,3,3-Tetramethylurea (Aldrich) was distilled from calcium hydride under reduced pressure. Silver tetrafluoroborate and silver hexafluoroantimonate, obtained from the Ozark-Mahoning Co., were dried at room temperature over P_2O_5 at 0.3 mm for a minimum of 3 days and stored in amber bottles under dry nitrogen. Silver acetate (Fischer) was used as commercially obtained. Silver trifluoroacetate was prepared from trifluoroacetic acid and silver oxide according to the procedure of Janseen and Wilson.[22] Commercial vinyl acetate (Eastman) and vinyl trifluoroacetate (Pfaltz and Bauer) were distilled at atmospheric pressure. Vinyl chloroformate (**1**) was purchased from Penninsular ChemResearch and purified by distillation, bp 66–68° (lit.[23] bp 69°). The impurities 1,1- and 1,3-dichloroethane remained after distillation and amounted to 8–14% in different samples. These were present during reactions and all weights and yields have been corrected accordingly. All other commercial reagent grade materials were used as obtained unless otherwise noted.

Vinyl fluoroformate was prepared by halogen exchange of vinyl chloroformate and sodium floride in acetone and purified by preparative glpc (column D, 75°): ir (CCl_4) 3086, 1840 (C=O), 1678, 1650, 1357, 1300, 1248, 1218, 1134, 1041, 938, 889 cm^{-1}; nmr (CCl_4) δ 7.01 (q, 1, X of ABX), 5.12 and 4.81 (m, 2, AB of ABX split by fluorine, $J_{AX} = 13.9$, $J_{BX} = 6.1$, $J_{AB} = 2.6$ Hz); ^{19}F nmr (CCl_4) δ (relative to internal $CFCl_3$) -19.6 (d of d, $J_{AF} = 2.0$, $J_{BF} = 4.8$ Hz); mass spectrum (70 eV) *m/e* (rel intensity) 90 (100, M$\cdot^+$), 47 (67), 46 (28).

Anal. Calcd for $C_3H_3FO_2$: C, 40.01; H, 3.36. Found: C, 39.82; H, 3.33.

Ethyl vinyl carbonate was prepared from vinyl chloroformate and absolute ethanol by preparative glpc (column F, 80°): ir (CCl_4) 3077, 2976, 2882, 1764 (C=O), 1653, 1368, 1299, 1258, 1163, 1095, 1007, 948, 878 cm^{-1}; nmr (CCl_4) δ 7.02 (q, 1, X of ABX), 4.70 (m, 2, AB of ABX, $J_{AX} = 13.8$, $J_{BX} = 6.3$, $J_{AB} = 18$ Hz), 4.18 (q, 2, $J = 7.0$ Hz), 1.32 (t, 3, $J = 7.0$ Hz).

Anal. Calcd for $C_5H_8O_3$: C, 51.72; H, 6.94. Found: C, 51.85; H, 6.88.

***N*-(*p*-Toly)benzamide** was prepared from benzoyl chloride and *p*-toluidine, mp 157–159° (lit.[24] mp 158°).

***N*-Phenyl-*p*-toluimide** was prepared from *p*-toluic acid chloride and aniline, mp 146–148° (lit.[24] mp 145–146°).

4-Methylbenzophenone oxime was prepared from 4-methylbenzophenone, and the syn and anti isomers were separated by fractional crystallization from absolute ethanol. *syn*-4-Methylbenzophenone oxime crystallizes preferentially: mp 156.5–158° (lit.[24] mp 155–156°); nmr ($CDCl_3$) δ 7.40 (m, 9), 2.42 (s, 3). *anti*-4-Methylbenzophenone oxime is obtained from the concentrated mother liquor: mp 135–137° (lit.[24] mp 136–137.5°); nmr ($CDCl_3$) δ 7.28 (m, 9), 2.34 (s, 3).

Reaction of Vinyl Chloroformate with Silver Acetate in Chlorobenzene.—To a suspension of 2.57 g (15.4 mmol) of silver acetate in chlorobenzene was added 1.31 g (12.3 mmol) of vinyl chloroformate. After the reaction had been stirred at 60° for 34 hr, filtration and glpc analysis (column A, 80°) showed two peaks, which were collected by preparative glpc (column C, 150°) and isolated in pure form by further preparative glpc (column B, 110°). The compound of shortest retention time was identified as vinyl acetate (**2**) by comparison of its ir and nmr spectra to those of the commercially available authentic material. The yield of silver chloride, measured as the ammonium hydroxide soluble residue after filtration, was 1.38 g (78%).

The second compound gave spectra and analytical data consistent with the structure of divinyl carbonate[25] (**3**): ir ($CHCl_3$) 3125, 3030, 1786 (C=O), 1656, 1302, 1258, 1117, 945, 909, 885 cm^{-1}; nmr (CCl_4) δ 7.03 (q, 1, X of ABX), 4.73 (m, 2, AB of ABX, $J_{AX} = 13.5$, $J_{BX} = 6.3$, $J_{AB} = 2.0$ Hz); mass spectrum (70 eV) *m/e* (rel intensity) 114 (M$\cdot^+$, 21.5), 71 (4.33), 69 (5.68), 44 (100), 43 (66.8).

Anal. Calcd for $C_5H_6O_3$: C, 52.63; H, 5.30. Found: C, 52.44; H, 5.39.

In a separate experiment 5.0 mmol of silver acetate and 4.8 mmol of vinyl chloroformate in chlorobenzene gave 17% vinyl acetate and 65% divinyl carbonate by glpc analysis (column A, 75°), using benzene as an internal standard. The divinyl carbonate yield is uncorrected for differences in thermal conductivity between the product and internal standard.

Reaction of Vinyl Chloroformate with Silver Trifluoroacetate in Chlorobenzene.—To a solution of 1.51 g (6.84 mmol) of silver trifluoroacetate in 10 ml of chlorobenzene heated to 60°, 0.73 g (6.85 mmol) of vinyl chloroformate was added. After 24 hr a slow nitrogen sweep was introduced and a clear, colorless liquid was collected in two Dry Ice cooled traps. The compound was isolated by preparative glpc (column A, 90°) and found to be identical with authentic vinyl trifluoroacetate by ir and nmr spectroscopy and mass spectrometry. The yield of silver chloride was 0.86 g (87%).

The yield of vinyl trifluoroacetate was determined in a separate experiment carried out under Dry Ice cooled condensers by glpc (column E, 65°, cyclohexane as internal standard) to be 77%.

Preparation of Silver Trifluoroacetate-^{18}*O*.—Trifluoroacetic acid (Aldrich), 0.70 g (6.1 mmol), and water, 3.6 g (200 mmol, 6.55 atom % excess ^{18}O), were heated at 55–60° for 48 hr followed by the addition of silver oxide, 1.5 g (16 mmol). After removal of excess water by distillation, extractive procedures with ether gave 0.70 g (52%) of silver trifluoroacetate-^{18}O. The amount of label shown in Table I was determined by conversion of the silver salt to methyl trifluoroacetate with methyl iodide and mass spectral comparison of the isotope ratios of the *m/e* 59 ($[CH_3OC{=}O]\cdot^+$) fragment for the labeled methyl ester and a sample prepared in a similar manner from unlabeled silver salt. The fragment peak was used for the analysis because methyl trifluoroacetate does not give a molecular ion.

Reaction of Vinyl Chloroformate with ^{18}O-Labeled Silver Trifluoroacetate in Chlorobenzene.—Reactions were carried out with 0.0555 g (0.52 mmol) of vinyl chloroformate and 0.112 g (0.51 mmol) of labeled and unlabeled silver trifluoroacetate in chlorobenzene at 60° for 24 hr, respectively. The vinyl trifluoroacetate was isolated directly from the reaction mixture by preparative glpc (column A, 90°) into a gas bulb for mass spectral analysis. The molecular ion peaks were used to provide the results summarized in Table I.

Reaction of Vinyl Chloroformate and Silver Acetate in Acetic Acid.—To silver acetate, 1.062 g (6.40 mmol), suspended in 41 ml of acetic acid and heated to 60°, 0.626 g (5.90 mmol) of vinyl chloroformate was added while a slow nitrogen sweep into a trap containing 2,4-dinitrophenylhydrazine solution was maintained. From the trap was obtained 1.01 g (77%) of the 2,4-dinitrophenylhydrazone derivative of acetaldehyde, authenticated by comparison of melting point and mixture melting point with those of an authentic sample.

In a control experiment carried out to establish that the 2,4-dinitrophenylhydrazone of acetaldehyde did not result from vinyl acetate, equimolar amounts of vinyl acetate and vinyl chloroformate were allowed to react with a slight excess of silver acetate in acetic acid at 60° and the reaction mixture was swept with nitrogen as before, but the 2,4-dinitrophenylhydrazone trap was replaced by a collection trap cooled in a Dry Ice–isopropyl alcohol slush. Analysis of the collected liquid by nmr showed it to be a mixture of acetaldehyde and vinyl acetate. A similar experiment without added vinyl acetate gave only acetaldehyde by nmr analysis.

Reaction of Vinyl Chloroformate with Silver Tetrafluoroborate in Chlorobenzene.—To silver tetrafluoroborate, 1.63 g (8.4 mmol), dissolved in 10 ml of chlorobenzene heated to 60°, 0.876 g (8.3 mmol) of vinyl chloroformate was added. After 4 hr at 60°, analyses by glpc (column D, 75°) revealed the one volatile product, which was isolated by preparative glpc (column D, 80°) and found by ir and nmr spectral criteria to be identical with those of a sample of vinyl fluoroformate. The yield of silver chloride was determined to be 1.19 g (100%).

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The yield of vinyl fluoroformate was determined to be a minimum of 36% by conversion to ethyl vinyl carbonate in a separate experiment.

Reaction of Vinyl Chloroformate with Silver Hexafluoroantimonate in Chlorobenzene and Tetramethylurea.—Vinyl chloroformate, 0.223 g (2.09 mmol), silver hexafluoroantimonate, 0.754 g (2.18 mmol), and tetramethylurea, 0.5 g (4 mmol), were allowed to react in 7 ml of chlorobenzene at 42° for 4 hr. Filtration gave a solid which was washed with chlorobenzene and pentane and then leached with acetone. The residue was 0.270 g (90.5%) of silver chloride. Concentration of the acetone washings gave 0.710 g (80%) of *O*-(carboxyvinyl)tetramethyluronium hexafluoroantimonate (**7**) as a white solid recrystallized from acetone–benzene: mp 97–98.5°; ir (solid film) 2924, 1795 (C=O), 1709 (C=O), 1657, 1536, 1468, 1412, 1304, 1232, 1182, 1120, 1062, 991, 929, 886, 760, 741 cm^{-1}; nmr (acetone-d_6) δ 7.10 (q, 1, X of ABX), 5.10 (m, 2, AB of ABX), 3.42 (s, 12).

Anal. Calcd for $C_8H_{15}F_6N_2O_3Sb$: C, 22.72; H, 3.55; N, 6.62. Found: C, 22.81; H, 3.65; N, 6.64.

The uronium salt **7**, 0.337 g (0.795 mmol), was allowed to react with excess absolute ethanol, 0.080 g (1.74 mmol), in 2.5 ml of acetone at 42° for 22 hr to give a 100 ± 5% yield of ethyl vinyl carbonate by glpc analysis on column D at 90° with 1,2-dichloroethane as internal standard.

Reaction of Phenyl Chloroformate with Silver Hexafluoroantimonate and Tetramethylurea in Chlorobenzene.—To a solution of 0.656 g (1.9 mmol) of silver hexafluoroantimonate and 0.403 g (3.5 mmol) of tetramethylurea in 6 ml of chlorobenzene stirred and heated to 80° was added 0.281 g (1.8 mmol) of phenyl chloroformate. After 20 hr at 80° the yield of **8** was determined directly by glpc analysis (column H, 175°) and uncorrected for thermal conductivity differences between the product and the internal standard, benzophenone (84.5%).

A similar reaction carried out at ambient temperature gave a precipitate which was washed repeatedly with chlorobenzene, then with pentane, and then leached with acetone. Concentration of the acetone solution gave a clear oil: ir (liquid film) 2933, 1808 (C=O), 1773 (C=O), 1706 (C=O), 1592, 1524, 1458, 1408, 1225, 1161, 1068, 969, 749, 763 cm^{-1} (shoulder); nmr (acetone-d_6) δ 7.45 (s, 5), 3.43 (s, 12), tentatively attributed to *O*-(carboxyphenyl)tetramethyluronium hexafluoroantimonate (**9**). The nmr spectrum also has a singlet at δ 3.0, which is attributed to an unidentified impurity.

Preparation of oxime chloroformates was carried out by reaction of the oxime at −10° with a five- to tenfold excess of phosgene in ether. Products were isolated from the organic phase after evaporation to dryness, addition of ether, and washing with a 5% solution of cold aqueous sodium bicarbonate.

Benzophenone oxime chloroformate is a white solid: mp 57–60° (lit.[26] mp 34–36°); ir ($CHCl_3$) 1790 (C=O), 1595 (C=N), 1110 cm^{-1} (COC). The material is sensitive to the atmosphere, and many attempts at further purification failed. The material was used as prepared and the structure was confirmed by the formation of a carbamate derivative.

Benzophenone imine *N*-benzylcarbamate was prepared from benzophenone oxime chloroformate and benzyl amine in benzene in 87% yield: mp 124–125° (lit.[26] mp 123–124°); ir ($CHCl_3$) 3480 (NH), 3070 (CH_2), 1740 (C=O), 1600 (C=N), 1110 (COC); nmr ($CDCl_3$) δ 7.35 (m, 15), 6.66 (broad s, 1), 4.35 (d, 2); mass spectrum (70 eV) m/e 180, 105, 90.

Anal. Calcd for $C_{20}H_{18}N_2O_2$: C, 76.36; H, 5.45; N, 8.48. Found: C, 76.38; H, 5.66; N, 8.54.

***syn*-4-Methylbenzophenone oxime chloroformate (10)** was prepared from *syn*-4-methylbenzophenone oxime in 90% yield: mp 79–82°; ir ($CHCl_3$) 3010 (CH_3), 1790 (C=O), 1601 (C=N), 1601 (C=N), 1100 (COC); nmr ($CDCl_3$) δ 7.52 (m, 9), 2.44, 2.38 (pair s, 3), ratio 18:1. The δ 2.38 singlet represents 5 ± 2% of the anti isomer.

***anti*-4-Methylbenzophenone oxime chloroformate (11)** was prepared from *anti*-4-methylbenzophenone oxime in 75% yield. The product was obtained as an unstable oil, nmr ($CDCl_3$) δ 7.30 (m, 9), 2.44, 2.38 (pair s, 3), ratio 15:85. The δ 2.44 singlet is 15 ± 3% of the syn isomer.

9-Fluorenone oxime chloroformate was prepared from 9-fluorenone oxime and phosgene in 95–100% yield as a yellow solid: mp 110–112°; ir ($CHCl_3$) 1795 (C=O), 1600 (C=N), 1100 (COC).

Reactions of oxime chloroformates with silver tetrafluoroborate were carried out in chlorobenzene for 4 hr, followed by heating to reflux with water for 20–30 min, filtration of precipitated silver chloride, and analysis of amide products in the organic layer by either glpc or direct isolation. Silver chloride was determined as the ammonium hydroxide soluble precipitate in the reaction mixture; carbon dioxide was determined as the acid-soluble precipitate from the barium hydroxide traps. The yields of both materials were consistently 90–100%.

Reaction of benzophenone oxime chloroformate with silver tetrafluoroborate in chlorobenzene gives 75 ± 5% benzanilide (glpc, column F). A preparative run gave a light brown solid, mp 157–160°. Chromatography on neutral alumina gave 66% benzanilide, mp 161–162°, mmp with authentic material 161–162°; the ir spectrum was identical with that of authentic benzanilide.

Reaction of 9-fluorenone oxime chloroformate with silver tetrafluoroborate in chlorobenzene was carried out at 55°. A pale brown solid was isolated from the organic layer in 87% yield. Recrystallization from methanol gave phenanthridinone: mp 290–292°, mmp 290–292°; the ir spectrum (Nujol mull), 1660 (C=O), 1600, 1460, 1370 cm^{-1}, was identical with that of authentic phenanthridinone.

Reaction of *syn*-4-methylbenzophenone oxime chloroformate (**10**) with silver tetrafluoroborate in chlorobenzene gave 90% of a brown solid: mp 130–136°; ir ($CHCl_3$) 3400, 2950, 1650, 1595, 1500, 1425, 1310, 1200 cm^{-1}; nmr ($CDCl_3$) δ 8.05 (broad s, 1), 7.50 (m, 9), 2.38, 2.32 (pair s, 3), ratio 6.8:1. Comparison of these spectra with those of mixtures of authentic samples indicates a 79 ± 3% yield of *N*-phenyl-*p*-toluamide (**12**) and an 11 ± 3% yield of *N*-(*p*-toly)benzamide (**13**).

Reaction of *anti*-4-methylbenzophenone oxime chloroformate (**11**) with silver tetrafluoroborate in chlorobenzene gave a pale brown solid: 96%; ir ($CHCl_3$) 3400, 3000, 1670, 1600, 1510, 1480, 1440, 1320 cm^{-1}; nmr ($CDCl_3$) δ 7.50 (m, 9), 2.38, 2.32 (pair s, 3), ratio 1:5.7. Comparison to known spectra indicates a 14 ± 3% yield of *N*-phenyl-*p*-toluamide (**12**) and an 82 ± 3% yield of *N*-(*p*-tolyl)benzamide (**13**).

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Registry No.—**1**, 5130-24-5; **3**, 7570-02-7; **7**, 40463-58-9; **9**, 40463-59-0; **10**, 40463-60-3; **11**, 40463-61-4; **12**, 6833-18-7; **13**, 582-78-5; vinyl fluoroformate, 40463-64-7; sodium fluoride, 7681-49-4; ethyl vinyl carbonate, 7570-06-1; *syn*-4-methylbenzophenone oxime, 2998-92-7; *anti*-4-methylbenzophenone oxime, 2998-91-6; 4-methylbenzophenone, 134-84-9; silver acetate, 563-63-3; silver trifluoroacetate, 2966-50-9; silver tetrafluoroborate, 14104-20-2; silver hexafluoroantimonate, 26042-64-8; phenyl chloroformate, 1885-14-9; benzophenone oxime chloroformate, 18304-44-4; benzophenone oxime, 574-66-3; benzophenone imine *N*-benzylcarbamate, 18304-48-8; 9-fluorenone oxime, 2157-52-0; 9-fluorenone oxime chloroformate, 40463-70-5.

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