51043-40-4; **15a**, 128243-19-6; **15b**, 128243-20-9; **16**, 128243-21-0; **17a**, 128243-22-1; **17b**, 128243-23-2; $PhCOCH_3$, 98-86-2; cyclohexanone, 108-94-1; 2-methylcyclohexanone, 583-60-8; cyclopentanone, 120-92-3; cycloheptanone, 502-42-1; cyclooctanone, 502-49-8; ethyl 2-oxocyclohexanecarboxylate, 1655-07-8; ethyl 2-(bromomethyl)acrylate, 17435-72-2.

Supplementary Material Available: ^1H and ^{13}C NMR spectra for **12a–b** and **9a/b** mixture (4 pages). Ordering information is given on any current masthead page.

An Efficient Synthesis of Some Substituted Vinylic Chloroformates: Reaction Scope and Limitations

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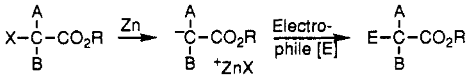
2,2-Dichlorovinyl chloroformate is isolated in 50% distilled yield when chloral is treated with phosgene and zinc dust in 2:1 methyl acetate/ether. The reaction has been extended to other α-chloro and α-bromo aldehydes and ketones in which both other α-positions are occupied by either halo and/or alkyl groups. The reaction fails with hydrogen in an α-position. Examples include the synthesis of $Cl_2C{=}C(Me)OC({=}O)Cl$ in 23% yield, $MeC(Cl){=}CHOC({=}O)Cl$ (56%, $E{:}Z$ = 1:1.1), $Cl_2C{=}C(C_6H_5)OC({=}O)Cl$ (66%), and 2-methyl-1-cyclohexenyl chloroformate (68%). Similar treatment of α-halo esters gives only the C-acylated products expected from a Reformatsky type reaction, while ketenes are the well-known products from α-halo acid chlorides. However, acyl cyanides and acyl phosphonates, with leaving groups intermediate between fluoride and alkoxide, are converted to chloroformates; e.g., $Me_2C{=}C(CN)OC({=}O)Cl$ in 67% yield and $Me_2C{=}C[P(O)(OMe)_2]OC({=}O)Cl$ in 83% yield. Carbonates and urethans from these chloroformates are of interest as monomers, pesticides, and chemical intermediates.

Since Reformatsky first treated α-bromo esters with zinc in 1887,[2] the ester zinc enolates **1** thus generated have become widely useful in synthetic chemistry. Part of the value of these ambident anions may be attributed to their exclusive reactivity at carbon. Whether the added electrophile is an aldehyde or a ketone (the Reformatsky reaction), an acid chloride or an anhydride, carbon dioxide, or an alkylating agent, no O-product is obtained.[2] Even reagents with strong affinities for oxygen such as TMS-Cl afford only C-silylated products.[3] The chemistry is the same whether the α-carbon substituents of **1** are H, alkyl, aryl, or halogen. For example, the products from reaction of trichloroethyl acetate with zinc and (a) aldehydes or ketones, (b) acetic anhydride, or (c) active alkylating agents all have structure **2** (A = B = Cl).[2]



$$X{-}\overset{\displaystyle A}{\underset{\displaystyle B}{C}}{-}CO_2R \xrightarrow{Zn} {}^{-}\overset{\displaystyle A}{\underset{\displaystyle B}{C}}{-}CO_2R \;\; {}^{+}ZnX \xrightarrow[\text{phile [E]}]{\text{Electro-}} E{-}\overset{\displaystyle A}{\underset{\displaystyle B}{C}}{-}CO_2R$$

X = Cl, Br **1** **2**

Treatment of α-chloro or α-bromo ketones with zinc is widely used to reduce these reactants to the parent ketones.[4] Sometimes, however, the intermediate zinc enolates have been intercepted by other electrophiles, including active alkylating agents, aldehydes and ketones, acid halides and sulfenyl chlorides, and Michael acceptors.[4] Again in all of these processes, the electrophile is attached to the carbon originally bearing the halogen. The only apparent exception is the reaction with TMS-Cl, which yields O-silylated enol ethers.[5] Even this may not be real, since C-silylated ketones readily undergo Lewis acid catalyzed isomerization to their *O*-silyl tautomers.[6]

While a long bibliography on the zinc plus α-halo ester reaction can be compiled and the literature on the chemistry of α-halo ketones with zinc is substantial, references to the treatment of α-halo aldehydes with zinc are virtually nonexistent.[7] This would be anticipated, given the expected tar-forming side reactions involving the highly reactive aldehyde carbonyl as a nucleophile acceptor.

Recently we reported[8] a simple synthesis of the previously unknown 2,2-dihalovinyl chloroformates **4** and **5** by a zinc-induced Boord elimination from the readily available tetrahaloethyl precursors **3**.[9] The process is significant because of the expected pesticidal activity of derived 2,2-dihalovinyl carbonates and carbamates.[10,11] Also, Chevalier at SNPE has found that 2,2-dichlorovinyl carbonates are too hindered to self-polymerize but do give alternating 1:1 copolymers with vinyl acetate with an unusual head to head structure.[12]

[†] The Pennsylvania State University.

[‡] SNPE.

(1) Adapted and condensed from the Ph.D. Dissertation of M. P. Bowman, The Pennsylvania State University, University Park, PA 1986.

(2) Rathke, M. W. *Org. React.* **1975**, *22*, 423.

(3) Fessenden, R. J.; Fessenden, J. S. *J. Org. Chem.* **1967**, *32*, 3535.

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(5) Rubottom, G. M.; Mott, R. C.; Krueger, D. S. *Synth. Commun.* **1977**, *7*, 327.

(6) Even with the very weak Lewis acid ZnI_2, $Et_3SiCH_2C({=}O)CH_3$ rearranges to its *O*-silyl tautomer in 20 min at 40 °C in ether: Lutsenko, I. F.; Baukov, Y. I.; Dudukina, O. V.; Kramarova, E. N. *J. Organomet. Chem.* **1968**, *11*, 35.

(7) Shchepin, V. V.; Lapkin, I. I. *Zh. Org. Khim.* **1981**, *17*, 1580. Although the related zinc reaction failed, these workers obtained $Cl_2C{=}CHOCO_2Me$ in 31% yield from chloral, $ClCO_2Me$, and magnesium.

(8) Bowman, M. P.; Olofson, R. A.; Senet, J.-P.; Malfroot, T. *J. Org. Chem.* **1990**, *55*, 2240.

(9) Treatment of chloral with phosgene in the presence of a reusable "naked Cl^-" catalyst ($PhCH_2N^+Bu_3Cl^-$) gives **3**.[8] Cagnon, G.; Piteau, M.; Senet, J.-P.; Olofson, R. A.; Martz, J. T.; Eur. Pat. 40153, 1981; *Chem. Abstr.* **1982**, *96*, 142281y; U.S. 4,592,874, 1986.

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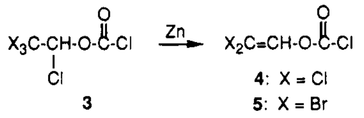
(12) To be published [$-CH(OCO_2R)CCl_2CH_2CH(OAc)CH(OCO_2R)CCl_2-$, etc.]. We thank S. Chevalier and co-workers at SNPE for permission to quote this result.

0022-3263/90/1955-5982$02.50/0



$X_3C\text{-}CH(Cl)\text{-}O\text{-}C(=O)\text{-}Cl \xrightarrow{Zn} X_2C{=}CH\text{-}O\text{-}C(=O)\text{-}Cl$

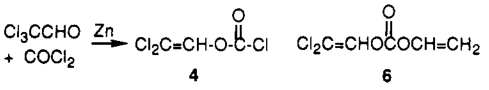
3

4: X = Cl

5: X = Br

This clean conversion, 3 → 4, was surprising since loss of the chloroformate anion could have been competitive with loss of chloride (when Favorskii treated 2,2,2-trichloroethyl acetate with zinc in 1899, he made 1,1-dichloroethylene in a very exothermic process[13]). Chloroformate also could have been lost in a subsequent elimination[14] to give the explosive chloroacetylene. Finally, the high reactivity of acid chlorides toward zinc and the $ZnCl_2$-catalyzed decomposition of chloroformates[15] presented other potential problems.

In this paper, we describe the even more surprising formation of 2,2-dichlorovinyl chloroformate (4) by direct treatment of a mixture of chloral and phosgene with zinc dust. Most of the factors favoring a negative outcome for the scheme 3 → 4 also apply to this new process. Also, under some conditions, zinc reacts exothermically with phosgene. In addition, complications from the powerful acceptor properties of the aldehyde carbonyl and the preference for reaction at carbon in Reformatsky type processes would be expected. Nevertheless, the desired reaction occurred.



$Cl_3CCHO + COCl_2 \xrightarrow{Zn} Cl_2C{=}CH\text{-}O\text{-}C(=O)\text{-}Cl \qquad Cl_2C{=}CHOC(=O)OCH{=}CH_2$

4

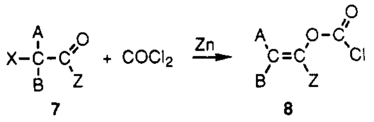
6

In the preferred process, a little zinc dust was added to a stirred solution of chloral and phosgene in MeOAc/ether. No more zinc was added until this was consumed, and initiation of the reaction was certain (usually 5–30 min but sometimes 1–2 h). Then the remaining zinc was added in portions, being sure that most was consumed before more was added. Otherwise the reaction could end in an uncontrollable exotherm. After removal of much of the solvent by vacuum evaporation, the remaining liquid was triturated with pentane to eliminate the insoluble zinc salts. Vacuum distillation then gave pure 4 in 50% yield.

Less satisfactory was a workup in which volatiles first were collected by vacuum distillation with 1,2,4-trichlorobenzene as a chaser. Then 4 was isolated by redistillation in 51% yield. The yield was 44% in EtOAc, 42% in EtOAc/ether (2:1), 19% in ether, 26% in dioxane, and 10% in diethyl oxalate. With magnesium instead of zinc, reaction was rapid (after 40 min, 16% of the chloral remained) but the yield was only 6%.

The reaction of bromal and phosgene with zinc was very slow, and 5 could not be separated from remaining bromal by simple distillation. The distilled product after a 7-day reaction still contained bromal and 5 in a 57:43 wt % ratio (26% yield of 5). A few reactions of 5 can be performed in the presence of bromal. In an attempt to extend the synthesis of 4 to include dihalovinyl carbonates, vinyl chloroformate was substituted for phosgene. Then 6 was isolated, but only in 6% yield (see the supplementary material).

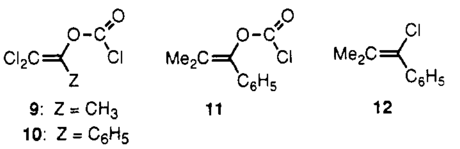
Efforts also were made to generalize the synthesis by replacing the chloral by other α-halo carbonyl compounds 7. Some of these reactions were successful. However, many were not, and several experiments were performed before a predictively useful pattern was recognized. When Z in 7 is hydrogen, alkyl, or aryl, the chloroformate 8 is obtained only when A and B are halogen or alkyl but not hydrogen.



7

8

While bromoacetone, chloroacetone, and 1,1-dichloroacetone all reacted with zinc and phosgene, no chloroformate 8 was found. However, 1,1,1-trichloroacetone[16] afforded pure chloroformate 9 in 23% yield. Similarly α-bromo and α,α-dichloroacetophenone reacted without yielding 8, but trichloroacetophenone[17] was converted to the styryl chloroformate 10 in 66% distilled yield. Reaction of α-chloroisobutyrophenone[18] in EtOAc gave 54% of the desired chloroformate 11 along with 34% of the chlorostyrene 12. This process was difficult to reproduce and usually gave low yields of 11 along with more 12 (from $ZnCl_2$-catalyzed decomposition of 11). The reaction failed using 2-chlorocyclohexanone but 2-chloro-2-methylcyclohexanone[19] gave 13 in 68% distilled yield.

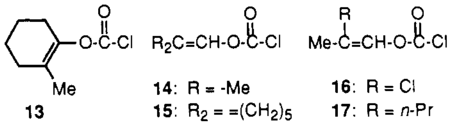


9: Z = CH_3

10: Z = C_6H_5

11

12



13

14: R = -Me

15: R_2 = $=(CH_2)_5$

16: R = Cl

17: R = n-Pr

In other successful reactions, α-chloroisobutyraldehyde[20] and 1-chlorocyclohexanecarboxaldehyde[21] were converted to the chloroformates, 14 (19%) and 15 (59%). The low yield of 14 is partly attributed to its volatility. Similarly, 16 (56% yield, *E*:*Z* = 1:1.1) and 17 (27% yield, *E*:*Z* = 1.5:1) were obtained from the corresponding α-chloroaldehydes.[22] In the only experiment which did not fit the pattern established for A, B, and Z in 7, no enol chloroformate was obtained from 1-chloro-1,1-difluoro-2-butanone, although the zinc was consumed. The reason for this failure is not known, but further reaction is suspected.

So far, this outline of the scope of the scheme 7 → 8 has been confined to systems 7 in which Z is H, alkyl, or aryl. Examples with other Z residues include 2,2-dichloro-1,3-cyclohexanedione,[23] which was converted to the chloroformate 18 in 30% distilled yield. Thus, the reaction seems to tolerate electron-withdrawing functions as Z. Interestingly, 18 is unstable at room temperature. Over 2 days it cleanly decomposed to the previously unknown di-

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[13] Favorskii, A. *Chem. Zentrablatt* **1899**, 778. For nucleofugacity of $ClCO_2^-$, see: Wong, C.-P.; Jackman, L. M.; Portman, R. G. *Tetrahedron Lett.* **1974**, 921.

[14] See, e.g.: Ballester, M.; Castaner, J.; Riera, J.; Tabernaero, I. *J. Org. Chem.* **1986**, *51*, 1413.

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[16] Villieras, J.; Castro, B. *Bull. Soc. Chim. Fr.* **1970**, 1189.

[17] Hiegel, G. A.; Peyton, K. B. *Synth. Commun.* **1985**, *15*, 385.

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[19] Warnhoff, E. W.; Martin, D. G.; Johnson, W. S. *Organic Syntheses*; Wiley: New York, 1963; Collec. Vol. IV, p 162.

[20] Stevens, C. L.; Gillis, B. T. *J. Am. Chem. Soc.* **1957**, *79*, 3448.

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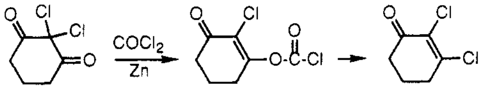
[22] DeBuyck, L.; Verhe, R.; DeKimpe, N.; Courtheyn, D.; Schamp, N. *Bull. Soc. Chim. Belg.* **1980**, *89*, 442. 2-Chloro-2-methylpentanal is new.

[23] Wanzlick, H.-W.; Mohrmann, S. *Chem. Ber.* **1963**, *96*, 2257.

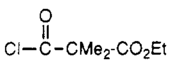
chlorocyclohexenone **19**, probably by Michael addition of Cl^- to **18** followed by Michael elimination to release CO_2 and regenerate Cl^-.



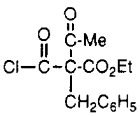
18 **19**

The course of the reaction when Z is not only electron withdrawing but also a leaving group (as Z^-) is more complex. When bromoacetyl fluoride or trichloroacetyl fluoride[24] was reacted with zinc and phosgene, no chloroformates were detected (IR). However, the acyl fluorides and zinc were consumed, yielding unidentified products. This was not unexpected since reaction of acid chlorides with zinc is a preferred route to ketenes.[25]

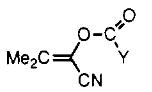
Attack at carbon in the reaction of ethyl trichloroacetate with zinc in the presence of a variety of electrophiles already has been documented.[4] However, there is no published example of the reaction of an α-halo ester with zinc in the presence of phosgene. Such experiments were performed as part of this investigation. With ethyl α-bromoisobutyrate, the acid chloride **20**[26] was obtained in 56% yield. The result was similar with the more complex ethyl 2-chloro-2-benzylacetoacetate, which gave **21** in 54% yield. Thus, the known regiospecificity of ester zinc enolates toward attack by electrophiles at carbon can be extended to include phosgene as the electrophile.


$Cl{-}C(O){-}CMe_2{-}CO_2Et$

20


$Cl{-}C(O){-}C(C(O){-}Me)(CH_2C_6H_5){-}CO_2Et$

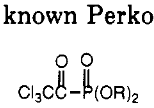
21



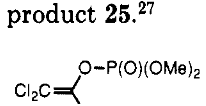
22: Y = -Cl
23: Y = $-N(CH_2CH_2)_2O$

Two other permutations of Z were tested with interesting results. If leaving group ability is used to characterize Z, both moieties would rank between fluoride and alkoxide. In the first study, reaction of 2-bromoisobutyryl cyanide with zinc and phosgene afforded the chloroformate **22** in 67% distilled yield. Derivatives of **22** can be made directly without isolating the chloroformate. The carbamate **23** was obtained in 72% overall yield by treatment of the reaction mixture with morpholine.

In the second study, the reactants were acyl phosphonates. The trichloroacetyl phosphonates **24** (R = Me or Et) could not be made by a standard Arbuzov process. Reaction of trichloroacetyl chloride with $(MeO)_3P$ gave only the known Perkow product **25**.[27]

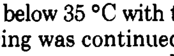

$Cl_3C{-}C(O){-}P(O)(OR)_2$

24

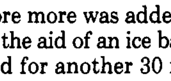


25

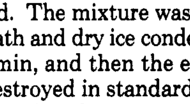
However, 2-bromoisobutyryl bromide was converted to the acyl phosphonates **26** (91% yield) and **27** (75%) when reacted with $P(OR)_3$. Subsequent treatment with zinc and phosgene gave the chloroformates **28** and **29**. The standard ways to remove zinc salts from high-boiling chloroformates are filtration through silica or triturative extraction into pentane. However, both **28** and **29** were rapidly decomposed by silica and insoluble in pentane. Thus, although **28** and **29** were characterized, they could not be distilled and some zinc salts remained. Yields were determined by ^1H NMR spectroscopy: 83% for **28** and 74% for **29**. Carbamates **30** and **31** were made by adding dioctylamine or morpholine to a reaction mixture containing **29**.


$BrMe_2C{-}C(O){-}P(O)(OR)_2$

26: R = Me
27: R = Et



28: R = Me
29: R = Et



30: R = Octyl
31: $R_2 = (CH_2CH_2)_2O$

The value of being able to include cyano and phosphonato among allowed Z substituents in **7** in this synthesis of enol chloroformates **8** is easily seen. One need only peruse a list of important pesticides in agricultural chemistry noting the prevalence of both functionalities.[10] Uses of carbonates and urethans from such chloroformates in preparative chemistry also can be foreseen. Note that Michael addition of a nucleophile to **30** (**31**) would yield directly a Wittig–Horner type reagent. Our collaborators at SNPE are now actively engaged in the conversion of **8** into candidates for biological screening. Investigations of the uses of **8** in synthetic chemistry also have begun.

Experimental Section[28]

Before using phosgene, it is *imperative* to first learn all safety procedures involved in handling this toxic gas. The efficient hood used for all experiments should contain phosgene indicator strips[29] and an open solution of concentrated NH_4OH, an indicator which smokes in the presence of $COCl_2$ or HCl and can be used to neutralize a trace spill. Excess phosgene was removed through a series of five bubble traps (empty, H_2SO_4, empty, aqueous NaOH, NH_4OH, to hood exhaust) with the aid of an aspirator before workup.

2,2-Dichlorovinyl Chloroformate (4). A small portion of zinc dust (ca. 1 g) was added to a stirred mixture of phosgene (18 mL, 0.25 mol) and chloral (23.0 g, 0.16 mol) (distilled) in 100 mL of 2:1 MeOAc/ether. Once the first portion of zinc dust had been consumed (initiation period varied from min to h), the remainder of the zinc (13.5 g, 0.21 mol) was added through a Teflon screw powder funnel over 40 min with care taken that each portion was mostly consumed before more was added. The mixture was kept at or below 35 °C with the aid of an ice bath and dry ice condenser. Stirring was continued for another 30 min, and then the excess phosgene was removed by aspiration (destroyed in standard trap system). Most of the solvent was removed under vacuum, and the product was extracted from the viscous oil by trituration with pentane (6 × 25 mL). The solution was concentrated and distilled to isolate pure **4**: bp 54–56 °C at 30 mm (lit.[8] bp 82–85 °C at 120 mm); 13.6 g (50% yield); IR (CCl_4) 1785 cm^{-1} (s); ^1H NMR ($CDCl_3$) δ 7.50 (s).

As with many heterogeneous reactions using zinc dust, the process was sometimes difficult to initiate. Addition of traces of iodine or $TiCl_4$ to the reaction medium had no obvious effect on initiation time while increasing side reactions.

In another study, zinc dust (8.0 g, 0.12 mol) was reacted as above with phosgene (10 mL, 0.14 mol) and dry chloral (13.8 g, 0.094 mol) in 45 mL of 2:1 MeOAc/ether. After another 2 h, excess phosgene was removed by aspiration, and the brown mixture was filtered through a fritted glass funnel (pore size 25–50 μm), yielding a gray white precipitate (zinc and salts) and a dark orange filtrate which was vacuum distilled (1.5 mm) at room temperature into a −78 °C trap. To obtain the last of the product from the still residue (a brown solid, mostly $ZnCl_2$), nitrobenzene (3 mL, distilled from P_2O_5) was added and the room temperature distillation

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[24] Kitano, H.; Fukui, K. *J. Chem. Soc. Jpn. Ind. Chem. Sect.* **1955**, *58*, 453. Made by general process of: Mashentsev, A. I. *J. Gen. Chem. (USSR)* **1946**, *16*, 203.

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[29] Hakashi, M. *J. Soc. Org. Synth. Chem. Jpn.* **1956**, *12*, 273. Liddell, H. F. *Analyst* **1957**, *82*, 375.

process was continued. Subsequent fractional distillation of the total volatile liquid afforded **4**: bp 37–40 °C (15 mm); 8.4 g (51% yield, >98% pure, NMR).

In another experiment, zinc dust (ca. 1 g, 30 mesh) was added to a stirred solution of phosgene (96 mL, 1.3 mol) and chloral (151 g, 1.0 mol) in EtOAc (250 mL) followed over 2 days by the rest of the zinc (70 g, 1.1 mol). Excess phosgene was removed. Next, 100 mL of 1,2,4-trichlorobenzene was added, and volatiles were distilled (1 mm) into a -78 °C trap. A second distillation afforded **4**: bp 80–81 °C at 90 mm, 78.3 g (44% yield). Initiation of the reaction with magnesium decreased the yield of **4** to 30%.

2,2-Dibromovinyl Chloroformate (5). Activated zinc dust[30] (10 g, 0.15 mol, 0.5 equiv) was added in small portions over 5 days via a powder dropping funnel to a stirred solution of bromal (80.2 g, 0.29 mol) in 75 mL of 2:1 EtOAc/ether and phosgene (38 mL, 0.5 mol). After 7 days with some zinc dust remaining, the excess phosgene was removed by aspiration and the mixture was filtered. Most of the zinc salts were precipitated and filtered off by adding 50 mL of hexane and 30 mL of dioxane to the solution. The hexane/dioxane precipitation was repeated twice more. The filtrate was distilled to remove solvents and collect higher boiling fractions at reduced pressure. These higher boiling fractions were combined and fractionally distilled to obtain **5**: bp 104–109 °C at 72 mm; 45.8 g (the product contained 57 wt % bromal by ^1H NMR analysis; corrected yield 26%, 38% yield based on consumed bromal). The spectra of **5** purified by preparative VPC are in accord with the reported data:[8] IR (CCl_4) 3090 (w), 1780 cm^{-1} (s); ^1H NMR ($CDCl_3$) δ 7.75 (s). Unless the zinc salts are completely removed, **5** begins to decompose within 1 h at 20 °C.

2-Chloro-2-methylpentanal. SO_2Cl_2 was reacted with 2-methylpentanal in CCl_4: bp 48–50 °C at 26 mm; 58% yield; IR (CCl_4) 1735 cm^{-1} (s); ^1H NMR ($CDCl_3$) δ 9.60 (s, 1 H), 2.1–0.8 (m, with spike at 1.60 (Me), 10 H).

1-Methyl-2,2-dichlorovinyl Chloroformate (9). Phosgene (5 mL, 0.070 mol, 3.0 equiv) and then 1,1,1-trichloroacetone[16] (3.69 g, 0.023 mol) were added to a stirred, ice bath cooled mixture of zinc dust (3.50 g, 0.054 mol) in EtOAc (50 mL). After 4 h, the solvent was removed under vacuum, and **9** was extracted from the viscous oil by trituration with pentane (4 × 20 mL). The extract was concentrated and distilled: bp 56–58 °C at 17 mm; 1.0 g (23% yield, 98% pure by VPC); IR (CCl_4) 1780 cm^{-1} (s); ^1H NMR ($CDCl_3$) δ 2.17 (s); ^{13}C NMR ($CDCl_3$) (^1H coupled) 147.3 (s, C=O), 143.4 (q, J = 7.8 Hz, =CO), 116.5 (q, J = 6.1 Hz, CCl_2), 16.5 ppm (q, J = 131.1 Hz, Me).

1-Phenyl-2,2-dichlorovinyl Chloroformate (10). Phosgene (6.0 mL, 0.084 mol) was added to cooled stirred zinc dust (4.34 g, 0.066 mol) in MeOAc (90 mL). Then α,α,α-trichloroacetophenone[25] (9.80 g, 0.044 mol) was added (2 min) with immediate reaction. After 2 h, workup as above gave **10**: bp 86–88 °C at 0.4 mm; 7.3 g (66% yield, 99% pure, VPC); IR (CCl_4) 1795 (s) 1680 cm^{-1} (w); ^1H NMR ($CDCl_3$) δ 7.7–7.3 (m); ^{13}C NMR ($CDCl_3$) 147.5 (C=O), 145.0 (Ar quat C), 130.3, 128.4, 128.3 (Ar CH's), 129.8 (=CO), 118.4 ppm (CCl_2).

1-Phenyl-2-methyl-1-propenyl Chloroformate (11). Zinc dust (3 g, 0.05 mol) was added over 3 h to α-chloroisobutyrophenone[18] (4.23 g, 0.023 mol) and phosgene (6.5 g, 0.07 mol) in EtOAc (20 mL). The mixture was stirred overnight, and excess phosgene was removed. The mixture then was filtered through silica with 300 mL of CH_2Cl_2 and fractionally distilled: bp 54–74 °C at 0.5 mm; 4.47 g (2.6 g of **11**, corrected for 1.3 g of 1-chloro-2-methyl-1-phenyl-1-propene (**12**) and 0.5 g isobutyrophenone; yield 54%). Some **11** was purified by VPC for spectroscopic analysis: IR ($CDCl_3$) 1780 cm^{-1} (s); ^1H NMR ($CDCl_3$) δ 7.32 (s, 5 H), 1.83 (s, 3 H), 1.78 (s, 3 H); ^{13}C NMR ($CDCl_3$) (^1H coupled) 149.0 (s, C=O), 143.4 (m), 133.4 (m, =CHPh), 128.9 (m), 128.6 (m), 128.3 (m), 123.6 (m, Me_2C=), 19.6 and 18.2 ppm (Me).

2-Methyl-1-cyclohexenyl Chloroformate (13). Phosgene (6.5 mL, 0.09 mol) and then 2-chloro-2-methylcyclohexanone[19] (11.0 g, 0.075 mol) were added to a stirred, ice bath cooled mixture of zinc dust (7.1 g, 0.11 mol) in EtOAc (50 mL). After 2 h, the mixture was worked up as above: bp 80–82 °C at 8 mm; 8.9 g (68% yield, 99% pure by VPC); IR (CCl_4) 1780 cm^{-1} (s); ^1H NMR ($CDCl_3$) δ 2.4–1.9 (m, 7 H), 1.8–1.4 (m, 4 H): ^{13}C NMR ($CDCl_3$) 148.5 (C=O), 144.4 (=CO), 122.2 (=C), 30.0, 26.3, 23.0 and 22.1 (CH_2), 15.9 ppm (Me).

2-Methyl-1-propenyl Chloroformate (14). A mixture of zinc dust (3.99 g, 0.06 mol), α-chloroisobutyraldehyde[20] (5.41 g, 0.05 mol), and phosgene (5.5 mL, 0.08 mol) in 30 mL of MeOAc was stirred overnight. After removal of excess phosgene, the mixture was concentrated, and **14** was extracted by trituration with pentane. The concentrated extract was distilled: bp 119–121 °C; 1.3 g (19% yield); IR (CCl_4) 3085 (w), 1780 cm^{-1} (s); ^1H NMR ($CDCl_3$) δ 7.9–7.6 (m, 1 H), 1.8–1.5 (m, 6 H); ^{13}C NMR ($CDCl_3$) (^1H coupled) 148.2 (d, J = 1.2 Hz, C=O), 131.7 (d of m, J = 198 Hz, =CHO), 121.7 (m, Me_2C=), 19.0 and 15.4 ppm (Me).

(Cyclohexan-1-ylidenemethoxy)carbonyl Chloride (15). 1-Chlorocyclohexanecarboxaldehyde[21] (7.0 g, 0.048 mol) in 15 mL of EtOAc was added in two parts over 2 h to stirred phosgene (5.5 mL, 0.077 mol) and zinc dust (4.13 g) in EtOAc (35 mL). Next another 1.0 g of zinc (total 0.08 mol) was added, and after 3 h the mixture was diluted with 30 mL of pentane/dioxane (2:1) and filtered, and the filtrate was concentrated in vacuo. Dry pentane (20 mL) was added to the residue, which was filtered, and the filtrate was distilled: bp 48–50 °C at 0.7 mm; 5.0 g (59% yield); IR (CCl_4) 1775 (s), 1680 cm^{-1} (w); ^1H NMR ($CDCl_3$) δ 6.70 (br s, 1 H), 2.5–1.3 (m, 10 H); ^{13}C NMR ($CDCl_3$) (^1H coupled) 148.3 (d, J = 1.6 Hz, C=O), 129.0 (dm, J = 197.8 Hz, =CH), 128.8 (m, =C), 30.0, 27.6, 26.5, 26.1, 25.9 ppm (CH_2).

2-Chloro-1-propenyl Chloroformate (16). Zinc dust (6 g, 0.09 mol) was added over 2.5 h to 2,2-dichloropropanal[22] (10.7 g, 0.084 mol) and phosgene (10 mL, 0.14 mol) in MeOAc (50 mL), which then was stirred for another 20 min. The mixture was filtered under pressure through silica with CH_2Cl_2 and distilled: bp 68–71 °C at 52 mm; 7.2 g (56% yield) (*E*:*Z* 1:1.1 from ^{13}C NMR); IR (CCl_4) 3070 (w), 1780 cm^{-1} (s); ^1H NMR ($CDCl_3$) δ 7.2–7.0 (m, 1 H), 2.10 (d, ca. 1.5 H, J = 3 Hz), 2.05 (d, ca. 1.5 H, J = 3 Hz); ^{13}C NMR ($CDCl_3$) (^1H coupled) *E* isomer 147.9 (d, J = 2.4 Hz, C=O), 131.8 (dq, J = 198.9, 6.7 Hz, =CH), 120.1 (m), 18.4 (qd, J = 130.6, 4.7 Hz); *Z* isomer 147.5 (d, J = 2.0 Hz, C=O), 133.8 (dq, J = 203.3, 4.4 Hz, =CH), 123.9 (m), 20.6 ppm (qd, J = 130.5, 2.6 Hz).

2-Methyl-1-pentenyl Chloroformate (17). 2-Chloro-2-methylpentanal (9.16 g, 0.068 mol) was added in three parts over 2 h to a stirred mixture of phosgene (7.0 mL, 0.098 mol, 1.4 equiv), zinc dust (4.49 g, 0.069 mol), and EtOAc (70 mL). The mixture was stirred for 3 h and aspirated, and then 70 mL of pentane/dioxane (2:1) was added. Solids were filtered off, the filtrate was concentrated in vacuo and then rapidly distilled at 4 mm. Fractional redistillation afforded **17**: bp 67–68 °C at 15 mm; 3.0 g (27% yield, *E*:*Z* ratio ca. 1.5:1, ^{13}C NMR); IR (CCl_4) 3090 (w), 1780 (s), 1680 cm^{-1} (m); ^1H NMR ($CDCl_3$) δ 6.9–6.7 (m, 1 H), 2.3–0.7 (m, 10 H); ^{13}C NMR ($CDCl_3$) *E* isomer 148.5 (C=O), 132.3 (=CO), 125.4 (=C), 35.5 and 20.4 (CH_2), 13.5 and 13.5 ppm (Me); *Z* isomer 148.5 (C=O), 132.0 (=CO), 125.6 (=C), 31.3 and 20.1 (CH_2), 17.0 (CH_3C=), 13.6 ppm (Me).

3-[(Chlorocarbonyl)oxy]-2-chloro-2-cyclohexen-1-one (18). 2,2-Dichloro-1,3-cyclohexanedione[23] (6.64 g, 0.037 mol) in 15 mL of EtOAc was added to a stirred mixture of phosgene (3.0 mL, 0.042 mol), zinc dust (3.01 g, 0.046 mol), and EtOAc (40 mL) in three parts over 1 h. After 2 h, excess phosgene was removed in vacuo, 40 mL of pentane–dioxane (2:1) was added, the mixture was filtered, and the filtrate was concentrated in vacuo. **18** was extracted from the residue by trituration with pentane (4 × 20 mL) and isolated by distillation: bp 108–110 °C at 0.8 mm; 2.3 g (30% yield); IR (CCl_4) 1790 (s), 1705 (s), 1630 cm^{-1} (m); ^1H NMR ($CDCl_3$) δ 2.9–2.5 (m, 4 H), 2.4–1.8 (m, 2 H).

2,3-Dichloro-2-cyclohexen-1-one (19). When **18** was kept in a vial for 2 days at room temperature, it cleanly decomposed to the white solid **19**: recrystallized from hot EtOH; mp 64.5–65.5 °C; IR (CCl_4) 1700 (s), 1590 cm^{-1} (s); ^1H NMR ($CDCl_3$) δ 3.1–2.5 (m, 4 H), 2.12 (like q, 2 H, J = 6 Hz).

Ethyl 2,2-Dimethylmalonyl Chloride (20). Ethyl 2-bromo-2-methylpropanoate (4.32 g, 0.022 mol) was stirred overnight with zinc dust (1.76 g, 0.027 mol) and phosgene (3.5 mL, 0.049 mol) in MeOAc (25 mL). The solvent was removed in vacuo, and **20** was triturated into pentane. The triturate was distilled under aspirator vacuum (ca. 20 mm); bp 77–82 °C (lit.[26] bp 74–78 °C at 19 mm), 2.2 g (56% crude yield, 90% pure, VPC, no reactant left).

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Ethyl 2-Acetyl-2-benzylmalonyl Chloride (21). Phosgene (1.4 g, 0.014 mol) was added to a stirred mixture of ethyl 2-benzyl-2-chloroacetoacetate[31] (2.87 g, 0.011 mol) and zinc dust (0.75 g, 0.011 mol) in EtOAc (25 mL). After 3 h, the mixture was concentrated in vacuo. Next 20 mL of pentane/dioxane (2:1) was added, and the mixture was filtered and concentrated in vacuo overnight: 1.7 g (54% crude yield, ^{13}C NMR analysis shows only C-acylated **21** with no O-acylation); IR (CCl_4) 1795 (s), 1750 (s), 1715 cm^{-1} (s); ^{1}H NMR ($CDCl_3$) δ 7.22 (s, 5 H), 4.25 (q, 2 H, J = 7 Hz), 3.60 (s, 2 H), 2.25 (s, 3 H), 1.27 (t, 3 H, J = 7 Hz).

1-Cyano-2-methyl-1-propenyl Chloroformate (22). Zinc dust (2.3 g, 0.03 mol) was added over 4 h to stirred phosgene (3.5 mL, 0.05 mol) and 2-bromo-2-methylpropanoyl cyanide[32] (4.11 g, 0.023 mol) in EtOAc (25 mL). After another 30 min, the mixture was filtered through silica with 200 mL of CH_2Cl_2, concentrated, and distilled: bp 80–83 °C at 10 mm; 2.5 g (67% yield); IR (CCl_4) 2180 (m), 1780 cm^{-1} (s); ^{1}H NMR ($CDCl_3$) δ 2.09 (s, 3 H), 1.90 (s, 3 H); ^{13}C NMR ($CDCl_3$) (^{1}H coupled) 148.4 (s, C=O), 146.5 (quintet, J = 6.6 Hz, =C), 118.5 (m, =CO), 111.7 (s, CN), 23.0 and 17.9 ppm (Me).

***N*-[[(2-Methyl-1-cyano-1-propenyl)oxy]carbonyl]morpholine (23).** After reaction of phosgene (0.09 mol), zinc dust (0.067 mol), and 2-bromo-2-methylpropanoyl cyanide (0.050 mol) as above, the phosgene was removed, and CH_2Cl_2 (30 mL) and morpholine (9.69 g, 0.11 mol) were added (10 min) to the cooled (0 °C) mixture. After 2 days at room temperature, the mixture was filtered, concentrated, diluted with CH_2Cl_2, washed with water and 10% HCl, dried (Na_2SO_4), concentrated, and distilled: bp 128–130 °C at 0.3 mm; 7.5 g (72% yield); IR (CCl_4) 2175 (m), 1740 cm^{-1} (s); ^{1}H NMR ($CDCl_3$) δ 3.8–3.4 (m, 8 H), 2.05 (s, 3 H), 1.81 (s, 3 H).

Dimethyl (2-Bromo-2-methylpropanoyl)phosphonate (26). $(MeO)_3P$ (41 mL, 0.35 mol) was added to stirred, ice bath cooled 2-bromoisobutyryl bromide (79.9 g, 0.35 mol) in CH_2Cl_2 (200 mL). The solution then was warmed to room temperature, stirred for 1 day, and fractionally distilled: bp 107–109 °C at 2 mm; 82.2 g (91% yield, VPC pure); IR (CCl_4) 1685 cm^{-1} (s); ^{1}H NMR ($CDCl_3$) δ 3.85 (dd, 6 H, J = 11, 3 Hz), 1.98 (s, 6 H).

Diethyl (2-Bromo-2-methylpropanoyl)phosphonate (27). By reaction as above with $(EtO)_3P$: bp 115–125 °C at 2 mm; 47.5 g (75% yield, 98% pure by VPC); IR (CCl_4) 1680 cm^{-1} (s); ^{1}H NMR ($CDCl_3$) δ 4.30 (quin, 4 H, J = 7 Hz), 2.00 (s, 6 H), 1.40 (t, 6 H, J = 7 Hz).

1-(Dimethoxyphosphonyl)-2-methyl-1-propenyl Chloroformate (28). Phosgene (2.5 mL, 0.35 mol) and then **26** (4.67 g, 0.018 mol) were added to stirred zinc dust (1.55 g, 0.024 mol) in EtOAc (25 mL). After 30 min, phosgene and solvent were removed, and 25 mL of 2:1 pentane/dioxane was added to precipitate zinc salts. The filtered mixture was concentrated (0.7 mm) for 2 h. The yield of **28** (^{1}H NMR, internal standard) was 83% (corrected for salts): IR (CCl_4) 1780 cm^{-1} (s); ^{1}H NMR ($CDCl_3$) δ 3.93 (d, 6 H, J = 12 Hz), 2.13 (d, 3 H, J = 3 Hz), 1.91 (d, 3 H, J = 3 Hz); ^{13}C NMR ($CDCl_3$) 150.4 (d, J_{PCC} = 19.5 Hz, $(Me)_2C$=, tentative assignment), 149.7 (s, C=O, tentative), 131.7 (d, J_{PC} = 250.6 Hz, =CP), 55.4 (d, J_{POC} = 6.2 Hz, OMe), 19.9 (d, J_{PCCC} = 7.6 Hz, Me), 19.8 ppm (s, Me).

1-(Diethoxyphosphonyl)-2-methyl-1-propenyl Chloroformate (29). **27** (4.21 g, 0.015 mol) was added to a stirred mixture of phosgene (2.0 mL, 0.03 mol), zinc dust (1.50 g, 0.023 mol), and MeOAc (25 mL). After 3 more h, workup as above gave **29** (74% yield, corrected for Zn salts); IR (CH_2Cl_2) 1780 (s), 1640 cm^{-1} (w); ^{1}H NMR ($CDCl_3$) δ 4.34 (quin, 4 H, J = 7 Hz), 2.13 (d, 3 H, J = 3 Hz), 1.89 (d, 3 H, J = 3 Hz), 1.40 (t, 6 H, J = 7 Hz); ^{13}C NMR ($CDCl_3$) 149.6 (d, J_{PCOC} = 1.1 Hz, C=O), 149.2 (d, J_{PCC} = 26.9 Hz, Me_2C=), 133.0 (d, J_{PC} = 250.2 Hz, =CO), 65.8 (d, J_{POC} = 6.3 Hz, OCH_2), 20.1, 19.9, 16.0 ppm (Me).

***N*-[[[2-Methyl-1-(diethoxyphosphonyl)-1-propenyl]oxy]carbonyl]dioctylamine (30).** After reaction of phosgene (1.2 mL, 0.017 mol), zinc dust (0.74 g, 0.011 mol), and **27** (2.13 g, 7.4 mmol) in EtOAc (25 mL) as above, volatiles were removed (1 mm). CH_2Cl_2 (10 mL) and dioctylamine (3.66 g, 0.015 mol) were added. The mixture was stirred 2 days, concentrated, diluted with 50 mL of pentane, washed with water (3 × 10 mL) and 10% HCl (4 × 15 mL), dried (Na_2SO_4), concentrated, filtered through silica with 100 mL of ether, and reconcentrated, and volatiles were removed in vacuo (0.7 mm) for 1 h, yielding **30** as a golden oil: 1.5 g (42% yield, one spot by TLC); IR (CCl_4) 1710 (s), 1640 cm^{-1} (w); ^{1}H NMR ($CDCl_3$) δ 4.11 (quintet, 4 H, J = 7 Hz), 3.5–3.0 (m, 4 H), 2.11 (d, 3 H, J = 3 Hz), 1.73 (d, 3 H, J = 3 Hz), 1.8–0.7 (m, 36 H); ^{13}C NMR ($CDCl_3$) 153.6 (s, C=O), 143.2 (d, J_{PCC} = 29.7 Hz, Me_2O=), 132.9 (d, J_{PC} = 230.3 Hz, =CO), 61.7 (d, J_{POC} = 5.0 Hz, OCH_2), 47.6, 47.3, 31.5, 29.0, 28.9, 28.5, 27.7, 26.7, 26.6, 26.4, 22.3, 19.4, 19.3, 19.2, 19.1, 19.1, 18.7, 16.0, 15.9, 13.7 ppm.

***N*-[[[2-Methyl-1-(diethoxyphosphonyl)-1-propenyl]oxy]carbonyl]morpholine (31).** After reaction of phosgene, zinc, and **27** in EtOAc, morpholine was added, the mixture filtered through silica (CH_2Cl_2), and 2:1 pentane/dioxane was added to the concentrated eluate. The filtered mixture was concentrated to 5.6 g of viscous oil, **31** with 1.4 g of noncombustable residue (combustion analysis), zinc salts: 53% corrected yield of **31**; IR (CH_2Cl_2) 1715 (s), 1645 cm^{-1} (w); ^{1}H NMR ($CDCl_3$) δ 4.27 (quin, 4 H, J = 8 Hz), 3.8–3.5 (m, 8 H), 2.06 (d, 3 H, J = 3 Hz), 1.80 (d, 3 H, J = 3 Hz), 1.36 (t, 3 H, J = 8 Hz); ^{13}C NMR ($CDCl_3$) 152.8 (s, C=O), 145.3 (d, J_{PCC} = 30.2 Hz, Me_2C=), 131.2 (d, J_{PC} = 242.1 Hz, =CO), 66.7, 66.1, 63.9 (d, J_{POC} = 5.7 Hz), 44.5, 43.9, 19.4 (m), 19.0 (d, J = 5.2 Hz), 15.7 ppm (d, J = 7.2 Hz, Me).

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Supplementary Material Available: Additional spectral-analytical (e.g., high-resolution MS and some ^{1}H NMR or ^{13}C NMR spectra) data and experimental detail on other experiments noted in the Discussion (24 pages). Ordering information is given on any current masthead page.

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