THE CHEMISTRY OF CHLOROFORMATES

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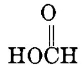
I. INTRODUCTION

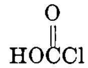
The chemistry of chloroformates has not been reviewed in depth previously, but has only received brief treatment in conjunction with reviews on phosgene. Dyson's review on phosgene which appeared in 1927 included four pages on the preparation and properties of chloroformates (193). A review on phosgene and its derivatives which appeared in 1938 by Criscuoli dealt with some of the lower alkyl and chloroalkyl chloroformates, particularly with their use as war gases (160). The chapter on carbonic acid derivatives by Petersen and Pieperbrink in Houben-Weyl devoted five pages to the preparation and properties of chloroformates (334).

Chloroformates have also been referred to in the literature as chlorocarbonates. The formulas shown below indicate the interrelationship.



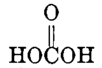
$\mathrm{HO\overset{O}{\overset{\|}{C}}H}$

formic acid



$\mathrm{HO\overset{O}{\overset{\|}{C}}Cl}$

chloroformic acid
chlorocarbonic acid



$\mathrm{HO\overset{O}{\overset{\|}{C}}OH}$

carbonic acid

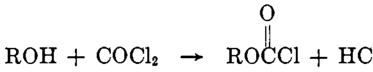
Throughout this review, the name of chloroformates has been used in order to be consistent with *Chemical Abstracts'* current practice of indexing these compounds under "formic acid, chloro-, esters of."

In view of the voluminous, published literature relating to chloroformates, the authors do not claim that this review contains every reference pertaining to this field. However, it can be stated that complete coverage through 1962 was our goal. In those instances where we have failed to attain this goal, it is our hope that we have included at least one example of the known uses and chemistry of chloroformates.

II. METHODS OF SYNTHESIS OF CHLOROFORMATES

A. ALIPHATIC CHLOROFORMATES

Phosgene reacts with aliphatic hydroxy compounds at room temperature or below to yield chloroformates in high yield (334). Low temperatures are preferred in many instances to minimize formation of dialkyl carbonates.



$$\mathrm{ROH + COCl_2 \rightarrow RO\overset{O}{\overset{\|}{C}}Cl + HCl\uparrow}$$

This synthesis can be carried out advantageously in the presence of a tertiary amine (51) as the hydrogen chloride acceptor, especially with tertiary alcohols. Removal of the hydrogen chloride in this way minimized deleterious acid-catalyzed side reactions in cases where acid-sensitive groups were present, and also increased the rate of reaction. As can be seen from Table I, chloroformates with the following additional functional groups have been synthesized: halogen (fluorine, chlorine, bromine), cyano, nitro, hydroxyl, amino, imino, amido, N-containing heterocycles, ether, ester

TABLE I

ALIPHATIC CHLOROFORMATES

1. Alkyl and Alicyclic Monochloroformates, ROCOCl

R	Method[a]	Yield, %	Reference
C_1			
Cl_3C			53, 160, 173, 267, 269, 306, 308, 327, 389, 391, 745
Cl_2CH			160, 173, 268, 269, 308, 327, 389, 391, 745
$ClCH_2$			41, 53, 160, 173, 267, 269, 306–309, 327, 389, 391, 745
CH_3			53, 98, 104, 140, 187, 189, 305, 307, 325, 388, 392, 409, 459, 521, 594, 602
C_2			
Cl_3CCCl_2			10, 140, 141, 489
Cl_2CHCCl_2	C		489
Cl_3CCHCl	D		50
Br_3CCH_2	A		101
$ClCH_2CCl_2$	C		498
$NCCH_2$	B		300
$CH_2{=}CH$	E		417
$ClCH_2CHCl$	C		489
$Cl(CH_2)_2$			154, 155, 172, 212, 360, 447, 453, 507, 519, 521, 626
CH_3CHCl	C		489
$F(CH_2)_2$	A	81	396, 532
$O_2N(CH_2)_2$	A		88
CH_3CH_2	B		43, 45, 46, 98, 104, 140, 183, 187, 289, 317, 404, 405, 464, 543, 594, 602, 659
C_3			
$CH{\equiv}CCH_2$	A	50	231
$CH_2{=}CClCH_2$			505
$ClCH{=}CHCH_2$	A	50	130
$(ClCH_2)(Cl_2CH)CH$	C	48	446
$CH_2{=}CHCH_2$			85, 227, 491, 493, 495, 500, 505, 630, 676
$CH_2{=}C(CH_3)$	D		451
$(ClCH_2)_2CH$	C	54	446, 536
$ClCH_2CHClCH_2$	A		536
$Cl(CH_2)_3$	A	>80	185, 557
$CH_3(CH_2)_2$			43, 287, 593, 594, 602
$(CH_3)_2CH$			287, 301, 325, 404, 405, 451, 460, 461, 491, 602, 647, 672, 676
$CH_3O(CH_2)_2$	A		199
C_4			
$ClCH_2C{\equiv}CCH_2$	A	70	330
$CH_2{=}C{=}CHCH_2$			105, 106
$OCOOCH_2CHCH_2$	A	90	658
$CH_2{=}CHCH(CH_2Cl)$	A	67	65
$CH_3CH{=}CHCH_2$	A		491, 495
$CH_2{=}C(CH_3)CH_2$	A		491, 493, 495, 505
$CH_2OCH_2CH_2CH$	A	93.3	544, 578
$Cl(CH_2)_4$	A		298
$CH_3CH_2CH(NO_2)CH_2$	A		66
$O_2NC(CH_3)_2CH_2$	A		66
$CH_3(CH_2)_3$			120, 351, 404, 405, 594
$(CH_3)_2CHCH_2$			287, 317, 404, 405, 594
$(CH_3)_3C$	B	20.4	57, 133
$CH_3CH_2CH(CH_3)$			6, 48, 367, 404, 405, 695
C_5			
$CH_2{=}CHCOO(CH_2)_2$	A		291
$CH_2{=}CHCH_2OCOCH_2$	A	60	341
$CH_2CH_2CH_2CH_2CH$	B	61	512
$OCH_2CH_2CH_2CHCH_2$	A	87	589
$CH_3CH(COOC_2H_5)$	A		248, 676
$Cl(CH_2)_5$	A		298
$Cl(CH_2)_2CH(C_2H_5)$			547
$ClCH_2C(CH_3)_2CH_2$			33
$CH_3(CH_2)_4$	A	80	6, 602
$CH_3(CH_2)_2CH(CH_3)$	B		43, 48
$(CH_3)_2CH(CH_2)_2$	B		404, 405, 456, 594
$C_2H_5C(CH_3)_2$	B		465
$(CH_3)_3CCH_2$	A	83	660
$(CH_3)_2CHCH(CH_3)$			48
$(C_2H_5)_2CH$			48
$H_2N(CH_2)_5$			344

TABLE I (*Continued*)

R	Method[a]	Yield, %	Reference
C_6			
$CH_2{=}C(CH_3)COO(CH_2)_2$	A		291
$\underline{CH_2CH_2CH_2CH_2CH_2CH}$	A	82	351, 404, 405, 594
$Cl(CH_2)_6$	A		298
$Cl(CH_2)_2CH(C_3H_7)$			547
$C_4H_9N{=}C(CH_3)$	A	95	299
$(CH_3)_2CHCH_2CH(CH_3)$	A	71	695
$CH_3CH_2CH(C_2H_5)CH_2$	A	56	695
$CH_3(CH_2)_3CH(CH_3)$			48
$(CH_3)_2CHCH(C_2H_5)$			48
$CH_3(CH_2)_2CH(C_2H_5)$			48
$(C_2H_5)_2N(CH_2)_2 \cdot HCl$	A	98	89
C_7			
C_6H_5CHCl	D		50
4-$(O_2N)C_6H_4CH_2$	A	95	107
$C_6H_5CH_2$	A	91	45, 46, 58, 80, 113, 223, 404, 405, 676
2-$(CH_3)C_6H_{10}$	B		404, 405
$C_2H_5CH(CH_3)CH(C_2H_5)$			49
$(n\text{-}C_3H_7)_2CH$			48
$CH_3(CH_2)_3CH(C_2H_5)$	A	33	695
$i\text{-}C_3H_7CH_2CH(C_2H_5)$			49
$(i\text{-}C_3H_7)_2CH$	A	34	669
C_8			
$CF_3(CF_2)_6CH_2$	B		520
$C_6H_5CH(CH_3)$	B		338
$Cl(CH_2)_8$	A		298
$CH_3(CH_2)_5CH(CH_3)$	B		335, 337, 339
$CH_3(CH_2)_7$	A	54	110, 404, 405, 602
C_9			
7-(β-Hydroxyethyl)theophylline	B		96
3,3,5-Trimethylcyclohexyl	A	81	695
$Cl(CH_2)_9$	A		298
$(i\text{-}C_4H_9)_2CH$	A	31	695
$(t\text{-}C_4H_9)_2CH$	B	93	379
$CH_3(CH_2)_8$	B	87	345
C_{10}			
$C_6H_5CH_2CONH(CH_2)_2$	A		55
$C_6H_5CH(i\text{-}C_3H_7)$	B		662, 663
l-Menthyl	B		404, 405
$Cl(CH_2)_{10}$	A		298
$CH_3(CH_2)_9$	A	87	508
C_{11}			
$CF_2Cl(CF_2)_9CH_2$	B		520
$CHF_2(CF_2)_9CH_2$	B	90	520
C_{12}			
Diacetone glucosyl	B	50–60	237
C_{13}			
$CHF_2(CF_2)_{11}CH_2$	B		520
$C_2H_5OCOC(CH_3)_2CH(C_6H_5)$	B		8
C_{15}			
$(C_6H_5)_2C(CH_2OH)CH_2$	B		56
C_n			
Complex unsaturated			492, 500, 501, 503
$Cl(CH_2)_n$			1
Various β-alkoxyethyl radicals	A	70–93	20
$-(CH_2CH_2O)_n(CH_2)_2(CH_2CH_2O)_n(CH_2)_2-$			127
2. Alkyl and Alicyclic Polychloroformates: $R(OCOCl)_n$			
C_2			
$-(CH_2)_2-$	B	>75	354, 373, 397, 398, 411, 529, 565, 648, 657
C_3			
$-(CH_2)_3-$	B	>75	354, 373, 397, 439, 529, 657
$-CH_2CH(CH_3)-$	A	65	657
C_4			
$-CH_2C{\equiv}CCH_2-$	B		275, 566
$-CH_2C(Cl){=}C(Cl)CH_2-$	C	96.5	275
$-CH_2CCl_2CCl_2CH_2-$	C	~95	275
$-(CH_2)_4-$	B	80	354, 397, 411, 565
$-CH_2CH(CH_3)CH_2-$	A		566
$-(CH_2)_2CH(CH_3)-$	A		566
$-(CH_2)_2O(CH_2)_2-$			297
$-(CH_2)_2S(CH_2)_2-$	A		380
C_5			
$-(CH_2)_5-$	B	75	354
$-CH_2C(CH_3)_2CH_2-$	A	90	246, 373, 439, 566

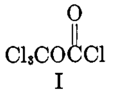
TABLE I (*Continued*)

R	Method[a]	Yield, %	Reference
C_6			
1,4-Cyclohexylene	A	~96	527, 566, 727
1,4-Cyclohexylene (*cis*)	B		354
1,4-Cyclohexylene (*trans*)	B	85	354
$-(CH_2)_2CHCH_2CH(CH_3)-$	A		411
$-CH_2C(CH_3)(C_2H_5)CH_2-$	B		439
$-(CH_2)_6-$	A	88	332, 354
$-CH_2CH(CH_3)OCH_2CH(CH_3)-$	A		494, 561
$-(CH_2)_2O(CH_2)_2O(CH_2)_2-$	A		494, 561
C_7			
$-(CH_2)_7-$	A	90	354
$-(CH_2)_2C(CH_3)_2(CH_2)_2-$	A		566
$-(CH_3)CHC(CH_3)_2CH(CH_3)-$	B		128
$-CH_2C(i\text{-}C_3H_7)(CH_3)CH_2-$	B		57, 439
$-CH_2C(C_2H_5)_2CH_2-$	B	75	439
$-CH_2C(CH_3)(n\text{-}C_3H_7)CH_2-$	B		57, 439
C_8			
1,1-Cyclohexylidene, dimethyl	A		373
1,4-Cyclohexylene, dimethyl			398
2,2,4,4-Tetramethyl-1,3-cyclobutylene	A		100
$-(CH_2)_8-$	A		354
C_9			
$-(CH_2)_9-$	A	80	354
$-CH_2C(n\text{-}C_3H_7)_2CH_2-$	B		439
$-CH_2C(C_2H_5)(n\text{-}C_4H_9)CH_2-$	B		439
C_{10}			
$-CH_2C(CH_3)(C_6H_5)CH_2-$	B		57, 439
$-(CH_2)_{10}-$	B	85	354, 468, 724
C_{11}			
$-CH_2C(C_2H_5)(C_6H_5)CH_2-$	B		439
C_{12}			
$1,4\text{-}[-(CH_2)_2OCO]_2C_6H_4-$	A		468
C_{14}			
$-(CH_2)_{14}-$	A		468
C_{15}			
$(CH_3)_2C(4\text{-}C_6H_{10})_2$			727
C_{18}			
$-(CH_2)_{18}-$	A		468
C_n			
$-(CH_2CH_2O)_n-$	A		468
$-[(CH_2)_4O]_n-$	A		468
$-(CH_2)_2[OCO(CH_2)_4COO(CH_2)_2]_n-$	A		468
$-(CH_2)_2[OCONH(1,3\text{-}C_6H_4)NHCOO(CH_2)_2]_n-$	A		468
Poly(ether–urethanes)	A		468, 654

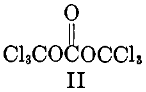
[a] A, alcohol and phosgene, no catalyst; B, alcohol and phosgene, added base; C, photolytic chlorination; D, **carbonyl** compound and phosgene; E, pyrolysis of dichloroformate.

(also cyclic carbonates), sulfide, and carbon-to-carbon unsaturation of various types. Chloroformates of partially protected sugar molecules have been prepared in 60% yield (237, 707). Conversion of the hydroxyl groups of cholesterol (393, 413, 711), deoxycholic acid (711), methyl and ethyl cholate (433, 711), and follicular hormones (180) to chloroformates has been reported. Bis- and polychloroformates have also been prepared.

Reaction of aliphatic hydroxy compounds with di- (I) and triphosgenes (II) yielded alkyl chloroformates (98, 140). This method has not been used extensively

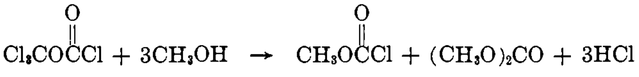

$Cl_3CO\overset{\overset{O}{\|}}{C}Cl$

I

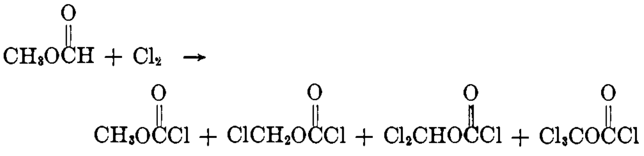

$Cl_3CO\overset{\overset{O}{\|}}{C}OCCl_3$

II

and possessed no advantage over direct reaction of the hydroxy compound with phosgene.


$$Cl_3CO\overset{\overset{O}{\|}}{C}Cl + 3CH_3OH \rightarrow CH_3O\overset{\overset{O}{\|}}{C}Cl + (CH_3O)_2CO + 3HCl$$

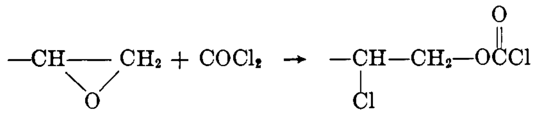
Formates have been chlorinated to yield chloroformates, but this synthesis is not very useful since all of the possible chlorinated chloroformates are usually produced in varying amounts (10, 53, 140, 141, 267, 269, 307, 389, 391, 745). In this reaction, methyl formate yielded a complex mixture of all the possible chlorinated chloroformates.


$$CH_3O\overset{\overset{O}{\|}}{C}H + Cl_2 \rightarrow CH_3O\overset{\overset{O}{\|}}{C}Cl + ClCH_2O\overset{\overset{O}{\|}}{C}Cl + Cl_2CHO\overset{\overset{O}{\|}}{C}Cl + Cl_3CO\overset{\overset{O}{\|}}{C}Cl$$

Alkyl chloroformates have been chlorinated to yield the same type of product mixture (10, 41, 53, 86, 140, 141, 173, 267, 269, 306, 308, 389, 391, 446, 489).

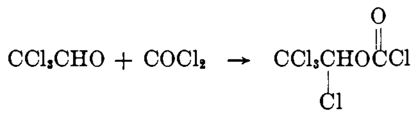
Chlorination of an acetylenic bis(chloroformate) has been effected without destruction of the dichloroformate groups (275).

β-Chlorochloroformates can be readily prepared in 50–100% yields from the reaction of epoxides with phosgene (360, 447).



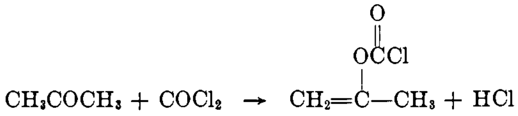
This reaction, though it proceeds uncatalyzed, is more efficient when catalyzed with either acids or bases.

α-Chlorochloroformates have been prepared in some cases by reaction of phosgene with carbonyl compounds, especially chloral (50).



$$\mathrm{CCl_3CHO + COCl_2 \rightarrow CCl_3\underset{\underset{Cl}{|}}{C}HO\overset{\overset{O}{\|}}{C}Cl}$$

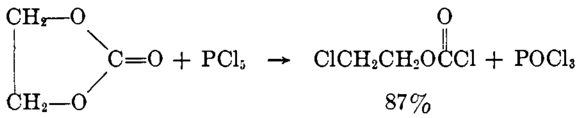
Where enolizable carbonyl groups are present, *e.g.*, acetone, unsaturated chloroformates were obtained (451).



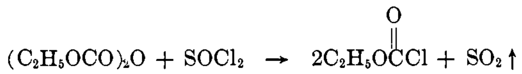
$$\mathrm{CH_3COCH_3 + COCl_2 \rightarrow CH_2{=}\overset{\overset{\overset{O}{\|}}{OCCl}}{\overset{|}{C}}{-}CH_3 + HCl}$$

The reaction of phosgene with carbonyl compounds has not been extensively investigated.

Alkyl chloroformates have been prepared by reaction of dialkyl and cyclic carbonates with phosphorus pentachloride (272, 594).

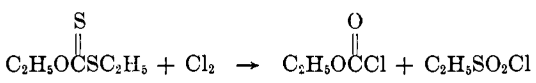


Reaction of diethyl pyrocarbonate with thionyl chloride has yielded ethyl chloroformate (543).

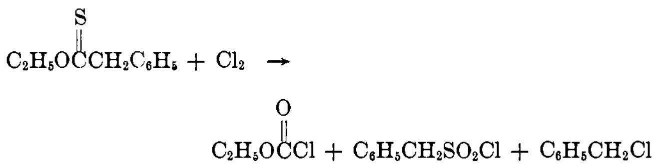


$$\mathrm{(C_2H_5OCO)_2O + SOCl_2 \rightarrow 2C_2H_5O\overset{\overset{O}{\|}}{C}Cl + SO_2\uparrow}$$

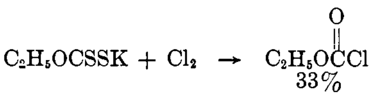
Chlorination of xanthates and thionoesters has yielded alkyl chloroformates (183).



$$\mathrm{C_2H_5O\overset{\overset{S}{\|}}{C}SC_2H_5 + Cl_2 \rightarrow C_2H_5O\overset{\overset{O}{\|}}{C}Cl + C_2H_5SO_2Cl}$$



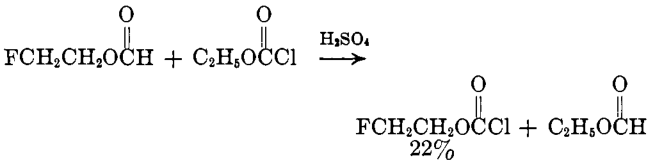
$$\mathrm{C_2H_5O\overset{\overset{S}{\|}}{C}CH_2C_6H_5 + Cl_2 \rightarrow C_2H_5O\overset{\overset{O}{\|}}{C}Cl + C_6H_5CH_2SO_2Cl + C_6H_5CH_2Cl}$$



$$\mathrm{C_2H_5OCSSK + Cl_2 \rightarrow \underset{33\%}{C_2H_5O\overset{\overset{O}{\|}}{C}Cl}}$$

Even though these routes may be general, they offer no advantage for the preparation of alkyl chloroformates.

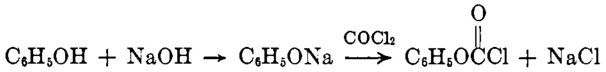
An interesting example of "chloroformate ester exchange" has also been reported (382).



$$\mathrm{FCH_2CH_2O\overset{\overset{O}{\|}}{C}H + C_2H_5O\overset{\overset{O}{\|}}{C}Cl \xrightarrow{H_2SO_4} \underset{22\%}{FCH_2CH_2O\overset{\overset{O}{\|}}{C}Cl} + C_2H_5O\overset{\overset{O}{\|}}{C}H}$$

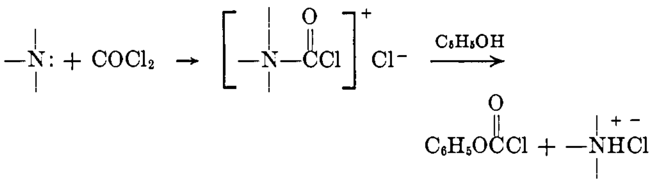
B. AROMATIC CHLOROFORMATES

In contrast to the facile reactivity of aliphatic alcohols toward phosgene, phenols are inert toward phosgene at temperatures below about 75°. However, aryl chloroformates are prepared easily in the presence of an acid acceptor (215, 322). Alkali metal hydroxides which yield the metal phenates are suitable. Early preparations of aryl chloroformates used these reagents. Conducting this reaction in the presence of an organic solvent for the chloroformate has been widely used (729).



$$\mathrm{C_6H_5OH + NaOH \rightarrow C_6H_5ONa \xrightarrow{COCl_2} C_6H_5O\overset{\overset{O}{\|}}{C}Cl + NaCl}$$

Many tertiary amines can be used as acid acceptors for the preparation of aryl chloroformates (45, 529). Amines of the dimethylaniline type gave the best results with this procedure, probably because of their low reactivity toward the chloroformates. Pyridines are also useful. The effectiveness of a tertiary amine in the synthesis of aryl chloroformates is probably not due solely to its ability to bind the hydrogen chloride that is formed. In addition, it probably forms an intermediate complex salt (7), *viz.*



$$\mathrm{-\underset{|}{\overset{|}{N}}: + COCl_2 \rightarrow \left[-\underset{|}{\overset{|}{N}}-\overset{\overset{O}{\|}}{C}Cl\right]^+ Cl^- \xrightarrow{C_6H_5OH} C_6H_5O\overset{\overset{O}{\|}}{C}Cl + -\underset{|}{\overset{|}{\overset{+}{N}}}H\overset{-}{Cl}}$$

which is a very reactive acylating agent for the phenol (45). The complex formed from 2 moles of pyridine and phosgene is well known to be a very active acylating agent (623). Aryl chloroformates (Table II) have been prepared which contained halogen (bromine, chlorine), nitro, methoxy, aldehyde, ester, sulfone, and double bond groupings.

III. PHYSICAL PROPERTIES OF CHLOROFORMATES

A. STRUCTURE

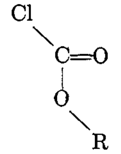
Electric dipole moments for various chloroformates are recorded throughout the literature (356, 476, 481, 639). The experimental values are similar to those for simple acyclic carboxylic esters. For methyl chloroformate, values of 1.62 (639) and 2.22 (356) have been

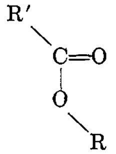
TABLE II

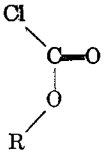
AROMATIC MONO- AND POLYCHLOROFORMATES: R(OCOCl)$_n$

R	Base type[a]	Yield, %	Reference
2,4,6-$(Br)_3C_6H_2$	O	74	348, 567
2,4,6-$(Cl)_3C_6H_2$	I		348
2,4-$(Cl)_2C_6H_3$	O	64	567
Various halogenated radicals	I		348
1,3-C_6H_4	O	>75	529
1,4-C_6H_4	O		566
2-$(Cl)C_6H_4$	O	>75	529
4-$(Cl)C_6H_4$	O	>75	351, 529, 568
2-$(NO_2)C_6H_4$	O	24	349, 567
3-$(NO_2)C_6H_4$	O	>75	323, 529
4-$(NO_2)C_6H_4$	O	80	351
C_6H_5	O	70	25, 37, 38, 45, 197, 290, 304 308, 323 351, 377, 421, 568
2-$(CHO)C_6H_4$			324
2-$(CH_3)C_6H_4$	I		38, 449, 556
3-$(CH_3)C_6H_4$	I		556
4-$(CH_3)C_6H_4$	O	82	156, 304, 351, 556
4-$(CH_3CO)C_6H_4$	I		421
2-$(CH_3OCO)C_6H_4$			438
4-$(CH_3OCO)C_6H_4$			438
4-$(C_2H_5O)C_6H_4$	O	65	351
2,6-$(CH_3)_2C_6H_3$	O		448
2,3,5-$(CH_3)_3C_6H_2$	I		421
2,4,6-$(CH_3)_3C_6H_2$	O		448
1-$C_{10}H_7$	I		119, 421, 434, 435, 529, 555
2-$C_{10}H_7$	O		52, 197, 198, 434, 435, 438, 570, 684, 734
2,4-$(CH_3O)(CH_3CH{=}CH)C_6H_3$			438
2,4-$(CH_3O)(CH_2{=}CHCH_2)C_6H_3$			438
2,4,5-$(i\text{-}C_3H_7)(Cl)(CH_3)C_6H_2$	O	80	567
2,5-$(i\text{-}C_3H_7)(CH_3)C_6H_3$			742
4-$(t\text{-}C_4H_9)C_6H_4$	I		421
4-$(C_4H_9OCO)C_6H_4$	O	91	425
S-$(4\text{-}C_6H_4)_2$	O	75.2	621
$(CH_3)_2C[4\text{-}(2,6\text{-}Cl_2C_6H_2)]_2$	O	87	621
$(CH_3)_2C(4\text{-}C_6H_4)_2$	O	93	146, 354, 621, 724, 726
$(CH_3)_2C[4\text{-}(3\text{-}CH_3C_6H_3)]_2$	O	78.3	621
$(CH_2)_4C(4\text{-}C_6H_4)_2$ └CH_2┘	O	79.4	621
Diradical from a hydroxyl-terminated polystyrene			468
Diradical from a low molecular hydroxyl-terminated bisphenol-A polycarbonate	I		148, 149

[a] I = inorganic base; O = organic base.


cis
III


IV


trans
V

published. The fact that chloroformates possessed dipole moments of this magnitude led to the postulate that they possessed a *cis*-planar structure (III) similar to that of acyclic carboxylic esters (IV). Confirmation of this structure in the case of methyl chloroformate was obtained from electron diffraction studies in the gas phase (530). The results of this study are tabulated in Table III. That this *cis*-planar configuration is due at least in part to resonance was supported by the marked shortening found for the carboxyl C–O bond as well as the widening of the C–O–C angle. The greater than tetrahedral value of the Cl–C–O angle in methyl chloroformate was also suggestive of double bond character of the C—O bond; the O—C═O angle being close to the value (125°) of the classical model. A similar study (372) of the structure of chloromethyl chloroformate indicated that it possessed the *trans* (V) configuration (Table III). The chlorine of the chloromethyl group was *trans* to the carboxyl carbon atom, and the carboxyl C–O bond showed about 5% double bond character. Since α-chlorochloroformates show differences in other properties, this effect on structure may be specific.

TABLE III

BOND DISTANCES AND ANGLES OF CHLOROFORMATES

Property	$CH_3O\overset{\overset{O}{\|}}{C}Cl$	$ClCH_2O\overset{\overset{O}{\|}}{C}Cl$
C═O	1.19 ± 0.03 Å.	1.20 ± 0.03 Å.
C–O (carboxyl)	1.36 ± 0.04 Å.	1.40 ± 0.04 Å.
C–O (methoxyl)	1.47 ± 0.04 Å.	1.40 ± 0.04 Å.
C–Cl	1.75 ± 0.02 Å.	1.74 ± 0.02 Å. (both)
∠O═C—O	126 ± 4°	126 ± 4°
∠C–O–C	111 ± 4°	110 ± 4°
∠Cl–C–O	112 ± 3°	112 ± 4°
∠O–C–Cl (chloromethyl)		109.5 ± 3°

Other physical properties including densities (26, 182, 234, 355, 371, 546, 680), refractive indices (26, 182, 234, 355, 371, 546, 680), molar refractions (26), and parachors (490) are available for many chloroformates.

B. SPECTRAL STUDIES

1. *Infrared*

The infrared absorptions of a series of chloroformates have been measured and reported (277, 366, 559). For simple aliphatic chloroformates, the carbonyl absorption occurred at 1770–1777 cm.$^{-1}$. Substitution of a chlorine atom on the β-carbon of an aliphatic chloroformate caused no change in the position of the carbonyl absorption, whereas a similar substitution on the α-carbon raised the carbonyl absorption to the 1793–

1806 cm.$^{-1}$ range. Similarly, aryl chloroformates possess carbonyl absorption at higher frequencies than aliphatic chloroformates. The C–O stretching frequency for chloroformates occurred in the 1050–1200 cm.$^{-1}$ range.

2. Raman

Raman spectra have been obtained for many chloroformates and are discussed in the literature (164, 358, 399, 400).

3. Nuclear Quadrupole Resonance

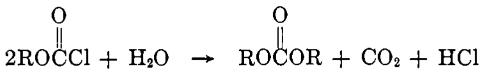
For ethyl chloroformate at liquid nitrogen temperatures, a resonance frequency of 33.858 Mc./sec. was obtained for $\mathrm{Cl^{35}}$ (704).

IV. CHEMICAL PROPERTIES OF CHLOROFORMATES

A. REACTIONS OF CHLOROFORMATES WITH HYDROXYLIC COMPOUNDS

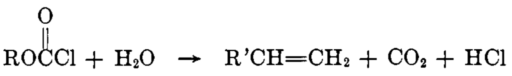
1. Water

The products from the reaction of a chloroformate with water are the hydroxy compound from which it was prepared, hydrogen chloride, and carbon dioxide (519, 594). High yields are generally obtainable. The symmetrical carbonate is also formed, presumably by reaction of the hydroxy compound with starting chloroformate (457, 483).



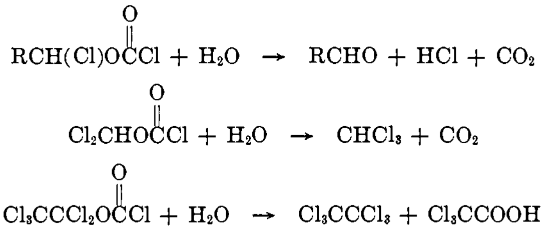
$$2\mathrm{RO\overset{O}{\overset{\|}{C}}Cl} + \mathrm{H_2O} \rightarrow \mathrm{RO\overset{O}{\overset{\|}{C}}OR} + \mathrm{CO_2} + \mathrm{HCl}$$

Ethylene has been obtained from hydrolysis of ethyl chloroformate (186, 188, 676).



$$\mathrm{RO\overset{O}{\overset{\|}{C}}Cl} + \mathrm{H_2O} \rightarrow \mathrm{R'CH{=}CH_2} + \mathrm{CO_2} + \mathrm{HCl}$$

Chlorine-substituted chloroformates have yielded different products on hydrolysis (140, 141, 268, 389–391, 489). A few cases are depicted below.

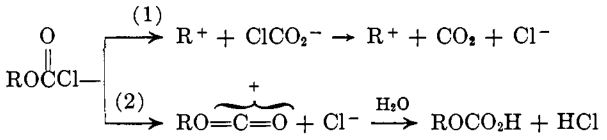


$$\mathrm{RCH(Cl)O\overset{O}{\overset{\|}{C}}Cl} + \mathrm{H_2O} \rightarrow \mathrm{RCHO} + \mathrm{HCl} + \mathrm{CO_2}$$

$$\mathrm{Cl_2CHO\overset{O}{\overset{\|}{C}}Cl} + \mathrm{H_2O} \rightarrow \mathrm{CHCl_3} + \mathrm{CO_2}$$

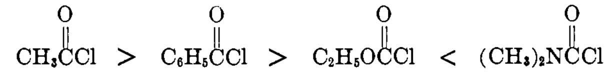
$$\mathrm{Cl_3CCCl_2O\overset{O}{\overset{\|}{C}}Cl} + \mathrm{H_2O} \rightarrow \mathrm{Cl_3CCCl_3} + \mathrm{Cl_3CCOOH}$$

The kinetics of the hydrolysis of chloroformates have been studied. An SN2 mechanism was found to be operative for the hydrolysis of chloroformates derived from primary and secondary alcohols (74, 75, 279, 687). Some recent work found an increase in the hydrolysis rate of chloroformates derived from secondary alcohols; hence a change in mechanism to SN1 has been postulated (161). Two postulated mechanisms for SN1 hydrolysis are shown. Path 1 was favored, although not conclusively proved. Chloroformates of tertiary alcohols are known to be unstable at room temperature, with their facile decomposition probably proceeding through a carbonium ion.



$$\mathrm{RO\overset{O}{\overset{\|}{C}}Cl}\!-\!\begin{cases} \xrightarrow{(1)} \mathrm{R^+ + ClCO_2^-} \rightarrow \mathrm{R^+ + CO_2 + Cl^-} \\ \xrightarrow{(2)} \mathrm{RO}\overbrace{\mathrm{{=}C{=}O}}^{+} + \mathrm{Cl^-} \xrightarrow{\mathrm{H_2O}} \mathrm{ROCO_2H + HCl} \end{cases}$$

The relative reactivity of ethyl chloroformate for SN2 hydrolysis, as compared to other acyl halides, is shown (278).

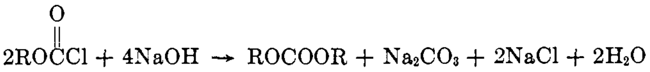


$$\mathrm{CH_3\overset{O}{\overset{\|}{C}}Cl} > \mathrm{C_6H_5\overset{O}{\overset{\|}{C}}Cl} > \mathrm{C_2H_5O\overset{O}{\overset{\|}{C}}Cl} < \mathrm{(CH_3)_2N\overset{O}{\overset{\|}{C}}Cl}$$

Hydrolysis of dimethylcarbamyl chloride proceeds *via* an SN1 mechanism accounting for the large increase in its rate.

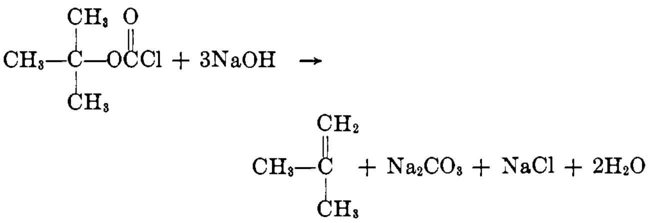
2. Alkali Metal Hydroxides

Addition of base to aqueous chloroformates can merely catalyze hydrolysis to yield the parent hydroxy compound (521). However, the use of a stoichiometric amount can yield the symmetrical carbonate, especially from aryl chloroformates (107, 483). Quantitative yields are readily obtained.



$$2\mathrm{RO\overset{O}{\overset{\|}{C}}Cl} + 4\mathrm{NaOH} \rightarrow \mathrm{ROCOOR} + \mathrm{Na_2CO_3} + 2\mathrm{NaCl} + 2\mathrm{H_2O}$$

Chloroformates derived from tertiary alkyl radicals yield olefins on treatment with base (465).



$$\mathrm{CH_3{-}\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}{-}O\overset{O}{\overset{\|}{C}}Cl} + 3\mathrm{NaOH} \rightarrow \mathrm{CH_3{-}\underset{CH_3}{\overset{CH_2}{\underset{|}{\overset{\|}{C}}}}} + \mathrm{Na_2CO_3} + \mathrm{NaCl} + 2\mathrm{H_2O}$$

An analytical method for chloromethyl and dichloromethyl chloroformates has been developed, based on their hydrolysis by sodium hydroxide (273).

3. Aliphatic Alcohols and Thiols

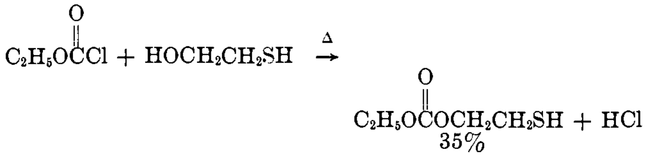
Aliphatic alcohols react with chloroformates to yield carbonates and hydrogen chloride (Table IV). In many cases, the reaction proceeds at room temperature without a catalyst or hydrogen chloride acceptor (140, 141). However, faster reactions and better yields are usually ensured if alkali metals or their hydroxides, or tertiary amines, are used to react with the hydrogen chloride that is formed.

Thiols yield the monothiolocarbonates on reaction with chloroformates (599). Reaction of 2-mercaptoethanol with ethyl chloroformate in bulk gave the mercaptocarbonate as the only isolable product (586, 587).

TABLE IV

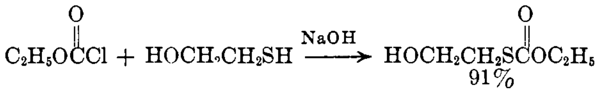
REACTIONS OF CHLOROFORMATES, ROCOCl, WITH ALCOHOLS, $R'(OH)_m$

R	R′	Yield, %	Reference
	1. Reactions of Monochloroformates with Monoalcohols		
Cl_3C	3-Cholesteryl		393
Cl_2CH	CH_3		392
Cl_2CH	3-Cholesteryl		393
$ClCH_2$	3-Cholesteryl		393
$CH_2{=}CH$	$CH_2{=}CHCH_2$		416
$ClCH_2CHCl$	C_2H_5		489
$Cl(CH_2)_2$	$Cl(CH_2)_2$	70	519
CH_3CHCl	C_2H_5		489
$F(CH_2)_2$	$F(CH_2)_2$	45	396, 532
$F(CH_2)_2$	C_2H_5	80	382
C_2H_5	$C_6H_5O(CH_2)_2$	86	715
C_2H_5	$1\text{-}(C{\equiv}CH)\text{-}1\text{-}C_6H_{10}$		184
C_2H_5	$C_6H_5(CH_2)_3$	83	715
C_2H_5	$4\text{-}(CH_3)\text{-}1\text{-}(C{\equiv}CH)\text{-}1\text{-}C_6H_{10}$		184
C_2H_5	Various radicals		628
$CH_2{=}CHCH_2$	CH_2OCHCH_2		487
$CH_2{=}C{=}CHCH_2$	Various radicals		105
C_4H_9	Various radicals		120
$CH_2{=}CHCH_2OCOCH_2$	$CH_2{=}CHCH_2OCOCH_2$	67	443
C_6H_5	C_2H_5		483
C_6H_5	$HC{\equiv}CC(R'')(R''')$ (R'' and R''' are various aliphatic radicals)		455
C_6H_5	$C_6H_5CH(CH_2R'')$ (R'' are N-pyrrolidinyl, N-piperidinyl, N-morpholinyl, and N-(N′-methyl)piperazinyl)	~70	294
C_6H_5	Various radicals		483, 422
$4\text{-}(NO_2)C_6H_4CH_2$	C_2H_5		107
$4\text{-}(NO_2)C_6H_4CH_2$	$4\text{-}(NO_2)C_6H_4CH_2$	52	107
Various aliphatic radicals	$R''NHCOCH_2$ (R'' are various aliphatic and aromatic radicals)	20–96	632
Various aliphatic radicals	$CH_3CH(COOR'')$ (R'' are various aliphatic radicals)	30–85	576
Various aliphatic radicals	$CH_3CH(CONHR'')$ (R'' are various aliphatic and aromatic radicals)	40–90	632
Various aliphatic radicals	$(CH_3)_2C(CONHR'')$ (R'' are various aliphatic and aromatic radicals)	30–90	632
Various aliphatic radicals	$C_6H_5CH(CH_2R'')$ (R'' are N-pyrrolidinyl, N-piperidinyl, N-morpholinyl, and N-(N′-methyl)piperazinyl)	~85	294
Various aliphatic radicals	$C_6H_5CH(CONHR'')$ (R'' are various aliphatic and aromatic radicals)	30–95	632
Various aliphatic radicals	CH_3		426, 540
Various aromatic radicals	Various radicals		197
Various aliphatic and aromatic radicals	Various radicals		339, 594, 630
Various steroidal radicals	CH_3		180
Various steroidal radicals	C_2H_5		180
	2. Reactions of Monochloroformates with Diols		
CH_3	Radical from cellulose		595
C_2H_5	$-CH_2CH{=}CHCH_2-$		54
C_2H_5	$1,4\text{-}CH_2C_6H_4CH_2$		583
C_2H_5	$1,4\text{-}(CH_2)_2C_6H_4(CH_2)_2$	80	585
C_2H_5	$1,4\text{-}(CH_2)_2OC_6H_4O(CH_2)_2$	>54	584
$CH_2{=}CHCH_2$	$O[\text{-}Si(CH_3)_2CH_2]_2$	30	9
$CH_3(CH_2)_4$	$1,4\text{-}CH_2C_6H_4CH_2$		583
C_6H_5	$1,4\text{-}CH_2C_6H_4CH_2$		583



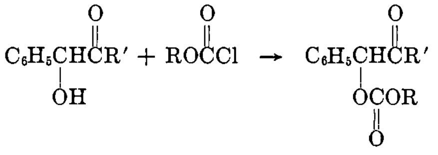
$$C_2H_5O\overset{O}{\overset{\|}{C}}Cl + HOCH_2CH_2SH \xrightarrow{\Delta} \underset{35\%}{C_2H_5O\overset{O}{\overset{\|}{C}}OCH_2CH_2SH + HCl}$$

However, the greater reactivity of the anion from a thiol as compared to that from an alcohol was shown by the formation of the monothiolcarbonate from the same reaction when carried out with added sodium hydroxide (506, 586, 587).



$$C_2H_5O\overset{O}{\overset{\|}{C}}Cl + HOCH_2CH_2SH \xrightarrow{NaOH} \underset{91\%}{HOCH_2CH_2S\overset{O}{\overset{\|}{C}}OC_2H_5}$$

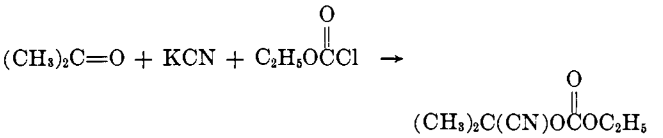
α-Hydroxy esters (676) and α-hydroxy amides (632) reacted with chloroformates to yield the expected carbonates. The reported yields were variable.



$$C_6H_5\underset{OH}{\underset{|}{C}}H\overset{O}{\overset{\|}{C}}R' + RO\overset{O}{\overset{\|}{C}}Cl \rightarrow C_6H_5\underset{\underset{\underset{O}{\|}}{OCOR}}{\underset{|}{C}}H\overset{O}{\overset{\|}{C}}R'$$

$R' = -NHR''$ or $-OR''$

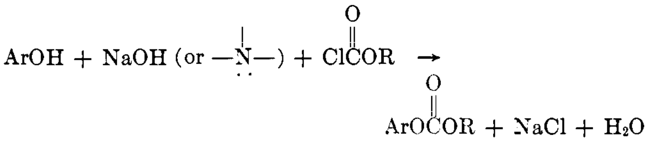
A carbonate has been prepared in low yield from a cyanohydrin by reaction of ethyl chloroformate with acetone in the presence of potassium cyanide (168).



$$(CH_3)_2C{=}O + KCN + C_2H_5O\overset{O}{\overset{\|}{C}}Cl \rightarrow (CH_3)_2C(CN)O\overset{O}{\overset{\|}{C}}OC_2H_5$$

4. Phenols

Phenols are unreactive toward chloroformates at room temperature, and at elevated temperatures only small yields (<10%) of the expected carbonates are produced. However, phenols react readily with chloroformates when bases are used (224), and high yields of the expected carbonates are obtainable (Table V).



$$ArOH + NaOH\ (\text{or} -\overset{|}{\underset{\cdot\cdot}{N}}-) + Cl\overset{O}{\overset{\|}{C}}OR \rightarrow Ar\overset{O}{\overset{\|}{O C}}OR + NaCl + H_2O$$

TABLE V

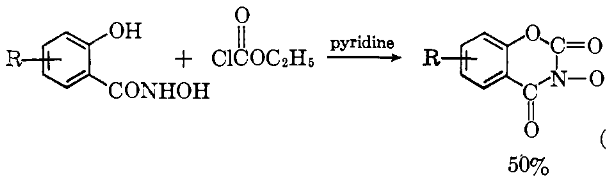
REACTIONS OF CHLOROFORMATES, ROCOCl, WITH PHENOLS, $Ar(OH)_m$

R	Ar	Yield, %	Reference
1. In the Presence of a Stoichiometric Amount of Base			
CH_3	$2,4,5,6\text{-}(Cl)_3(NO_2)C_6H$		635
CH_3	5-Acetyl-8-quinolyl		318, 319
CH_3	5-Butyryl-8-quinolyl		318, 319
CH_3	5-Valeryl-8-quinolyl		318, 319
CH_3	$(CH_3)_2C(4\text{-}C_6H_4)_2$		59
CH_3	Various radicals		312, 313
C_2H_5	$2,4,5,6\text{-}(Cl)_3(NO_2)C_6H$		635
C_2H_5	C_6H_5	71	138, 195, 225, 718
C_2H_5	$2\text{-}(COOH)C_6H_4$		395
C_2H_5	$4\text{-}(COOH)C_6H_4$		682
C_2H_5	5-Acetyl-8-quinolyl		318, 319
C_2H_5	5-Butyryl-8-quinolyl		318, 319
C_2H_5	5-Valeryl-8-quinolyl		318, 319
C_2H_5	2-Formyl-5-acetyl-8-quinolyl		319, 318
C_2H_5	Various radicals		312, 313
$CH_2{=}CHCH_2$	$4\text{-}Cl\text{-}1,3\text{-}C_6H_4$		84
$CH_3(CH_2)_2$	$2,4,5,6\text{-}(Cl)_3(NO_2)C_6H$		635
$(CH_3)_2CH$	$2,4,5,6\text{-}(Cl)_3(NO_2)C_6H$		635
$CH_3(CH_2)_2$	5-Acetyl-8-quinolyl		318, 319
$CH_3(CH_2)_2$	5-Butyryl-8-quinolyl		318, 319
$CH_3(CH_2)_2$	5-Valeryl-8-quinolyl		318, 319
$CH_2{=}C{=}CHCH_2$	Various radicals		105
$CH_3(CH_2)_3$	$2,4,5,6\text{-}(Cl)_3(NO_2)C_6H$		635
$CH_3(CH_2)_3$	5-Acetyl-8-quinolyl		318, 319
$CH_3(CH_2)_3$	5-Butyryl-8-quinolyl		318, 319
$CH_3(CH_2)_3$	5-Valeryl-8-quinolyl		318, 319
$CH_3(CH_2)_4$	$2,4,5,6\text{-}(Cl)_3(NO_2)C_6H$		635
$CH_3(CH_2)_4$	5-Acetyl-8-quinolyl		318, 319
$CH_3(CH_2)_4$	5-Butyryl-8-quinolyl		318, 319
$CH_3(CH_2)_4$	5-Valeryl-8-quinolyl		318, 319
$4\text{-}(Cl)C_6H_4$	$1,4\text{-}C_6H_4$	58	568
C_6H_5	C_6H_5		314
C_6H_5	5-Acetyl-8-quinolyl		318, 319
C_6H_5	5-Butyryl-8-quinolyl		318, 319
C_6H_5	5-Valeryl-8-quinolyl		318, 319
C_6H_5	$(CH_3)_2C(4\text{-}C_6H_4)_2$		79
Various halogenated aromatic radicals	5-Acetyl-8-quinolyl		318, 319
Various halogenated aromatic radicals	5-Butyryl-8-quinolyl		318, 319
Various halogenated aromatic radicals	5-Valeryl-8-quinolyl		318, 319
Various aromatic radicals	2-Formyl-5-acetyl-8-quinolyl		318, 319
Various aromatic radicals	Various radicals		314
Various aliphatic and aromatic radicals	Various radicals	~90	229, 230, 667
Various aliphatic radicals	$2\text{-}(NO_2)C_6H_4$	70–95	381
Various aliphatic radicals	Various diradicals	~90	229, 230, 667
Various aliphatic radicals	Various radicals		121
3-Cholesteryl	Various di- and polyradicals		604
3-Cholesteryl	Various radicals		604
2. Catalytic			
C_2H_5[a]	C_6H_5		545
C_9H_{19}[b]	C_6H_5		625

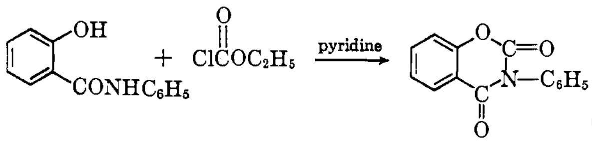
[a] With $AlCl_3$ as catalyst. [b] Activated carbon catalyst.

Sodium hydroxide and amines, such as pyridine and dimethylaniline, are particularly useful. Activated carbon has been claimed to be a very good catalyst for the reaction of phenol with an aliphatic chloroformate (345).

The cyclizations shown in eq. a (737), and b (364) have been reported.



(a)



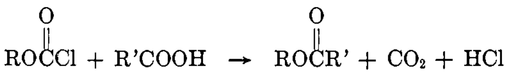
(b)

5. *Heterocyclic Alcohols*

Alcohols of nitrogen-containing heterocycles have been converted to carbonates by reaction with chloroformates (96, 171, 316, 514, 515, 647). Furan- and tetrahydrofuran-derived alcohols reacted similarly to give carbonates in 75% yield (715). As with aliphatic alcohols, inorganic bases and tertiary amines increased reactivity and the yields.

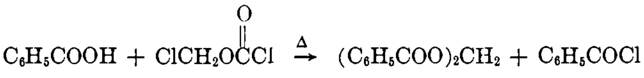
B. REACTION OF CHLOROFORMATES WITH CARBOXYLIC ACIDS

Most of the early literature pertaining to the reaction of a chloroformate with a carboxylic acid described the formation of esters as the main products (3, 29, 196, 310, 335, 336, 395, 538). The conditions that were used



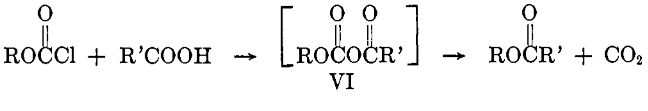
$$RO\overset{O}{\overset{\|}{C}}Cl + R'COOH \rightarrow RO\overset{O}{\overset{\|}{C}}R' + CO_2 + HCl$$

generally employed heating and/or acidic or basic catalysts. Good yields of esters were obtained. Esters of fluorinated carboxylic acids can also be advantageously prepared in 75–80% yields by this method (266). A variation from the usual result is shown in the following equation (174, 409).



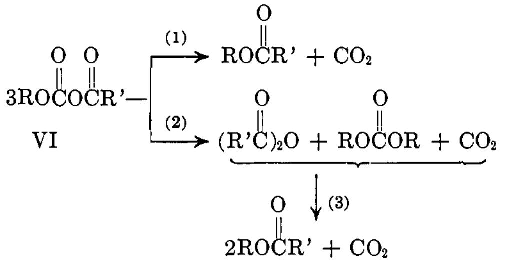
$$C_6H_5COOH + ClCH_2O\overset{O}{\overset{\|}{C}}Cl \xrightarrow{\Delta} (C_6H_5COO)_2CH_2 + C_6H_5COCl$$

For many years, the expected intermediates in this reaction, the mixed carboxylic–carbonic anhydrides (VI), *i.e.*



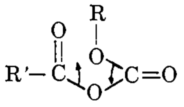
$$RO\overset{O}{\overset{\|}{C}}Cl + R'COOH \rightarrow \underset{\text{VI}}{\left[RO\overset{O}{\overset{\|}{C}}O\overset{O}{\overset{\|}{C}}R'\right]} \rightarrow RO\overset{O}{\overset{\|}{C}}R' + CO_2$$

were thought to be incapable of isolation and purification because of their thermal instability. However, several groups (216, 670, 721) have recently synthesized and isolated many examples of this class of compounds (VI). The mechanism of the thermal decomposition of these mixed carboxylic–carbonic anhydrides has been the subject of recent publications. Both Tarbell and Longosz (437, 671) and Windholz (722, 723) have observed paths 1 and 2 below. Reaction 3

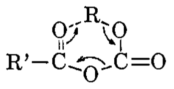


$$\underset{\text{VI}}{3RO\overset{O}{\overset{\|}{C}}O\overset{O}{\overset{\|}{C}}R'} \begin{cases} \xrightarrow{(1)} RO\overset{O}{\overset{\|}{C}}R' + CO_2 \\ \xrightarrow{(2)} \underbrace{(R'\overset{O}{\overset{\|}{C}})_2O + RO\overset{O}{\overset{\|}{C}}OR + CO_2}_{\downarrow (3)\ 2RO\overset{O}{\overset{\|}{C}}R' + CO_2} \end{cases}$$

was also demonstrated to occur, but temperatures much higher than those used for the mechanism studies were required to effect it. The preferred route (1 or 2) of decomposition was found to be dependent on the particular groups (R, R′) that were present, the temperature of decomposition, and the presence or absence of catalysts. For benzoic *n*-butylcarbonic anhydride (VI, R = C_4H_9, R′ = C_6H_5), Tarbell and Longosz found that their results agreed with the idea that the products were formed by a series of ionic chain reactions which were initiated by catalysts acting as nucleophiles (437). Cyclic transition states of types VII and VIII were ruled out on the basis of a study of the thermal decomposition of benzoic *sec*-butylcarbonic



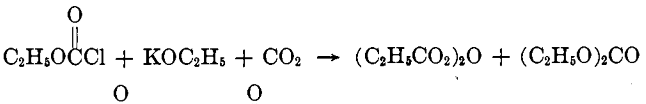
VII



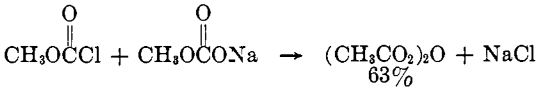
VIII

anhydride containing O^{18} in the alcohol fragment (475). No alkyl–oxygen cleavage was observed, and hence transition states of types VII and VIII could not be operative. It was pointed out, however, that when R is benzyl or a tertiary radical, alkyl–oxygen cleavage might occur to yield the more stable carbonium ions. Early workers (335) had shown that the reaction of potassium benzoate with (−)-2-octyl chloroformate resulted in the recovery, after hydrolysis, of only (−)-2-octanol. This retention of configuration was reconfirmed by Tarbell, *et al.*, by the preparation and decomposition of pure benzoic (−)-2-octylcarbonic anhydride (671). It was found that the resulting 2-octyl benzoate gave pure (−)-2-octanol on saponification. This stereochemical result is compatible with the ionic chain mechanism proposed above.

Pyrocarbonates (anhydrides of carbonic acids) have been prepared by the following routes (169, 406, 677).



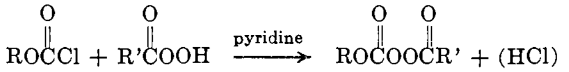
$$C_2H_5O\overset{O}{\overset{\|}{C}}Cl + KOC_2H_5 + CO_2 \rightarrow (C_2H_5CO_2)_2O + (C_2H_5O)_2CO$$



$$CH_3O\overset{O}{\overset{\|}{C}}Cl + CH_3O\overset{O}{\overset{\|}{C}}ONa \rightarrow \underset{63\%}{(CH_3CO_2)_2O} + NaCl$$

The two pyrocarbonates shown are fairly stable compounds but do decompose at temperatures over 100° to yield the corresponding ester and carbon dioxide.

Mixed anhydrides of peroxy carboxylic acids have been prepared and isolated from chloroformates using pyridine as a hydrogen chloride acceptor (541). They have been claimed to have utility as initiators for vinyl polymerization.

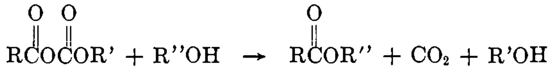

$$\mathrm{RO\overset{O}{\overset{\|}{C}}Cl + R'\overset{O}{\overset{\|}{C}}OOH \xrightarrow{pyridine} RO\overset{O}{\overset{\|}{C}}OO\overset{O}{\overset{\|}{C}}R' + (HCl)}$$

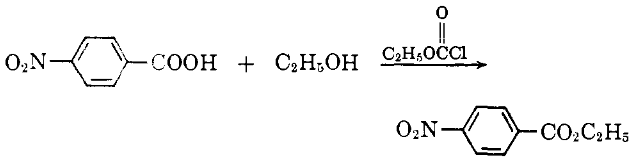
C. REACTIONS OF CARBOXYLIC–CARBONIC ANHYDRIDES

Carboxylic–carbonic anhydrides are very active acylating agents and were widely used for this purpose even before their isolation. Their reaction with nucleophiles proceeds readily under mild conditions to give good yields of the expected products.

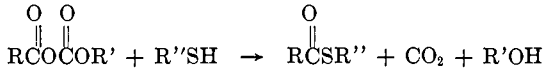
1. *With Alcohols* (*39, 335, 359*)

The preparation of esters by the route shown in the following equation is especially useful in cases where the acids are thermally or otherwise unstable. The use of chloroformates as esterification catalysts has been reported (238). Their utility may stem from the formation of the mixed anhydride which then reacts rapidly with the alcohol.

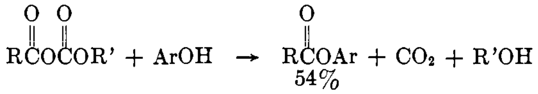

$$\mathrm{R\overset{O}{\overset{\|}{C}}O\overset{O}{\overset{\|}{C}}OR' + R''OH \rightarrow R\overset{O}{\overset{\|}{C}}OR'' + CO_2 + R'OH}$$

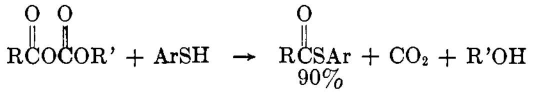


2. *With Thiols* (*39, 335, 359*)

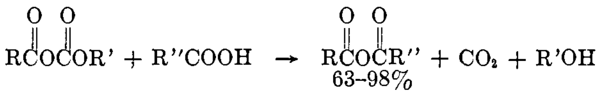

$$\mathrm{R\overset{O}{\overset{\|}{C}}O\overset{O}{\overset{\|}{C}}OR' + R''SH \rightarrow R\overset{O}{\overset{\|}{C}}SR'' + CO_2 + R'OH}$$

3. *With Phenols* (*669*) *and Thiophenols* (*714*)


$$\mathrm{R\overset{O}{\overset{\|}{C}}O\overset{O}{\overset{\|}{C}}OR' + ArOH \rightarrow \underset{54\%}{R\overset{O}{\overset{\|}{C}}OAr} + CO_2 + R'OH}$$

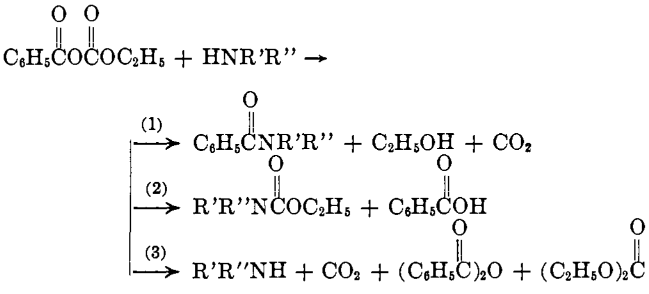

$$\mathrm{R\overset{O}{\overset{\|}{C}}O\overset{O}{\overset{\|}{C}}OR' + ArSH \rightarrow \underset{90\%}{R\overset{O}{\overset{\|}{C}}SAr} + CO_2 + R'OH}$$

4. *With Acids* (*611, 669*)

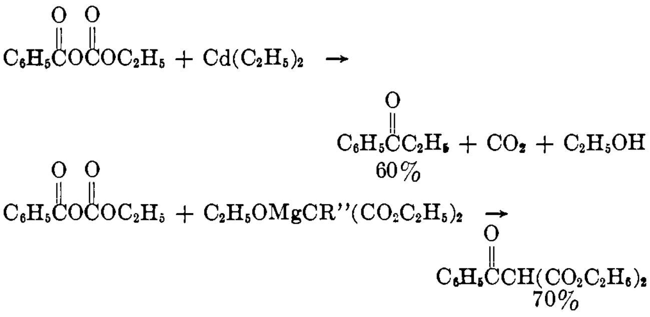

$$\mathrm{R\overset{O}{\overset{\|}{C}}O\overset{O}{\overset{\|}{C}}OR' + R''COOH \rightarrow \underset{63\text{–}98\%}{R\overset{O}{\overset{\|}{C}}O\overset{O}{\overset{\|}{C}}R''} + CO_2 + R'OH}$$

5. *With Amines*

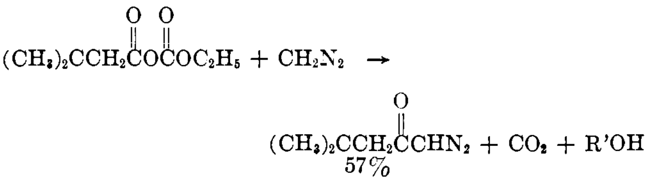
The reaction of amines (39, 73, 315, 335, 359, 581, 609, 611, 694–698, 702, 713) with carboxylic–carbonic anhydrides to yield amides has been used widely for the synthesis of peptide bonds because of the requisite mild reaction conditions. Excellent yields are obtainable. In a recent study, Tarbell and Leister (427) have shown that this reaction can proceed by the three routes shown below, depending on the particular structure of the carboxylic–carbonic anhydride. In many cases when benzoic–carbonic anhydrides were treated with amines, urethans (path 2) were the major products. Paths 1 and 2 are merely the result of attack at either the carboxylic or carbonic carbonyl groups, whereas path 3 is a disproportionation of the anhydride.


$$\mathrm{C_6H_5\overset{O}{\overset{\|}{C}}O\overset{O}{\overset{\|}{C}}OC_2H_5 + HNR'R'' \rightarrow}$$
$$\mathrm{\xrightarrow{(1)} C_6H_5\overset{O}{\overset{\|}{C}}NR'R'' + C_2H_5OH + CO_2}$$
$$\mathrm{\xrightarrow{(2)} R'R''N\overset{O}{\overset{\|}{C}}OC_2H_5 + C_6H_5\overset{O}{\overset{\|}{C}}OH}$$
$$\mathrm{\xrightarrow{(3)} R'R''NH + CO_2 + (C_6H_5\overset{O}{\overset{\|}{C}})_2O + (C_2H_5O)_2\overset{O}{\overset{\|}{C}}}$$

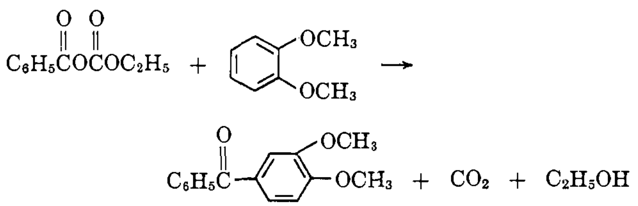
6. *With Organometallic Reagents* (*668, 669*)

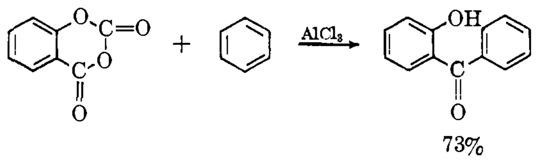

$$\mathrm{C_6H_5\overset{O}{\overset{\|}{C}}O\overset{O}{\overset{\|}{C}}OC_2H_5 + Cd(C_2H_5)_2 \rightarrow \underset{60\%}{C_6H_5\overset{O}{\overset{\|}{C}}C_2H_5} + CO_2 + C_2H_5OH}$$
$$\mathrm{C_6H_5\overset{O}{\overset{\|}{C}}O\overset{O}{\overset{\|}{C}}OC_2H_5 + C_2H_5OMgCR''(CO_2C_2H_5)_2 \rightarrow \underset{70\%}{C_6H_5\overset{O}{\overset{\|}{C}}CH(CO_2C_2H_5)_2}}$$

7. *With Diazoalkanes* (*34, 669*)


$$\mathrm{(CH_3)_2CCH_2\overset{O}{\overset{\|}{C}}O\overset{O}{\overset{\|}{C}}OC_2H_5 + CH_2N_2 \rightarrow \underset{57\%}{(CH_3)_2CCH_2\overset{O}{\overset{\|}{C}}CHN_2} + CO_2 + R'OH}$$

8. *With Hydrocarbons* (*129, 167, 191*)



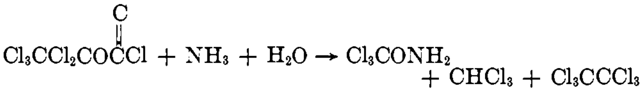


73%

D. REACTIONS OF CHLOROFORMATES WITH NITROGEN COMPOUNDS

1. Ammonia

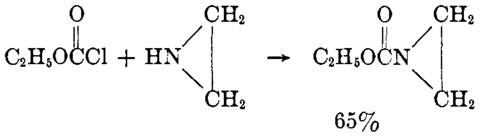
The reaction of chloroformates with ammonia is the classical method for preparing primary urethans and, therefore, has been used extensively in the past for this purpose. In most cases, ammonia is used in excess to remove the hydrogen chloride. The utility of primary urethans, and urethans in general, in diverse applications within the general areas of biological and agricultural chemicals has contributed to the widespread use of this reaction. As can be seen from the examples listed in Table VI, this reaction has been effected successfully in the presence of many types of reactive groups, even some of which are normally considered to be reactive towards ammonia. These include double and triple bonds, allenic groups, alkyl chlorides and fluorides, hydroxyl groups, cyclic and acyclic ethers, and esters of carbonic and carboxylic acids. Bis(urethans) have also been prepared by this method. The reaction of the chloroformate of pentachloroethanol with ammonia is a special case (140, 141, 489).



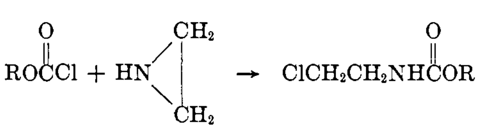
$$Cl_3CCl_2CO\overset{C}{\overset{\|}{C}}Cl + NH_3 + H_2O \rightarrow Cl_3CONH_2 + CHCl_3 + Cl_3CCCl_3$$

2. Primary and Secondary Aliphatic Amines

Primary and secondary aliphatic amines react rapidly with chloroformates to yield the urethans. Organic (excess amine) or inorganic bases can be used to remove the hydrogen chloride that is formed. For many of the same reasons mentioned above with respect to the reaction of ammonia with chloroformates, this reaction has been used extensively throughout the literature (Table VII). Reaction of ethylenimine with ethyl chloroformate in the presence of a tertiary amine as the hydrogen chloride acceptor gave the expected urethan (351) (Table VIII).



However, when no acid acceptor was present, ring opening occurred to give the β-chlorourethan (60).

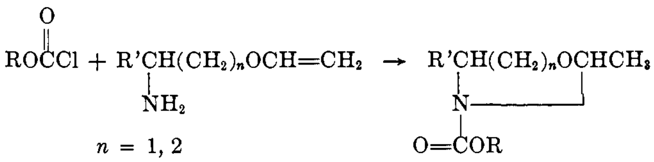


An interesting synthesis of oxazolidines and 1,3-oxazines resulted from the reaction of aminovinyl esters with alkyl or aryl chloroformates (462).

TABLE VI

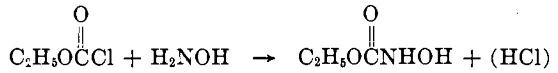
REACTIONS OF CHLOROFORMATES, R(OCOCl)$_n$, WITH AMMONIA

R	Yield, %	Reference
$-(CH_2)_2-$		354
$Cl(CH_2)_2$		155
$F(CH_2)_2$	85	382, 532
C_2H_5		186, 188
$-(CH_2)_3-$		354
$Cl(CH_2)_3$	71	185
C_3H_7		676
$HC\equiv CCH(CH_3)$		553, 554
$CH_2=C=CHCH_2$		105, 106
$OCOOCH_2CHCH_2$		658
$-CH_2CH=CHCH_2-$	90	276
$CH_2OCH_2CH_2CH$	~90	578
$-(CH_2)_4-C$		354
$CH_3CH(CH_3)CH_2$		676
$-(CH_2)_5-$		354
$CH_3C(CH_3)(C_2H_5)$		466
C_6H_5		377, 489
$-(CH_2)_6-$		354
$Cl(CH_2)_6$		298
$C_6H_5CH_2$	90	112
$-(CH_2)_7-$		354
$CH_3CHC(CH_3)_2CHCH_3$		128
$(i\text{-}C_3H_7)_2CH$		669
$CF_3(CF_2)_6CH_2$	~70	520
$-(CH_2)_8-$		354
$Cl(CH_2)_8$		298
1-(1-Cyclohexenyl)propargyl	40	553, 554
$-(CH_2)_9-$		354
$Cl(CH_2)_9$		298
$[(CH_3)_3C]_2CH$		379
1-(2-Bicyclo[2.2.1]heptenyl-2)-propargyl	53	553, 554
$(C_6H_5)(i\text{-}C_3H_7)CH$		662–664
$-(CH_2)_{10}-$		354
$Cl(CH_2)_{10}$		298
$ClCF_2(CF_2)_9CH_2$	~70	520
$CHF_2(CF_2)_9CH_2$	~70	520
$4\text{-}(C_4H_9OCO)C_6H_4$		425
$CHF_2(CF_2)_{11}CH_2$	~70	510
$C_2H_5OCOC(CH_3)_2CH(C_6H_5)$		8
$(C_6H_5)_2C(CH_2OH)CH_2$		56
3-Ethylcholatyl		701
$HC\equiv CC(R')(R'')$ (R′ and R″ are various aliphatic, cycloaliphatic, and/or aromatic radicals)		516
$HC\equiv CCH_2C(R')(R'')$ (R′ and R″ are various aliphatic and/or aromatic radicals; together they may form an alicyclic radical	60–70	422, 423
Various aromatic radicals		311
Various chlorinated aliphatic radicals		743
$R'O(CH_2)_2$ (R′ are various aliphatic radicals)	13–66	20
$-CH_2C(R')(R'')CH_2-$ (R′ and R″ are various aliphatic or aromatic radicals)	60–90	439
Various aliphatic radicals	55–80	48, 49, 440



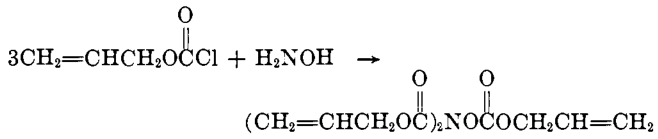
Recent kinetics studies have shown that the reaction of primary and secondary amines is an extremely fast one which proceeds by an SN2 mechanism (280, 282). This is due to the high nucleophilicity of the amines and the ease of displacing a chloride ion attached to a carbonyl group. Rate constants (k_2) of the order of 10^4 were found for piperidine; 10^2 for morpholine, 1-carboethoxypiperazine, 2-methylpiperidine, *n*-butylamine, and neopentylamine; 10 for *sec*-butylamine; and 1 for *t*-butylamine. The reaction is markedly subject to steric hindrance although it was surprising that neopentylamine did not exhibit a conspicuous degree of hindrance.

Reaction of hydroxylamine with a chloroformate leads to N-acylation preferentially, *viz.* (292)



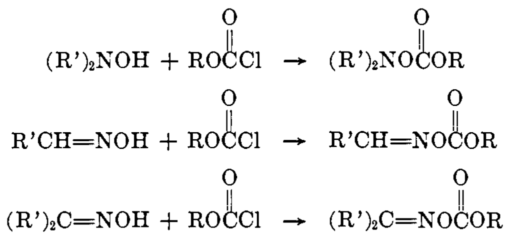
$$C_2H_5O\overset{O}{\overset{\|}{C}}Cl + H_2NOH \rightarrow C_2H_5O\overset{O}{\overset{\|}{C}}NHOH + (HCl)$$

However, the use of 3 equiv. of a chloroformate can lead to the replacement of the three active hydrogens of hydroxylamine (85). Other examples of this reaction have also been reported (749, 750).



$$3CH_2{=}CHCH_2O\overset{O}{\overset{\|}{C}}Cl + H_2NOH \rightarrow (CH_2{=}CHCH_2O\overset{O}{\overset{\|}{C}})_2NO\overset{O}{\overset{\|}{C}}OCH_2CH{=}CH_2$$

When N-acylation is not possible as with dialkylhydroxylamines, aldoximes, and ketoximes, O-acylation occurs readily, *viz.* (81, 82).



$$(R')_2NOH + RO\overset{O}{\overset{\|}{C}}Cl \rightarrow (R')_2NO\overset{O}{\overset{\|}{C}}OR$$

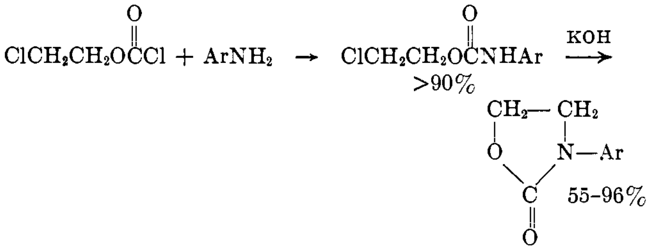
$$R'CH{=}NOH + RO\overset{O}{\overset{\|}{C}}Cl \rightarrow R'CH{=}NO\overset{O}{\overset{\|}{C}}OR$$

$$(R')_2C{=}NOH + RO\overset{O}{\overset{\|}{C}}Cl \rightarrow (R')_2C{=}NO\overset{O}{\overset{\|}{C}}OR$$

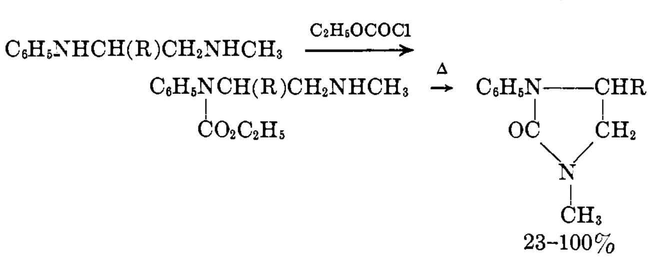
3. Primary and Secondary Aromatic Amines

Aromatic primary and secondary amines react with chloroformates in the same manner as do aliphatic amines. However, since aromatic amines are weaker bases (and weaker nucleophiles), the reactions are slower than with aliphatic amines. For reasons of economy, it is more advantageous to use inorganic bases as the hydrogen chloride acceptor instead of excess amine. The numerous examples shown in Table IX are indicative of the generality of this reaction, even with many types of other functional groups present.

An interesting use of an intermediate urethan prepared by this route in the synthesis of 3-aryl-substituted 2-oxazolidones has been reported (5, 453).

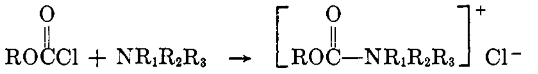


A similar cyclization has yielded cyclic ureas (738).



4. Tertiary Amines

Tertiary amines react with chloroformates to yield quaternary ammonium compounds of the general structure IX (42, 44, 47, 122–124, 329, 394, 543, 590).



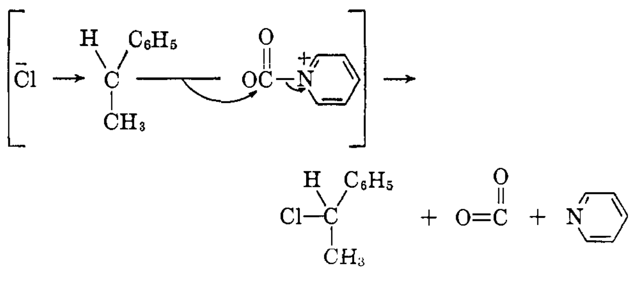
$$RO\overset{O}{\overset{\|}{C}}Cl + NR_1R_2R_3 \rightarrow \left[RO\overset{O}{\overset{\|}{C}}{-}NR_1R_2R_3\right]^+ Cl^-$$

IX

The properties of these salts vary depending on the specific R groups that are present.

a. Thermal Reactions of Tertiary Amine–Chloroformate Complexes

Complexes formed from aliphatic chloroformates with pyridine are unstable at room temperature (329). Reaction of pyridine with ethyl chloroformate at 0° gave ethyl chloride, carbon dioxide, pyridine, and pyridine hydrochloride. Chloroformates derived from secondary alcohols react with pyridine quite cleanly to yield the secondary chlorides (544). This reaction has been shown to proceed with inversion in the case of 1,2-octyl and 1,1-phenethyl chloroformates (335–338). Inversion probably occurs by backside attack of the chloride ion on the cationic complex ion.



Catalytic amounts of triethylamine have been used

TABLE VII

REACTIONS OF CHLOROFORMATES, $R(OCOCl)_n$, WITH ALIPHATIC AMINES

1. Primary Amines $R'(NH_2)_m$

R	R′	Yield, %	Reference
$-(CH_2)_2-$	C_4H_9		354
$Cl(CH_2)_2$	CH_3		626
$Cl(CH_2)_2$	Various radicals	~70	558, 626
$F(CH_2)_2$	CH_3	81	532
C_2H_5	HO		292
C_2H_5	$-(CH_2)_2-$		582
C_2H_5	$-(CH_2)_3-$		582
C_2H_5	$-(CH_2)_6-$		582
C_2H_5	$C_6H_5CH(CH_3)$		705
C_2H_5	$-(CH_2)_8-$		582
C_2H_5	Various radicals		282
$ClCH=CHCH_2$	$Cl(CH_2)_2$	46	130
$CH_2=CHCH_2$	HO		85
$-(CH_2)_3-$	C_4H_9		354
$Cl(CH_2)_3$	Various radicals	~70	558
$ClCH_2C\equiv CCH_2$	Various radicals	10–90	31, 330, 685
$CH_2OCOOCHCH_2$	Various radicals		658
$-CH_2CH=CHCH_2-$	CH_3		276
$CH_2O(CH_2)_2CH$	$-(CH_2)_6-$		578
$-(CH_2)_4-$	C_4H_9		354
$[-(CH_2)_2-]_2O$	2-(12-Hydroxyoleoyloxy)ethyl		170
$[-(CH_2)_2-]_2O$	Various radicals	64–99	661
$-(CH_2)_5-$	C_4H_9		354
$C_2H_5C(CH_3)_2$	Various radicals		466
1,4-C_6H_4	C_4H_9		354
C_6H_5	Various radicals		484
1,4-Cyclohexylene (*cis*)	C_4H_9		354
1,4-Cyclohexylene (*trans*)	C_4H_9		354
$-(CH_2)_6-$	C_4H_9		354
2-Chlorobenzyl	$(C_2H_5)_2N(CH_2)_2$		295
$-(CH_2)_7-$	C_4H_9		354
4-$(CH_3CO)C_6H_4$	CH_3		421
2,6-$(CH_3)_2C_6H_3$	Various radicals	70–80	448
$-(CH_2)_8-$	C_4H_9		354
2,6-Dimethylbenzyl	$(C_2H_5)_2N(CH_2)_2$		295
2,4,6-$(CH_3)_3C_6H_2$	Various radicals	70–80	448
$-(CH_2)_9-$	C_4H_9		354
1-Naphthyl	CH_3		420
1-Naphthyl	C_4H_9	~70	434, 435
2-Naphthyl	C_4H_9	~70	434, 435
1-Naphthyl	Various radicals		421
5,6,7,8-Tetrahydro-2-naphthyl	C_4H_9	~70	434, 435
1,4-$[-(CH_2)_2OCO]_2C_6H_4$	C_4H_9		354
$(CH_3)_2C(4\text{-}C_6H_4)_2$	C_4H_9		354
3-Cholesteryl	$C_6H_5CH_2$	89	413, 454
Various aromatic radicals	1-Menthyl		556
Various aliphatic and aromatic radicals	$(CH_3)_2N(CH_2)_3$	50–55	404, 405
Various aliphatic and aromatic radicals	$(C_2H_5)_2N(CH_2)_3$	25–85	404, 405
Various aliphatic and aromatic radicals	$(CH_2(CH_2)_4N(CH_2)_2$	50–80	404, 405
1-Propargyl alicyclic radicals	Various radicals		423
$(R_1)(R_2)(HC\equiv C)C$ (R_1 and R_2 are various aliphatic radicals)	Various radicals		516
$-CH_2C(C_2H_5)_2CH_2-$	Various radicals	50–60	439
Various aliphatic radicals	Camphoryl	~90–95	227
Various tertiary aliphatic radicals	Various radicals		466
Various aliphatic, alicyclic, and heterocyclic radicals	Various bivalent radicals		346

TABLE VII (*Continued*)

2. Secondary Amines, R'R''NH

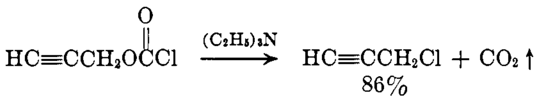
R	R'	R''	Yield, %	Reference
$F(CH_2)_2$	CH_3	CH_3	85	532
C_2H_5	Cyclopropyl	$C_6H_5CH_2$		2
$CH_2{=}C{=}CHCH_2$	CH_3	CH_3		105, 106
$+(CH_2)_2+_2O$	C_4H_9	C_4H_9		70
C_6H_5	CH_3	CH_3		421
C_6H_5	Various radicals	Various radicals		484
1-Naphthyl	CH_3	CH_3		421, 434, 435
2-Naphthyl	CH_3	CH_3		434, 435
1-Naphthyl	$Cl(CH_2)_2$	$Cl(CH_2)_2$	80	434, 435
2-Naphthyl	$Cl(CH_2)_2$	$Cl(CH_2)_2$	60	434, 435
1-Naphthyl	C_2H_5	C_2H_5		434, 435
2-Naphthyl	C_2H_5	C_2H_5		434, 435
1-Naphthyl	C_3H_7	C_3H_7		434, 435
1-Naphthyl	C_4H_9	C_4H_9		421, 434, 435
1-Naphthyl	$(CH_3)_2CH(CH_2)_2$	$(CH_3)_2CH(CH_2)_2$	70	434, 435
1-Naphthyl	C_5H_{11}	C_5H_{11}	60	434, 435
5,6,7,8-Tetrahydro-1-naphthyl	C_2H_5	C_2H_5	70	434, 435
5,6,7,8-Tetrahydro-2-naphthyl	C_2H_5	C_2H_5		434, 435
5,6,7,8-Tetrahydro-1-naphthyl	C_4H_9	C_4H_9		434, 435
$4\text{-}[(CH_3)_3C]C_6H_4$	CH_3	CH_3		421
Various aromatic radicals	Various radicals	Various radicals		691
$(R_1)(R_2)(HC{\equiv}C)C$ (R_1 and R_2 are various aliphatic radicals)	Various radicals	Various radicals		516
Various tertiary aliphatic radicals	Various radicals	Various radicals		466
$-(CH_2CH_2NH)_n-$	Various radicals	Various radicals		688

TABLE VIII

REACTION OF CHLOROFORMATES, $R(OCOCl)_n$, WITH ETHYLENIMINE

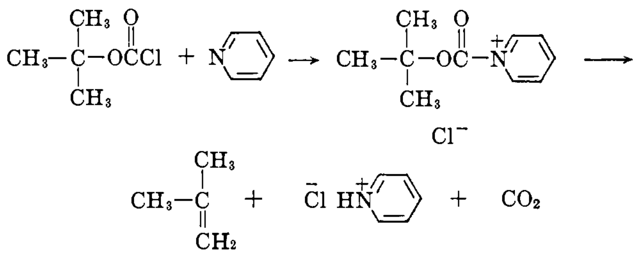
R	Yield, %	Reference
$-(CH_2)_2-$		354
C_2H_5	60–65	60
$-(CH_2)_3-$	25	354
$-(CH_2)_4-$	50–60	354
$CH_3(CH_2)_3$	78	351
$-(CH_2)_5-$	38	354
$1,4\text{-}C_6H_4$	58	354
$4\text{-}(Cl)C_6H_4$	70–80	351
$4\text{-}(NO_2)C_6H_4$	70–80	351
C_6H_5	70–80	351
1,4-Cyclohexylene (*cis*)		354
1,4-Cyclohexylene (*trans*)	53	354
Cyclohexyl	72	351
$-(CH_2)_6-$	60	354
$4\text{-}(CH_3)C_6H_4$	70–80	351
$-(CH_2)_7-$		354
$4\text{-}(CH_3CH_2O)C_6H_4$	70–80	351
$-(CH_2)_8-$		354
$-(CH_2)_9-$	35	354
$-(CH_2)_{10}-$	77	354
$1,4\text{-}[-(CH_2)_2OCO]_2C_6H_4$	76	354
$(CH_3)_2C(4\text{-}C_6H_4)_2$		354
Various bivalent radicals		480
Polymeric polyoxyethylene radicals	88–91	352, 353

for the preparation of acetylenic chlorides from their respective chloroformates (28, 231).

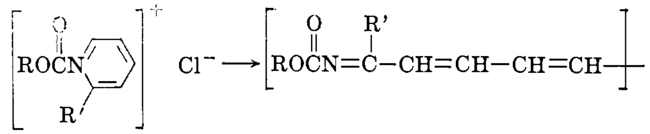


$$HC{\equiv}CCH_2O\overset{\overset{\large O}{\|}}{C}Cl \xrightarrow{(C_2H_5)_3N} \underset{86\%}{HC{\equiv}CCH_2Cl} + CO_2\uparrow$$

With chloroformates derived from tertiary alcohols, elimination occurs on reaction with pyridine (466). Extensive studies on the decomposition of chloroformates in the presence of organic bases have been made (108, 109, 111, 249).



Cleavage of the pyridine ring has been reported when 2- and 4-alkyl-substituted pyridines reacted with chloroformates (692, 693). This ring opening reaction



has been used for the degradation of some natural products (90, 232, 233, 242, 708).

Reaction of pyridine with ethyl chloroformate in the presence of zinc dust has been investigated (692, 693). The major products from this reaction are shown below.

TABLE IX

REACTIONS OF CHLOROFORMATES, $R(OCOCl)_n$, WITH AROMATIC AMINES

1. Primary Amines, $R'(NH_2)_m$

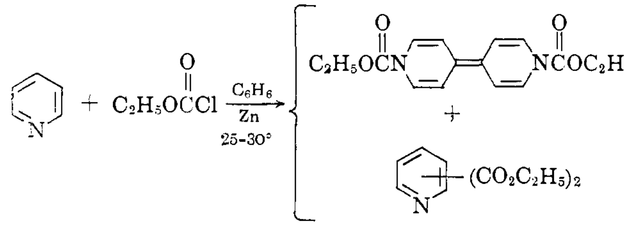
R	R'	Yield, %	Reference
CH_3	$4\text{-}(H_2O_3Sb)C_6H_4$	73	288
$-(CH_2)_2-$	C_6H_5		354
$Cl(CH_2)_2$	C_6H_5		521
$Cl(CH_2)_2$	2-Methyl-1-anthraquinonyl	70	507
$Cl(CH_2)_2$	Various radicals	>95	453
C_2H_5	C_6H_5	75	138, 719
C_2H_5	$4\text{-}(H_2O_3Sb)C_6H_4$	85	288
C_2H_5	$4\text{-}(NaO_3SCH_2O)C_6H_4$	77	36
C_2H_5	$2\text{-}(NaOCOCO)C_6H_4$		293
C_2H_5	$2,5\text{-}[CH_3COO(CH_2)_3](NO_2)C_6H_3$	74	539
C_2H_5	$CH_2(4\text{-}C_6H_4)_2$		99
$ClCH{=}CHCH_2$	C_6H_5		130
$-(CH_2)_3-$	C_6H_5		354
C_3H_7	$4\text{-}(H_2O_3Sb)C_6H_4$	87	288
$(CH_3)_2CH$	$4\text{-}(H_2O_3Sb)C_6H_4$	89	288
$CH_2OCOOCHCH_2$	Various radicals		658
$-CH_2CH{=}CHCH_2-$	C_6H_5		276
$BrCH_2C{\equiv}CCH_2$	Various radicals	>50	330, 331
$ClCH_2C{\equiv}CCH_2$	Various radicals	30–90	330, 331
$CH_2O(CH_2)_2CH$	C_6H_5		578
$-(CH_2)_4-$	C_6H_5		354
$+(CH_2)_2+_2O$	$3\text{-}(Cl)C_5H_4$	64	661
$+(CH_2)_2+_2O$	C_6H_5	78	661
C_4H_9	$4\text{-}(H_2O_3Sb)C_6H_4$	70	288
C_4H_9	Various radicals		120
$(CH_3)_2CHCH_2$	$4\text{-}(H_2O_3Sb)C_6H_4$	85	288
$-(CH_2)_5-$	C_6H_5		354
$1,4\text{-}C_6H_4$	C_6H_5		354
$4\text{-}(Cl)C_6H_4$	$1,4\text{-}C_6H_4$	91	568
C_6H_5	$1,4\text{-}C_6H_4$	57	568
C_6H_5	$2\text{-}(Cl)C_6H_4$		568
C_6H_5	C_6H_5	95	270, 484, 568
C_6H_5	Various radicals		484
$-(CH_2)_6-$	C_6H_5		354
$CH_3(CH_2)_5$	$4\text{-}[(C_2H_5)_2N(CH_2)_2OCO]C_6H_4$		508
$CH_3(CH_2)_5$	Various radicals		508
$-(CH_2)_7-$	C_6H_5		354
$-CH_2C(C_2H_5)_2CH_2-$	C_6H_5	67	439
$-CH_2C(CH_3)(C_3H_7)CH_2-$	C_6H_5		257
$-CH_2C(CH_3)(C_3H_7)CH_2-$	$4\text{-}(CH_3O)C_6H_4$		257
$-CH_2C(CH_3)(C_3H_7)CH_2-$	$4\text{-}(C_2H_5O)C_6H_4$		257
$CH_3(CH_2)_6$	$4\text{-}[(C_2H_5)_2N(CH_2)_2OCO]C_6H_4$		508
$CH_3(CH_2)_6$	Various radicals		508
$-(CH_2)_8-$	C_6H_5		354
$CH_3(CH_2)_7$	$4\text{-}[(C_2H_5)_2N(CH_2)_2OCO]C_6H_4$		508
$CH_3(CH_2)_7$	Various radicals		508
$2,3,5\text{-}(CH_3)_3C_6H_2$	C_6H_5		421
$-(CH_2)_9-$	C_6H_5		354
1-Naphthyl	1-Naphthyl		421
$-(CH_2)_{10}-$	C_6H_5		354
$CH_3(CH_2)_9$	$4\text{-}[(C_2H_5)_2N(CH_2)_2OCO]C_6H_4$		508
$CH_3(CH_2)_9$	Various radicals		508
$4\text{-}[CH_3(CH_2)_3OCO]C_6H_4$	$2\text{-}(CH_3O)C_6H_4$	71	425
$4\text{-}[CH_3(CH_2)_3OCO]C_6H_4$	Various radicals	72–98	425
$1,4\text{-}[(CH_2)_2OCO]_2C_6H_4$	C_6H_5		354
3-Cholesteryl	C_6H_5	85.2	413
3-Cholesteryl	$4\text{-}(H_2O_3As)C_6H_4$		433
Various aliphatic radicals	$4\text{-}(H_2O_3Sb)C_6H_4$	70–90	288
Various aliphatic radicals	1-Naphthyl		683
Various aliphatic radicals	2-Naphthyl		683

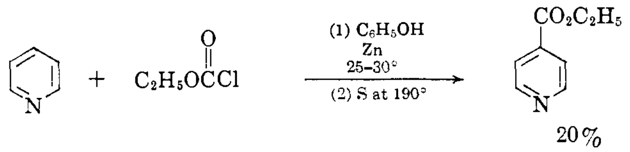
TABLE IX (*Continued*)

R	R′	Yield, %	Reference
Various aliphatic and cycloaliphatic radicals	4-[$(C_2H_5)_2N(CH_2)_2OCO]C_6H_4$	80-99	566
Various radicals	Various radicals containing the AsO_3H_2 substituent		1

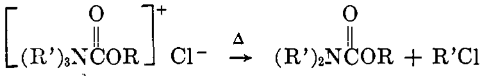
2. Secondary Amines R′R′′NH

R	R′	R′′	Reference
$Cl(CH_2)_2$	C_6H_5	CH_3	155
$Cl(CH_2)_2$	C_6H_5	C_6H_5	509
$CH_3O(CH_2)_2$	2-$(CH_3)C_6H_4$	C_2H_5	199
$CH_2{=}C{=}CHCH_2$	C_6H_5	CH_3	105, 106
3-Cholesteryl	C_6H_5	CH_3	454

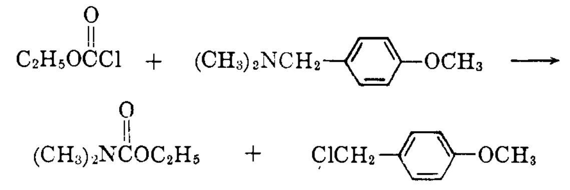




Trialkylamines react with chloroformates at higher temperatures to yield urethans; presumably the complex salts are intermediates. This reaction proceeds in high yields with trimethyl- and triethylamines (52, 103, 335). Suitably activated benzyl tertiary amines have given a slightly different reaction with ethyl chloroformate (409). Dimethylbenzylamine did not react under the same conditions which indicates the need for an electron-donating group on the ring of the benzylamine. However, more recent work has uncovered other examples of the debenzylation of tertiary amines with ethyl chloroformate (739).



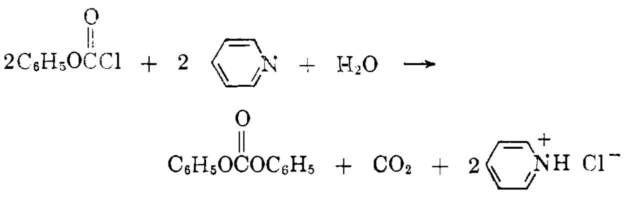
$$\left[(R')_3N\overset{O}{\overset{\|}{C}}OR\right]^+ Cl^- \xrightarrow{\Delta} (R')_2N\overset{O}{\overset{\|}{C}}OR + R'Cl$$

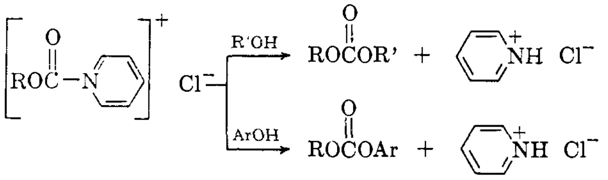


Complexes of chloroformates with dimethylaniline have not been studied extensively (590). It has been reported that the complex between phenyl chloroformate and dimethylaniline decomposes at 100° to yield phenol, carbon dioxide, and dimethylaniline.

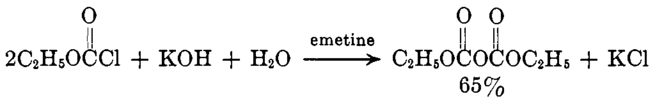
b. Reaction of Tertiary Amine–Chloroformate Complexes with Hydroxylic Compounds

It has been reported in the literature that the thermal reaction of pyridine with an aryl chloroformate leads directly to a diaryl carbonate (449, 484). Work has shown that water is a necessary reactant for this reaction to proceed (47). The complex of pyridine and phenyl chloroformate can be heated at 130° in chlorobenzene with only traces of diphenyl carbonate being formed. Reaction of this complex with water at room temperature, however, gave quantitative yields of diphenyl carbonate. Similarly, reaction of these pyridine–chloroformate complexes with alcohols and phenols gave the expected carbonates in high yields (123). Although complexes derived from the other types of tertiary amines have not been studied in any detail, they should behave similarly.





One difference that has been noted, however, is the reported (69, 543) preparation of pyrocarbonates by treatment of chloroformates with aqueous potassium hydroxide in the presence of the alkaloid amine, emetine. Other amines were tried in this reaction but none was as useful as emetine.



$$2C_2H_5O\overset{O}{\overset{\|}{C}}Cl + KOH + H_2O \xrightarrow{\text{emetine}} C_2H_5O\overset{O}{\overset{\|}{C}}O\overset{O}{\overset{\|}{C}}OC_2H_5 + KCl$$

65%

5. *Heterocyclic Amines*

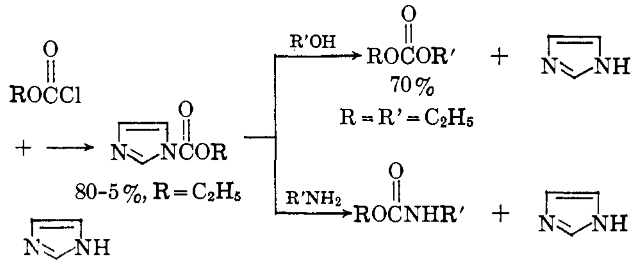
Chloroformates have been treated with many nitrogen-containing heterocycles to yield urethans. Inorganic base was used as the acid acceptor. Table X is illustrative of the various types of chloroformates and heterocycles that have been used.

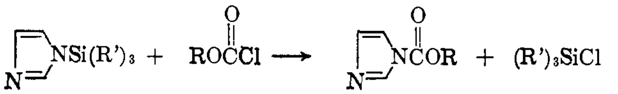
Table X

Reactions of Chloroformates, $R(OCOCl)_n$, with Heterocyclic Amines, R'R''NH

R	R'R''NH	Yield, %	Reference
CH_3	Benzopyrazole	90	24
CH_3	Carbazol		424
CH_3CH_2	Imidazol	80–85	649
CH_3CH_2	2,4-Diamino-6-methyl-s-triazine	32	192
CH_3CH_2	Piperidine		627
CH_3CH_2	Benzopyrazol	97	24
CH_3CH_2	2,4-Diamino-6-phenyl-s-triazine	77	192
CH_3CH_2	Carbazol		424
CH_3CH_2	Various aminopyrimidines		259
$ClCH_2C{\equiv}CCH_2$	2-Aminopyridine	11	330
$ClCH_2C{\equiv}CCH_2$	Various heterocyclic amines	17–66	330
$-CH_2CH{=}CHCH_2-$	Piperidine		276
$(CH_3)_2CH(CH_2)_2$	Benzopyrazol	90	24
C_6H_5	Benzopyrazol	86	24
C_6H_5	Various aminopyrimidines		259
$C_6H_5CH_2$	Benzopyrazol	83	24

Urethans prepared from imidazole and chloroformates are very reactive acylating agents (649). These compounds have been used in the synthesis of monomers and polymers by their further reaction with compounds containing active hydrogen. The use of N-trimethylsilyl derivatives of nitrogen-containing heterocycles for reaction with chloroformates has been reported to give better yields and reaction rates (64).

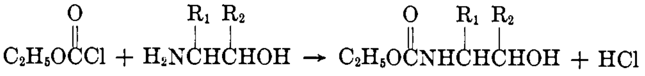




95%, $R = C_2H_5$

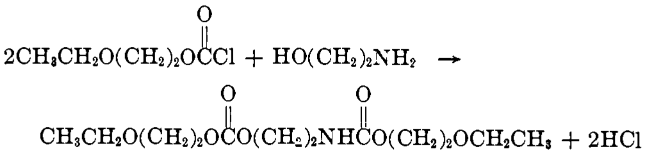
6. *Amino Alcohols*

Chloroformates react with primary or secondary amino alcohols at the amino group more rapidly than at the hydroxyl group (127, 510, 511). Examples are shown in the following equation and in Table XI. Acid



$$C_2H_5O\overset{O}{\overset{\|}{C}}Cl + H_2N\overset{R_1}{\overset{|}{C}}H\overset{R_2}{\overset{|}{C}}HOH \rightarrow C_2H_5O\overset{O}{\overset{\|}{C}}NH\overset{R_1}{\overset{|}{C}}H\overset{R_2}{\overset{|}{C}}HOH + HCl$$

acceptors can be used in this reaction. Hydroxyurethans of this type can be cyclized with base to yield 2-oxazolidones (5). Further reaction with additional chloroformate leads to acylation of the hydroxyl group.



$$2CH_3CH_2O(CH_2)_2O\overset{O}{\overset{\|}{C}}Cl + HO(CH_2)_2NH_2 \rightarrow$$
$$CH_3CH_2O(CH_2)_2O\overset{O}{\overset{\|}{C}}O(CH_2)_2NH\overset{O}{\overset{\|}{C}}O(CH_2)_2OCH_2CH_3 + 2HCl$$

When the amino group of the amino alcohol is tertiary, the hydrochloride of the aminocarbonate is isolated

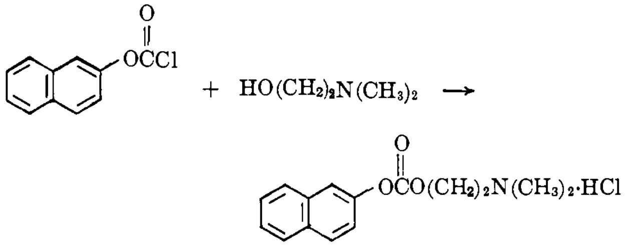


Table XI

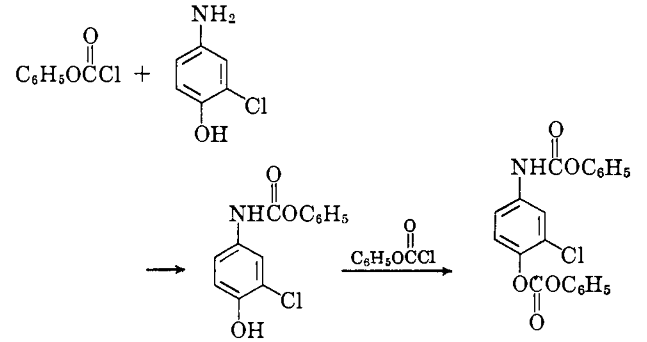
Reactions of Chloroformates, ROCOCl, with Amino Alcohols, $R_1R_2NR_3OH$

R	$R_1R_2NR_3OH$	Acylation site	Yield, %	Reference
Br_3CCH_2	$(CH_3)_2N(CH_2)_2OH$	O		101
CH_3CH_2	$H_2N(CH_2)_2OH$	N	79	597
CH_3CH_2	2-Hydroxycyclohexylamine	N	75	597
CH_3CH_2	$H_2NCHR'CHR''OH$ (R' and R'' are various alkyl radicals)	N	Varied	510, 511
$CH_3CH_2O(CH_2)_2$	$H_2N(CH_2)_2OH$	O and N		525
6-Bromo-2-naphthyl	$(CH_3)_2N(CH_2)_2OH$	O	82	570
2-Naphthyl	$(CH_3)_2N(CH_2)_2OH$	O	80	570
3-Methyl-6-isopropylphenyl	$(C_2H_5)_2N(CH_2)_2OH$	O		742
Various aliphatic and aromatic radicals	$\underbrace{CH_2(CH_2)_3N}CH_2CH(C_6H_5)OH$	O	Varied	294
Various aliphatic and aromatic radicals	$\underbrace{(CH_2)_2O(CH_2)_2N}CH_2CH(C_6H_5)OH$	O	Varied	294
Various aliphatic and aromatic radicals	$\underbrace{CH_2(CH_2)_4N}CH_2CH(C_6H_5)OH$	O	Varied	294
Various aliphatic and aromatic radicals	$\underbrace{(CH_2)_2N(CH_3)(CH_2)_2N}CH_2CH(C_6H_5)OH$	O	Varied	294
$-(CH_2CH_2O)_n-$	$CH_3(CH_2)_{11}N(CH_3)(CH_2CH_2O)_nH$	O		127

(101, 294, 570, 742). Generation of the free amine can be accomplished by reaction of the hydrochloride with base. Nonionic detergents have been prepared from polyethylene glycol bis(chloroformates) and long-chain tertiary amino alcohols (127).

7. *Aminophenols*

As with amino alcohols, the amino group of aminophenols is more reactive toward a chloroformate (568). An example is shown and others are tabulated in Table XII. With *o*-aminophenol, benzoxazolones are produced *via* cyclization of the intermediate phenolic urethan (567).



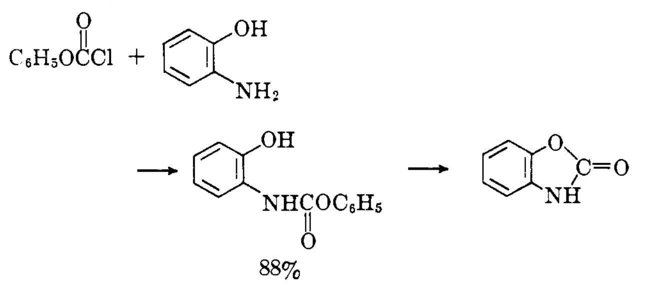


TABLE XII

REACTIONS OF CHLOROFORMATES, ROCOCl, WITH AMINOPHENOLS, H_2NArOH

R	ArOH	Yield, %	Reference
CH_3	4-Hydroxyphenyl		572
CH_3CH_2	4-Hydroxyphenyl		572
CH_3CH_2	2-Hydroxyphenyl		572
$CH_3(CH_2)_2$	4-Hydroxyphenyl		572
$CH_3(CH_2)_3$	4-Hydroxyphenyl		572
$CH_3(CH_2)_3$	2-Hydroxyphenyl		572
$CH_3CH_2CH(CH_3)$	4-Hydroxyphenyl		572
$CH_3(CH_2)_4$	4-Hydroxyphenyl		572
C_6H_5	3,5-Dichloro-4-hydroxyphenyl	64	572
$CH_3(CH_2)_5$	2-Hydroxyphenyl		572
$C_6H_5CH_2$	4-Hydroxyphenyl		572
$C_6H_5CH_2$	2-Hydroxyphenyl		572
$CH_3(CH_2)_6$	4-Hydroxyphenyl	93	573
$CH_3(CH_2)_6$	2-Hydroxyphenyl		573
$C_6H_5(CH_2)_2$	4-Hydroxyphenyl	95	573
$CH_3(CH_2)_7$	4-Hydroxyphenyl	83	573
$CH_3(CH_2)_7$	2-Hydroxyphenyl		573
$CH_3(CH_2)_9$	4-Hydroxyphenyl	86	573
$CH_3(CH_2)_{13}$	4-Hydroxyphenyl	51	573
Various aryl radicals	2-Hydroxyphenyl	88	567

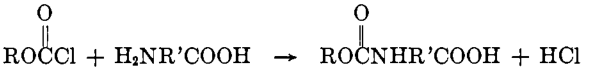
8. *Amino Acids*

The reaction of chloroformates with amino acids has been used for the protection of the amine group during peptide synthesis (Table XIII). In particular, benzyl chloroformate has been preferred for this purpose. The derived urethan can be hydrogenolyzed easily to free the amine after the carboxyl group has reacted further (58, 223, 350, 542). The above equation illustrates the greater reactivity of the amine group toward the chloroformate than the acid group in amino acids. A similar reactivity was found with *p*-aminophenylarsinic acid (217).

TABLE XIII

REACTIONS OF CHLOROFORMATES, $R(OCOCl)_n$, WITH AMINO ACIDS, $NH_2R'H$

R	R'H	Yield, %	Reference
CH_3	Various aminoaryl arsonic acids	65-91	287, 460, 461
C_2H_5	Various aminoaryl arsonic acid	59-90	287, 460, 461
C_3H_7	Various aminoaryl arsonic acids	35-90	287, 460, 461
$(CH_3)_2CH$	Various aminoaryl arsonic acids	45-85	287, 460 461
$XCH_2C{\equiv}CCH_2$ (X is a halogen)	CH_2COOH	26	330
$XCH_2C{\equiv}CCH_2$ (X is a halogen)	Various radicals	11-96	330
$-CH_2CH{=}CHCH_2-$	CH_2COOH		276
$-CH_2CH{=}CHCH_2-$	$(CH_2)_3COOH$		276
$-CH_2CH{=}CHCH_2-$	4-$(HOCO)C_6H_4$		276
$CH_3(CH_2)_3$	Various radicals	40-90	287, 460, 461
$(CH_3)_2CHCH_2$	Various radicals	50-90	287, 460, 461
2-$(NO_2)C_6H_4$	$CH(CH_3)COOH$		349
4-$(Br)C_6H_4CH_2$	CH_2COOH		119
4-$(NO_2)C_6H_4CH_2$	CH_2COOH	78	107
$C_6H_5CH_2$	CH_2COOH	90	112
$C_6H_5CH_2$	$CH(CH_3)(CH_2)_{10}COOH$		350
$C_6H_5CH_2$	$CH(CH_3)(CH_2)_{11}COOH$	38	350
$C_6H_5CH_2$	Various radicals	Varied	58, 63, 223, 542
4-$(CH_3)C_6H_4$	$-CH_2COOH$		119
4-$(CH_3)C_6H_4$	$-CH(CH_3)COOH$		349
1-Naphthyl	$-CH_2COOH$		119
2-Naphthyl	Various radicals	40-90	734
Various aliphatic and aromatic radicals	Various degraded peptides		646



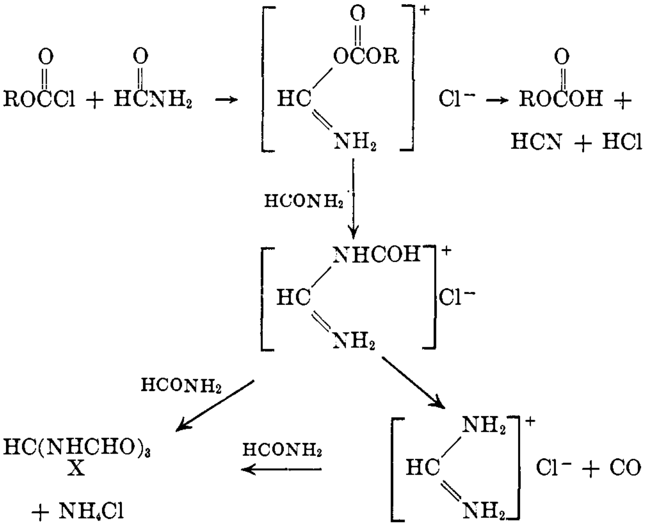
$$RO\overset{O}{\overset{\|}{C}}Cl + H_2NR'COOH \rightarrow RO\overset{O}{\overset{\|}{C}}NHR'COOH + HCl$$

This reaction has found utility for the resolution of optically active alcohols (6). A racemic alcohol is converted to its chloroformate ester which is then treated with an optically active amino acid. The resulting urethan–acid was then separated into its antipodes, followed by regeneration of the original alcohol.

No examples have been found in the literature where the urethan acid has been reacted further with another mole of chloroformate to yield the ester or the mixed carboxylic–carbonic anhydride. This reaction should be possible in view of the recent synthesis and isolation of mixed carboxylic–carbonic anhydrides. A patent describing the preparation of useful surface active agents by the reaction of chloroformates with amino acids or partially degraded peptides has been issued (646).

9. Amides

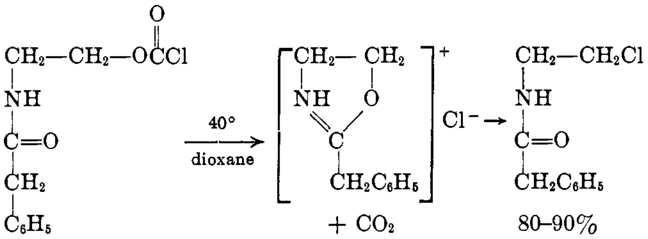
Only a few examples of the reaction of a chloroformate with an amide have appeared in the literature. Apparently, either O- or N-acylation can occur depending on the specific reactants. Formamide reacted with ethyl chloroformate to yield tris(formylamino)-methane (X) in 31% yield along with other products (87). The initial step was postulated to be O-acylation followed by reaction along the paths shown in the diagram.



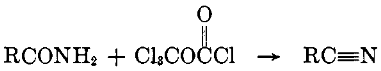
Hall has found that chloroformates form conducting solutions in dimethylformamide (281). This observation was attributed to the following reaction for which he has obtained additional evidence based on the reactivity of these complexes.

$$RO\overset{O}{\overset{\|}{C}}Cl + OHCN(CH_3)_2 \rightarrow \left[RO\overset{O}{\overset{\|}{C}}OCH{=}N(CH_3)_2\right]^+ Cl^-$$

An intramolecular assist by an amide group has been postulated to aid the decomposition of a chloroformate prepared from a β-hydroxyethylamide (55).

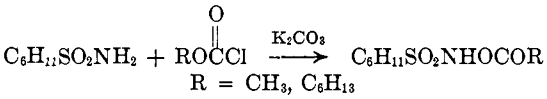


Trichloromethyl chloroformate has been used to dehydrate amides to nitriles on simple heating in an inert solvent (303).



$$RCONH_2 + Cl_3CO\overset{O}{\overset{\|}{C}}Cl \rightarrow RC{\equiv}N$$

Examples of the acylation of a sulfonamide have appeared recently (22).



$$C_6H_{11}SO_2NH_2 + RO\overset{O}{\overset{\|}{C}}Cl \xrightarrow{K_2CO_3} C_6H_{11}SO_2NHOCOR$$

$$R = CH_3, C_6H_{13}$$

Additional examples are listed in Table XIV.

TABLE XIV

REACTIONS OF CHLOROFORMATES, ROCOCl, WITH SULFONAMIDES, R'SO$_2$NH$_2$

R	R'	Yield, %	Reference
CH_3	Cyclohexyl		23
C_2H_5	CH_3	60–80	114
C_2H_5	2-Thienyl		114
C_2H_5	$CH_3(CH_2)_3$		114
C_2H_5	Cyclopentyl		114
C_2H_5	$CH_3(CH_2)_4$		114
C_2H_5	Cyclohexyl		114
C_2H_5	$CH_3(CH_2)_5$		114
C_2H_5	4-$(CF_3)C_6H_4$		552
C_2H_5	2,4-$(NO_2)(CF_3)C_6H_3$		552
C_2H_5	4-$(COH)C_5H_4$		482
C_2H_5	$C_6H_5CH_2$		114
C_2H_5	4-$(CH_3CONHCH_2)C_6H_4$		482
C_2H_5	4-$[CH_3CONH(CH_2)_2]C_6H_4$		482
C_2H_5	4-$[CH_3CONHCH(CH_3)]C_6H_4$		482
C_2H_5	$CH_3(CH_2)_9$	60–80	114
C_3H_7	$CH_3(CH_2)_3$		114
$CH_3O(CH_2)_2$	4-$(CH_3)C_6H_4$		22
$CH_3(CH_2)_3$	$CH_3(CH_2)_3$	60–80	114
$CH_3(CH_2)_3$	$CH_3(CH_2)_4$		114
$CH_3CH(C_2H_5)$	$CH_3(CH_2)_4$		114
$CH_3(CH_2)_4$	$CH_3(CH_2)_3$		114
$CH_3(CH_2)_5$	$CH_3(CH_2)_3$		114
$CH_3(CH_2)_5$	Cyclohexyl		23

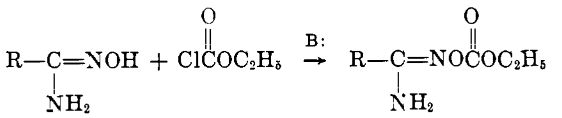
10. Amidoximes

Amidoximes are O-acylated by chloroformates (Table XV) in high yields. An equivalent of the amidoxime can act as the hydrogen chloride acceptor although aqueous base or organic amines can serve the same purpose (203, 563, 669, 735). Amidoximes derived from

TABLE XV

REACTIONS OF ETHYL CHLOROFORMATE WITH AMIDOXIMES, R'C(NH$_2$)=NOH

R'	Reference
3-Pyridyl	474
4-$(NO_2)C_6H_4$	706
3-$(NO_2)C_6H_4$	625
C_6H_5	4, 203, 204
2-$(HO)C_6H_4$	477
4-$(CH_3)C_6H_4$	629
4-$(CH_3O)C_6H_4$	624
$C_6H_5CH(OH)$	271
2,4-$(CH_3)_2C_6H_3$	535
6-Quinolyl	62
1-Naphthyl	588
2-Naphthyl	588
Various radicals	678, 679

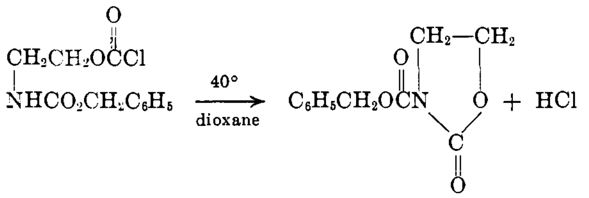


$$\underset{\mathrm{NH_2}}{\mathrm{R{-}C}}\mathrm{{=}NOH} + \mathrm{Cl\overset{O}{\overset{\|}{C}}OC_2H_5} \xrightarrow{B:} \underset{\mathrm{NH_2}}{\mathrm{R{-}C}}\mathrm{{=}NO\overset{O}{\overset{\|}{C}}OC_2H_5}$$

tertiary amides and bis(amidoximes) react similarly (83, 748). The products are very useful intermediates for the preparation of various types of heterocyclic ring systems.

11. Urethans

Heating chloroformates prepared from β-hydroxyethylurethans gives 2-oxazolidones in excellent yields (55).

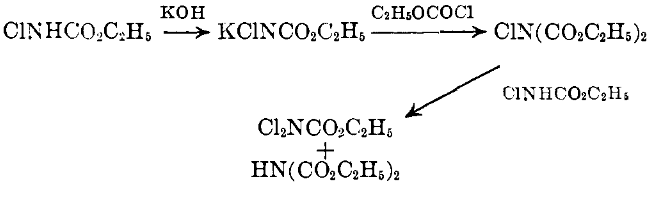


Acylation of ammonia with a chloroformate was described earlier. Further acylation with additional chloroformate is readily accomplished by using the sodium salt of the urethan as shown in the following equations (176, 407, 741). The use of different chloroformates at the different steps has provided mixed urethans. This reaction has also been carried out on the sodio derivatives of phenylurethan and the ethylurethan of glycine (177, 608, 636, 651).

$$\mathrm{H_2NCO_2C_2H_5} \xrightarrow{\mathrm{Na}} \mathrm{NaNHCO_2C_2H_5} \xrightarrow{\mathrm{C_2H_5OCOCl}} \mathrm{NH(CO_2C_2H_5)_2}$$

$$\mathrm{NH(CO_2C_2H_5)_2} \xrightarrow{\mathrm{Na}} \mathrm{NaN(CO_2C_2H_5)_2} \xrightarrow{\mathrm{C_2H_5OCOCl}} \mathrm{N(CO_2C_2H_5)_3}$$

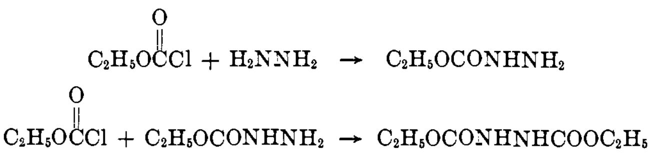
The reaction of N-chloroethylurethan with ethyl chloroformate in the presence of potassium hydroxide has been reported to yield N,N-dichloroethylurethan and diethyl azamalonate (681). A proposed reaction scheme is shown.



$$\mathrm{ClNHCO_2C_2H_5} \xrightarrow{\mathrm{KOH}} \mathrm{KClNCO_2C_2H_5} \xrightarrow{\mathrm{C_2H_5OCOCl}} \mathrm{ClN(CO_2C_2H_5)_2} \xrightarrow{\mathrm{ClNHCO_2C_2H_5}} \mathrm{Cl_2NCO_2C_2H_5} + \mathrm{HN(CO_2C_2H_5)_2}$$

12. Hydrazine

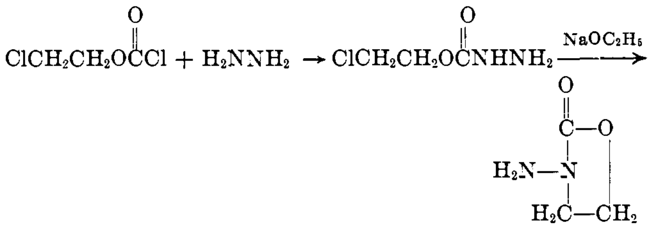
Hydrazine reacts with chloroformates to yield the expected hydrazides, depending on whether 1 or 2 moles of chloroformate is employed (162, 163, 274).



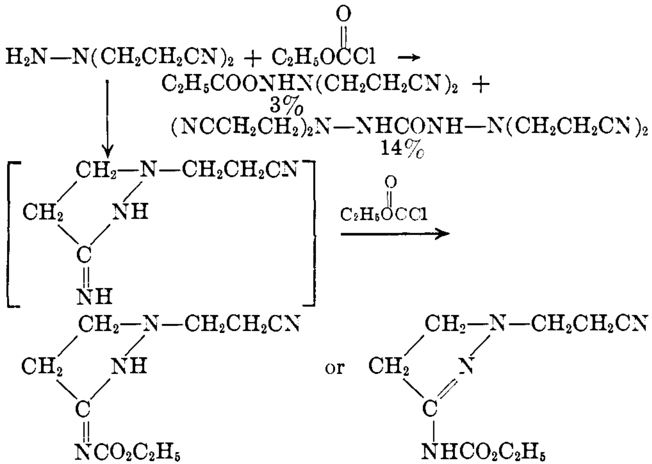
$$\mathrm{C_2H_5O\overset{O}{\overset{\|}{C}}Cl + H_2NNH_2 \rightarrow C_2H_5OCONHNH_2}$$

$$\mathrm{C_2H_5O\overset{O}{\overset{\|}{C}}Cl + C_2H_5OCONHNH_2 \rightarrow C_2H_5OCONHNHCOOC_2H_5}$$

Cyclization of the hydrazide formed from the chloroformate of 2-chloroethanol with sodium ethoxide offers a route to N-amino-2-oxazolidones (172).



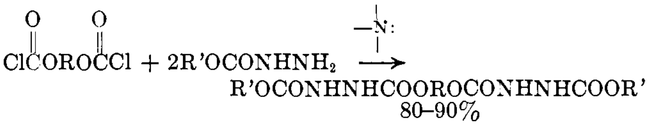
1,1-Bis(2-cyanoethyl) hydrazine reacted with ethyl chloroformate to yield a pyrazolidine (XI) in addition to low yields of the expected carbazate and carbohydrazide (442).



XI, 60%

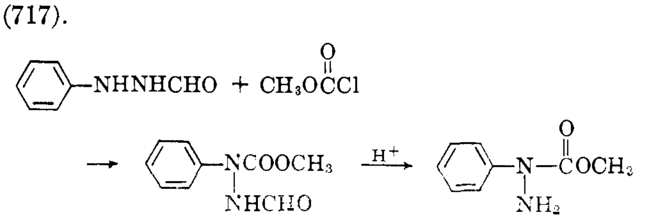
13. Hydrazides

A series of bis(hydrazodicarboxylates) has been prepared from aliphatic and aromatic bis(chloroformates) by reaction with hydrazides (565, 724).

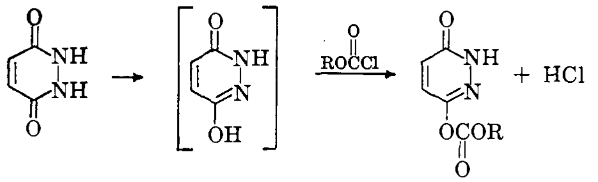


$$\mathrm{Cl\overset{O}{\overset{\|}{C}}ORO\overset{O}{\overset{\|}{C}}Cl + 2R'OCONHNH_2 \xrightarrow{-\overset{|}{N}:} \underset{80\text{–}90\%}{R'OCONHNHCOOROCONHNHCOOR'}}$$

An acid acceptor was used. The formyl hydrazide shown below was acylated with methyl chloroformate (717).

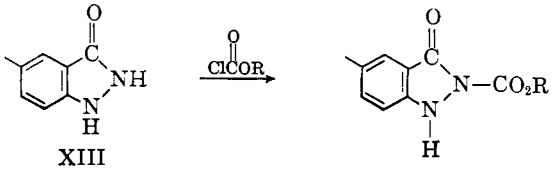


O-Acylation occurred by reaction of maleic hydrazide with ethyl chloroformate to yield XII (652). N-Acyl-



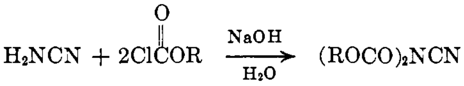
XII

ation has been observed with the cyclic hydrazide XIII to yield the depicted products, which have utility as color couplers in color photography (736).

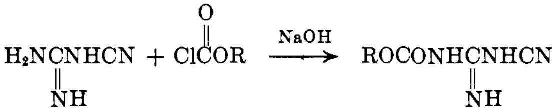

XIII

14. Cyanamid

Both hydrogens of cyanamid have been acylated by chloroformates in high yields (40, 179, 368, 463). Polymerizable derivatives of cyanamid have been prepared by using allyl chloroformate in this reaction (85, 258).


$$H_2NCN + 2Cl\overset{O}{\overset{\|}{C}}OR \xrightarrow[H_2O]{NaOH} (ROCO)_2NCN$$

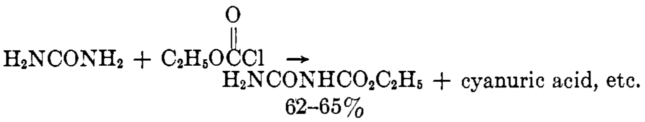
Dicyandiamide has been monoacylated (70–95% yields) under similar conditions (7, 560).


$$\underset{\underset{NH}{\|}}{H_2NCNHCN} + Cl\overset{O}{\overset{\|}{C}}OR \xrightarrow{NaOH} \underset{\underset{NH}{\|}}{ROCONHCNHCN}$$

These products have been described as possessing a variety of uses.

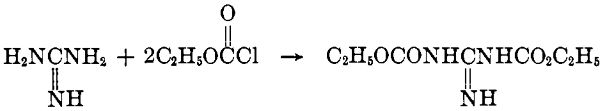
15. Urea

Urea has been monoacylated by a chloroformate (165, 610, 718).


$$H_2NCONH_2 + C_2H_5O\overset{O}{\overset{\|}{C}}Cl \rightarrow H_2NCONHCO_2C_2H_5 + \text{cyanuric acid, etc.}$$
$$62\text{–}65\%$$

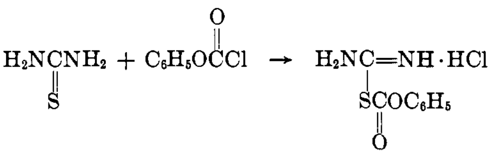
16. Guanidine

Guanidine has been diacylated with ethyl chloroformate (522).

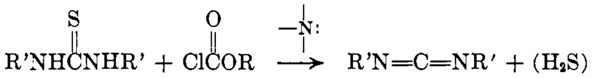

$$\underset{\underset{NH}{\|}}{H_2NCNH_2} + 2C_2H_5O\overset{O}{\overset{\|}{C}}Cl \rightarrow \underset{\underset{NH}{\|}}{C_2H_5OCONHCNHCO_2C_2H_5}$$

17. Thioureas

Thiourea has been reported to react with chloroformates as shown (181).


$$\underset{\underset{S}{\|}}{H_2NCNH_2} + C_6H_5O\overset{O}{\overset{\|}{C}}Cl \rightarrow \underset{\underset{\underset{O}{\|}}{SCOC_6H_5}}{\underset{|}{H_2NC{=}NH\cdot HCl}}$$

In the presence of an acid acceptor, substituted thioureas have yielded carbodiimides in fair yields on reaction with a chloroformate (144).


$$R'NH\overset{S}{\overset{\|}{C}}NHR' + Cl\overset{O}{\overset{\|}{C}}OR \xrightarrow{-\overset{|}{\underset{|}{N}}:} R'N{=}C{=}NR' + (H_2S)$$

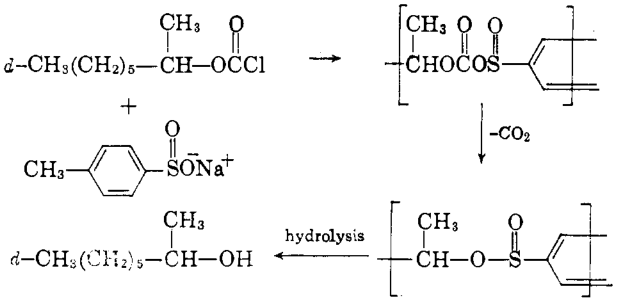
18. Miscellaneous Nitrogen-Containing Compounds

A series of Swiss patents describe several uses for the water-soluble products obtained from reaction of various chloroformates with imidazolsulfonic acids (*i.e.*, sodium hendecylbenzimidazolsulfonic acid). Foaming agents and textile-dyeing assistants are among the uses claimed (640–645).

E. MISCELLANEOUS REACTIONS AND SYNTHESES

1. Sulfinic Acids

Very little research has been done on this reaction (537). The reaction of sodium *p*-toluenesulfinate with *d*-2-octyl chloroformate yielded alkyl *p*-toluenesulfinates (335, 336). This result is in contrast to the fact that sulfones are obtained by reaction of alkyl halides with sodium *p*-toluenesulfinate. Hydrolysis of the sulfinate ester obtained from this reaction gave *d*-2-octanol of retained configuration. This fact was interpreted as evidence that an intermediate anhydride was formed which decomposed without alkyl–O cleavage, resulting in retention of configuration.



2. Active Methylene Compounds

There are many reported examples (Table XVI) of the acylation of various types of active methylene compounds by chloroformates. Apparently much of this work was done quite early, so that the poor yields that have been reported for these reactions might be increased by using modern techniques and condensing agents. Dimethyl malonate has been converted to the tetracarboxylate by this method (135, 136, 153, 517, 518, 622).

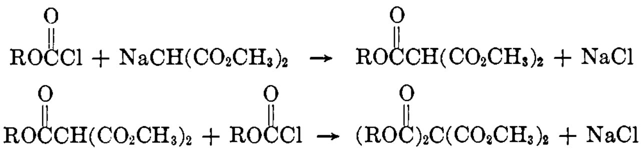
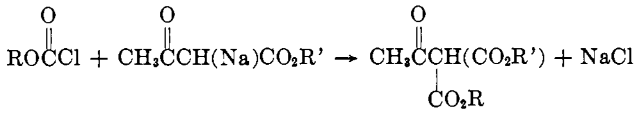

$$RO\overset{O}{\overset{\|}{C}}Cl + NaCH(CO_2CH_3)_2 \rightarrow RO\overset{O}{\overset{\|}{C}}CH(CO_2CH_3)_2 + NaCl$$
$$RO\overset{O}{\overset{\|}{C}}CH(CO_2CH_3)_2 + RO\overset{O}{\overset{\|}{C}}Cl \rightarrow (RO\overset{O}{\overset{\|}{C}})_2C(CO_2CH_3)_2 + NaCl$$

TABLE XVI

REACTIONS OF CHLOROFORMATES, ROCOCl, WITH ACTIVE METHYLENIC COMPOUNDS, R'H

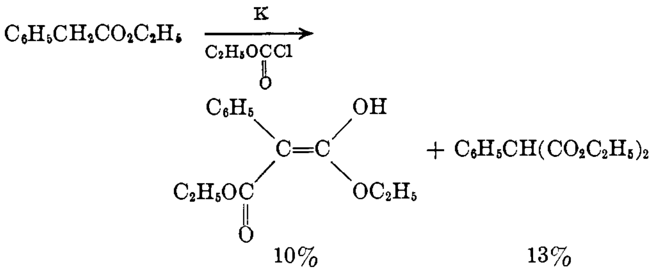
R	R'H	Site of carbalkoxylation	Yield, %	Reference
CH_3	5,5-Dimethyl-1,3-cyclohexanedione	O		633
CH_3	Dibenzoylmethane	C and O	Varies	473
C_2H_5	Ethyl acetate	C		606
C_2H_5	Ethyl cyanoacetate	C		283, 284, 302
C_2H_5	Dimethyl malonate	C		136, 153
C_2H_5	Cyclohexanone	O		285, 286
C_2H_5	Ethyl acetoacetate	C and O		153, 470, 471, 472, 606, 725
C_2H_5	Ethyl bis(methoxycarbonyl)acetate	C		153, 517, 518, 622
C_2H_5	Propiophenone	O		285, 286
C_2H_5	Butyrophenone	O		285, 286
C_2H_5	Isobutyrophenone	O		285, 286
C_2H_5	Ethyl phenylacetate	C		607
C_2H_5	Ethyl 2-(phenyl)butyrate	C		703

Acetoacetates are converted to acetyl malonates (137, 139, 153, 470, 471, 725).

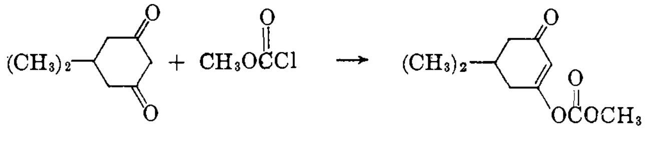


$$RO\overset{O}{\overset{\|}{C}}Cl + CH_3\overset{O}{\overset{\|}{C}}CH(Na)CO_2R' \rightarrow CH_3\overset{O}{\overset{\|}{C}}\underset{CO_2R}{\underset{|}{C}}H(CO_2R') + NaCl$$

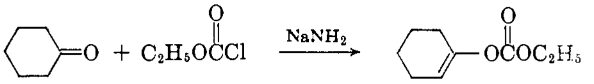
Cyanoacetates have been converted to cyanomalonates (283, 284, 302). α-Aryl acetates have also been acylated by chloroformates using potassium or sodamide as catalysts (473, 607, 703). Mixtures of products and low yields have been reported.



O-Acylation has been observed in this reaction. Dibenzoylmethane gave a mixture of the C- and O-acylated products on treatment with methyl chloroformate in the presence of sodamide (473). In some cases, O-acylation is the main reaction, as with the β-diketone, dimedon (633).

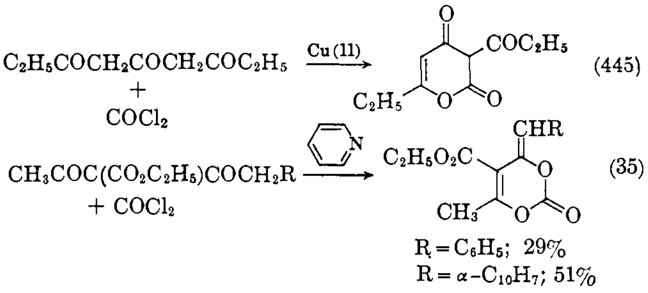


Cyclohexanone reacted similarly in the presence of sodamide (285, 286).



A series of phenyl alkyl ketones gave O-acylated products on reaction with ethyl chloroformate (285, 286).

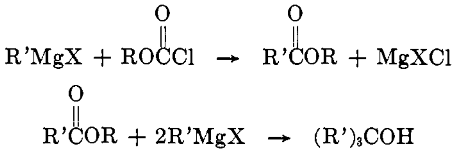
The copper(II) chelate of ethyl acetoacetate has been treated with ethyl chloroformate to yield the analogous chelate of acetylmalonic ester (472). Similar results were obtained with the Cu(II) chelate of benzoylacetic ester which yielded the expected benzoyl malonate. The following two reactions illustrate cyclizations of β-dicarbonyl compounds through C- and O-acylations.



3. *Organometallic Compounds*

Many diverse types of organometallic compounds react with chloroformates. They are shown in Table XVII.

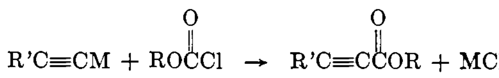
Organometallic compounds of the Grignard type react with chloroformates to yield esters (333, 410, 452, 571). However, with the more reactive organometallic compounds, the initially formed ester reacts further to yield the tertiary alcohol. Usually both products are formed although their relative amounts can be controlled by the molar amounts of the starting materials that are used and by the reaction conditions employed.



$$R'MgX + RO\overset{O}{\overset{\|}{C}}Cl \rightarrow R'\overset{O}{\overset{\|}{C}}OR + MgXCl$$

$$R'\overset{O}{\overset{\|}{C}}OR + 2R'MgX \rightarrow (R')_3COH$$

Acetylenic Grignard reagents or alkali metal acetylides yield the carboxylic ester with little or no tertiary carbinol being formed (190, 485, 486, 534). However, the reaction of ethyl chloroformate with the lithium derivative of ethoxyacetylene gave only a small yield of the expected ester. Surprisingly, the lithium derivatives of the sulfur analog of ethoxyacetylene gave a 56% yield of the expected ester in the same reaction (13).



$$R'C{\equiv}CM + RO\overset{O}{\overset{\|}{C}}Cl \rightarrow R'C{\equiv}C\overset{O}{\overset{\|}{C}}OR + MCl$$

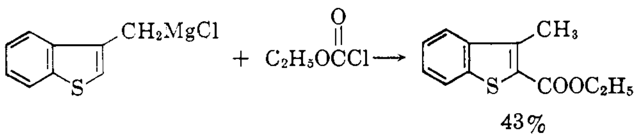
3-Thianapthenylmethylmagnesium chloride reacted

TABLE XVII

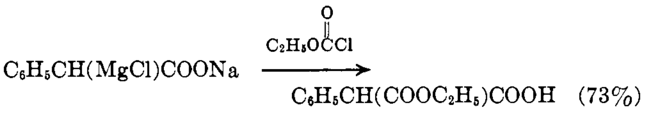
REACTIONS OF CHLOROFORMATES, ROCOCl, WITH ORGANOMETALLIC DERIVATIVES

R	Organometallic Derivative	Product(s)	Yield, %	Reference
CH_3	$(CH_3)_2Zn$			94
CH_3	$(CH_3)_2CHMgCl$			571
C_2H_5	C_2H_5MgBr			410, 452
C_2H_5	C_2H_5MgI			452
C_2H_5	$CH_3C{\equiv}CMgBr$			190, 485, 486
C_2H_5	$CH_3C{\equiv}CNa$			190, 485, 486
C_2H_5	$CH_2{=}CHCH_2MgBr$			410
C_2H_5	$CH_2{=}CHCH_2ZnI$	$(CH_2{=}CHCH_2).COH$	40	92, 574, 575
C_2H_5	$C_2H_5SC{\equiv}CLi$	$C_2H_5SC{\equiv}CCOOC_2H_5$	56	13
C_2H_5	$CH_3(CH_2)_3MgBr$			410
C_2H_5	$(CH_3)_2NCH_2C{\equiv}CNa$	$(CH_3)_2NCH_2C{\equiv}CCOOC_2H_5$	24	534
C_2H_5	C_6H_5MgBr	$C_6H_5COOC_2H_5$	16–75	333
		$(C_6H_5)_3COH$	9–34	
C_2H_5	$[C_6H_5Br + NaHg]$			102, 740
C_2H_5	$C_6H_5P(MgBr)_2$			357
C_2H_5	$(CH_3)_2N(CH_2)_2C{\equiv}CNa$	$(CH_3)_2N(CH_2)_2C{\equiv}CCOOC_2H_5$	23	534
C_2H_5	$C_6H_5CH_2MgBr$	$C_6H_5CH_2COOC_2H_5$	43	333
		$(C_6H_5CH_2)_3COH$		
C_2H_5	$C_6H_5CH(MgCl)COONa$			650
C_2H_5	1,4-$(CH_3)(SO_2CH_2MgBr)C_6H_4$	1,4-$(CH_3)(SO_2CH_3)C_6H_4$	70	226
C_2H_5	$(CH_3)_2N(CH_2)_5C{\equiv}CNa$	1,4-$(CH_3)(SO_2CH_2COOC_2H_5)C_6H_4$	22	534
C_2H_5	2-Methyl-2,5-(dimethylmethano)cyclohexylmagnesium chloride	$(CH_3)_2N(CH_2)_5C{\equiv}CCOOC_2H_5$	53	591, 700
C_2H_5	$(C_6H_5)_2PMgBr$			357
C_2H_5	$(CH_3)_2N(CH_2)_9C{\equiv}CNa$	$(CH_3)_2N(CH_2)_9C{\equiv}CCOOC_2H_5$		534
C_2H_5	$RC{\equiv}CMgBr$ (R are various aliphatic radicals)			190, 485, 486
C_2H_5	$RC{\equiv}CNa$ (R are various aliphatic radicals)			190, 485, 486

with ethyl chloroformate with rearrangement to yield the 2-carboxylate (243). None of the expected ester was found in the reaction product.

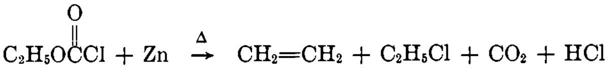


Half-esters of malonic acid have been prepared by the following reaction (650).



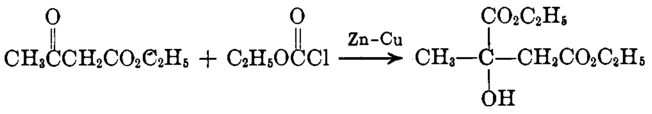
$$C_6H_5CH(MgCl)COONa \xrightarrow{C_2H_5O\overset{O}{\overset{\|}{C}}Cl} C_6H_5CH(COOC_2H_5)COOH \quad (73\%)$$

Reaction of alkylzinc compounds with chloroformates also gives tertiary alcohols but to a lesser degree (11, 91, 94, 574, 575). Heating ethyl chloroformate with zinc alone resulted in extensive decomposition (250).



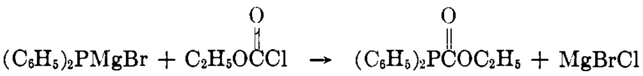
$$C_2H_5O\overset{O}{\overset{\|}{C}}Cl + Zn \xrightarrow{\Delta} CH_2{=}CH_2 + C_2H_5Cl + CO_2 + HCl$$

A Reformatsky-type reaction has been observed in the reaction of ethyl chloroformate with ethyl acetoacetate in the presence of zinc and reduced copper powder (11).



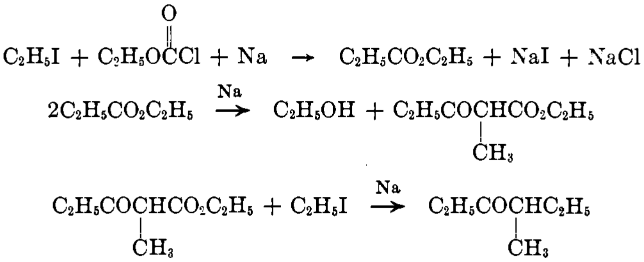
$$CH_3\overset{O}{\overset{\|}{C}}CH_2CO_2C_2H_5 + C_2H_5O\overset{O}{\overset{\|}{C}}Cl \xrightarrow{Zn\text{-}Cu} CH_3{-}\underset{OH}{\underset{|}{\overset{CO_2C_2H_5}{\overset{|}{C}}}}{-}CH_2CO_2C_2H_5$$

The phosphorus-containing Grignard reagent in the following equation reacted to yield the expected ester (357).



$$(C_6H_5)_2PMgBr + C_2H_5O\overset{O}{\overset{\|}{C}}Cl \rightarrow (C_6H_5)_2P\overset{O}{\overset{\|}{C}}OC_2H_5 + MgBrCl$$

The reaction of sodium with ethyl iodide and ethyl chloroformate led to the mixture of products shown (250).



$$C_2H_5I + C_2H_5O\overset{O}{\overset{\|}{C}}Cl + Na \rightarrow C_2H_5CO_2C_2H_5 + NaI + NaCl$$

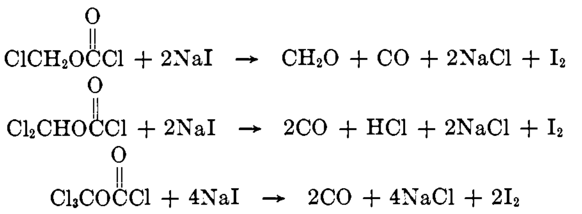
$$2C_2H_5CO_2C_2H_5 \xrightarrow{Na} C_2H_5OH + C_2H_5CO\underset{CH_3}{\underset{|}{C}}HCO_2C_2H_5$$

$$C_2H_5CO\underset{CH_3}{\underset{|}{C}}HCO_2C_2H_5 + C_2H_5I \xrightarrow{Na} C_2H_5CO\underset{CH_3}{\underset{|}{C}}HC_2H_5$$

4. Inorganic Salts

A comparative rate study of the reaction of various anions with ethyl chloroformate gave the following reactivity order (265): acetoxime pH (6 or 7) > OH^- > C_6H_5OH (pH 7) > NO_2^- > N_3^- > $S_2O_3^{-2}$ > F^-. In the reaction medium used (85:15 water–acetone), chloride, bromide, iodide, cyanate, thiocyanate, chlorate, and nitrate ions had no effect on the rate of reaction. The possible reasons for this entirely different rate order for the reaction of anions with ethyl chloroformate (acylation) as compared to their reactivity in alkylations was discussed. The rate of reaction of ethyl chloroformate with sodium iodide in acetone was studied by Conant in his classical study of the reactivity of organic chlorides (151, 152).

Reaction of sodium iodide with chloromethyl chloroformates led to the decomposition reactions shown in the following equations (550, 551).

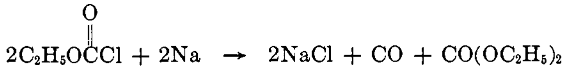


$$\mathrm{ClCH_2O\overset{O}{\overset{\|}{C}}Cl + 2NaI \rightarrow CH_2O + CO + 2NaCl + I_2}$$

$$\mathrm{Cl_2CHO\overset{O}{\overset{\|}{C}}Cl + 2NaI \rightarrow 2CO + HCl + 2NaCl + I_2}$$

$$\mathrm{Cl_3CO\overset{O}{\overset{\|}{C}}Cl + 4NaI \rightarrow 2CO + 4NaCl + 2I_2}$$

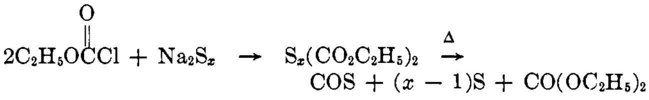
Alkali metals, especially, sodium, decomposed ethyl chloroformate to yield diethyl carbonate and carbon monoxide (250, 718).



$$\mathrm{2C_2H_5O\overset{O}{\overset{\|}{C}}Cl + 2Na \rightarrow 2NaCl + CO + CO(OC_2H_5)_2}$$

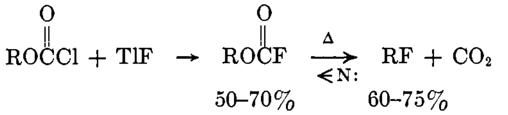
Two early reports described the conversion of alkyl chloroformates to the corresponding carbonates by lead oxide and water (159, 457). Water was thought to be necessary for the reaction to occur.

Alkylmetal sulfides and polysulfides react with chloroformates to yield bis(carbalkoxy) sulfides (326, 469, 686). This class of compound decomposes on heating to yield the carbonate, carbonoxysulfide, and sulfur.



$$\mathrm{2C_2H_5O\overset{O}{\overset{\|}{C}}Cl + Na_2S_x \rightarrow S_x(CO_2C_2H_5)_2 \xrightarrow{\Delta} COS + (}x\mathrm{ - 1)S + CO(OC_2H_5)_2}$$

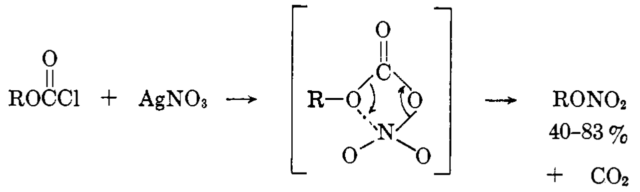
The reaction of chloroformates with inorganic fluorides yields the corresponding fluoroformates (512).

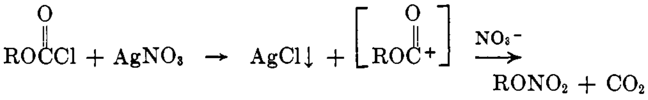


$$\mathrm{RO\overset{O}{\overset{\|}{C}}Cl + TlF \rightarrow \underset{50\text{–}70\%}{RO\overset{O}{\overset{\|}{C}}F} \xrightarrow[<N:]{\Delta} \underset{60\text{–}75\%}{RF + CO_2}}$$

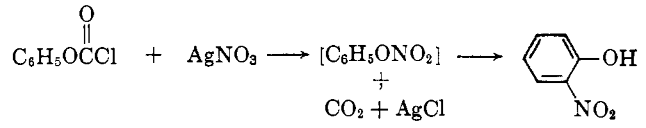
Thallous fluoride is a preferred reagent for this conversion, although conditions for the use of potassium fluoride have also been found (382, 531, 707). The facile catalyzed decomposition of fluoroformates to alkyl fluorides represents a convenient synthesis of the latter type of compound.

Silver nitrate has been treated with alkyl chloroformates to yield nitrate esters (68, 76). This reaction can be run in either heterogeneous or homogeneous systems and possesses advantages for the preparation of nitrates when oxidixable groups are present. In addition, it was shown by mechanism studies that this reaction proceeded mainly with retention of the configuration of the R group. Hence, it was postulated that an SNi-type decomposition of the intermediate was operative. Some reaction was thought to occur by the mechanism shown in the following equation. An attempt to prepare phenyl nitrate from phenyl chloroformate and silver nitrate resulted in a 64% yield of *o*-nitrophenol (118).

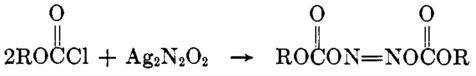




$$\mathrm{RO\overset{O}{\overset{\|}{C}}Cl + AgNO_3 \rightarrow AgCl\downarrow + \left[RO\overset{O}{\overset{\|}{C}}{+}\right] \xrightarrow{NO_3^-} RONO_2 + CO_2}$$

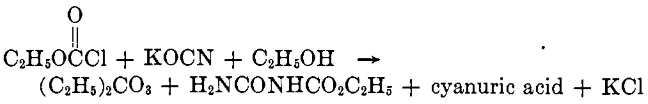


The reaction of silver hyponitrite with chloroformates has been described as leading to the formation of hyponitrous esters (631). The products, though not isolable, were found to be useful as polymerization catalysts for olefins. Their decomposition products are nitrogen, carbon dioxide, nitrous oxide, and free radicals, the latter functioning as polymerization initiators.

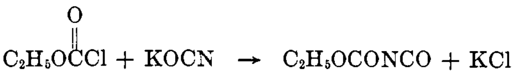


$$\mathrm{2RO\overset{O}{\overset{\|}{C}}Cl + Ag_2N_2O_2 \rightarrow RO\overset{O}{\overset{\|}{C}}ON{=}NO\overset{O}{\overset{\|}{C}}OR}$$

An early attempt to react potassium cyanate with ethyl chloroformate in the presence of ethanol gave a variety of products (718). Somewhat later, it was found that simple heating of ethyl chloroformate with potassium cyanate gave some carbethoxyethyl isocyanate with recoverable chloroformate (178, 250, 251, 720).

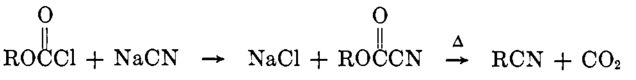


$$\mathrm{C_2H_5O\overset{O}{\overset{\|}{C}}Cl + KOCN + C_2H_5OH \rightarrow (C_2H_5)_2CO_3 + H_2NCONHCO_2C_2H_5 + \text{cyanuric acid} + KCl}$$



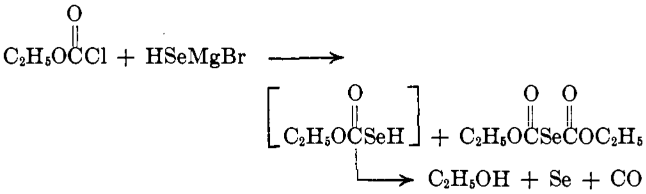
$$\mathrm{C_2H_5O\overset{O}{\overset{\|}{C}}Cl + KOCN \rightarrow C_2H_5OCONCO + KCl}$$

Cyanoformates have been prepared from chloroformates by reaction with sodium cyanide or hydrogen cyanide–pyridine in 5–40% yields. Pyrolysis of the cyanoformates at 700° yielded the corresponding nitrile (40–60%) in most cases.



$$\mathrm{RO\overset{O}{\overset{\|}{C}}Cl + NaCN \rightarrow NaCl + RO\overset{O}{\overset{\|}{C}}CN \xrightarrow{\Delta} RCN + CO_2}$$

Magnesyl selenohydrate (from ethylmagnesium bromide and hydrogen selenide) reacted with ethyl chloroformate to give the following products (478, 479). Pure



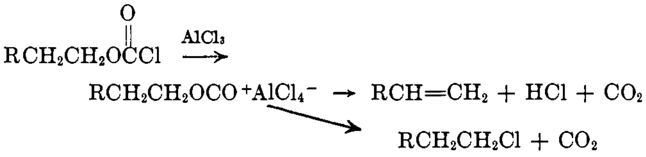
$$C_2H_5O\overset{O}{\overset{\|}{C}}Cl + HSeMgBr \longrightarrow \left[C_2H_5O\overset{O}{\overset{\|}{C}}SeH\right] + C_2H_5O\overset{O}{\overset{\|}{C}}Se\overset{O}{\overset{\|}{C}}OC_2H_5$$

$$\left[C_2H_5O\overset{O}{\overset{\|}{C}}SeH\right] \longrightarrow C_2H_5OH + Se + CO$$

compounds were not isolated in high yields in this work.

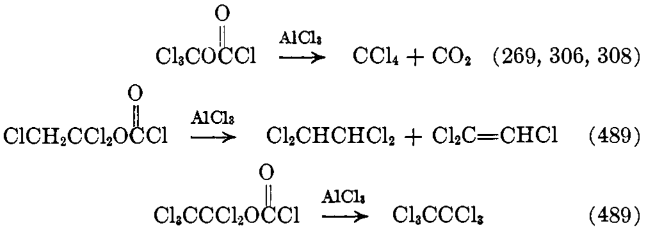
5. In the Presence of Lewis Acids

Aliphatic chloroformates undergo decomposition with Lewis acids according to the following equation (91, 93, 94, 513, 577, 689, 690). Yields of the products vary according to particular reactants, reagents, and reaction conditions. Chlorinated chloroformates yield the parent chloroalkane in many cases. Some examples are shown below. In some cases, free phosgene has been detected among the decomposition products. Table XVIII lists other examples of reactions of Lewis acids with chloroformates.



$$RCH_2CH_2O\overset{O}{\overset{\|}{C}}Cl \xrightarrow{AlCl_3} RCH_2CH_2OCO^+AlCl_4^- \rightarrow RCH{=}CH_2 + HCl + CO_2$$

$$RCH_2CH_2OCO^+AlCl_4^- \rightarrow RCH_2CH_2Cl + CO_2$$



$$Cl_3CO\overset{O}{\overset{\|}{C}}Cl \xrightarrow{AlCl_3} CCl_4 + CO_2 \quad (269, 306, 308)$$

$$ClCH_2CCl_2O\overset{O}{\overset{\|}{C}}Cl \xrightarrow{AlCl_3} Cl_2CHCHCl_2 + Cl_2C{=}CHCl \quad (489)$$

$$Cl_3CCCl_2O\overset{O}{\overset{\|}{C}}Cl \xrightarrow{AlCl_3} Cl_3CCCl_3 \quad (489)$$

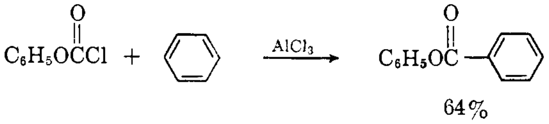
TABLE XVIII

REACTIONS OF CHLOROFORMATES, ROCOCl, WITH LEWIS ACIDS

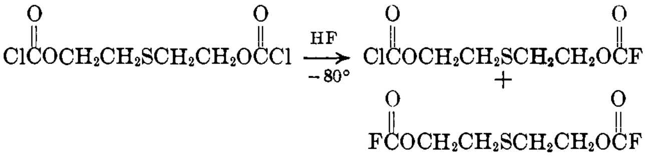
R	Lewis acid	Products (yield, %)	Reference
Cl_3C	$AlCl_3$	CO_2, CCl_4	269, 306
$ClCH_2$	$AlCl_3$	$COCl_2$, other products	390
$ClCH_2$	$FeCl_3$	$COCl_2$, other products	390
Cl_3CCCl_2	$AlCl_3$	Hexachloroethane, CO_2	489
Cl_2CHCCl_2	$AlCl_3$	Tetrachloroethylene, CO_2, HCl	489
$ClCH_2CCl_2$	$AlCl_3$	*sym*-Tetrachloroethane, trichloroethylene, CO_2, HCl	489
$ClCH_2CHCl$	$AlCl_3$	1,1,2-Trichloroethane, CO_2	489
CH_3CHCl	$AlCl_3$	CH_3CHCl_2, $CH_2{=}CHCl$, CO_2	489
C_2H_5	$AlBr_3$	C_2H_5Cl, C_2H_5Br, CO_2	403
C_2H_5	$AlCl_3$	C_2H_5Cl, CO_2	577
C_2H_5	BF_3·ether	C_2H_5Cl (62), CO_2 (64)	513
C_2H_5	$ZnCl_2$	C_2H_5Cl (26), ethylene (18), HCl, CO_2	91, 93, 94, 449, 689, 690
$(ClCH_2)(Cl_2CH)CH$	$FeCl_3$	CO_2, HCl, carbon	446
$(Cl_2CH)_2CH$	$AlCl_3$	$COCl_2$, HCl, carbon	446
n-C_3H_7	$ZnCl_2$	n-C_3H_7Cl (23), propylene (55), HCl, CO_2	690
Various aliphatic radicals	BF_3·ether	Alkyl chloride, olefins, HCl	513

Reaction of aliphatic chloroformates with Lewis acids in the presence of an aromatic hydrocarbon results in alkylation rather than acylation (95, 239–241, 403, 414, 415, 577, 744). Apparently the decomposition reaction occurs first to give the carbonium ion which then alkylates the aromatic ring. A patent claims to have upgraded isobutane to gasoline with high anti-knock value by treating it with alkyl chloroformates and a Friedel–Crafts catalyst (613).

In contrast to the aliphatic chloroformates, aromatic chloroformates are quite stable to Lewis acids (157). Complexes are undoubtedly formed, but extensive decomposition reactions are not observed up to temperatures of 130°. Because of this fact, aromatic chloroformates are good acylating agents under Friedel–Crafts conditions.



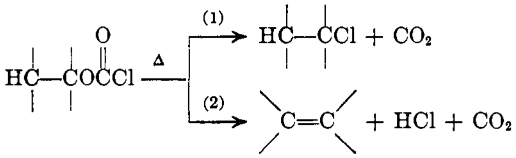
The use of hydrogen fluoride as a catalyst in a reaction of a chloroformate has resulted in halogen exchange to yield the fluoroformate (380).

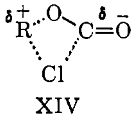


$$Cl\overset{O}{\overset{\|}{C}}OCH_2CH_2SCH_2CH_2O\overset{O}{\overset{\|}{C}}Cl \xrightarrow[-80°]{HF} Cl\overset{O}{\overset{\|}{C}}OCH_2CH_2SCH_2CH_2O\overset{O}{\overset{\|}{C}}F + F\overset{O}{\overset{\|}{C}}OCH_2CH_2SCH_2CH_2O\overset{O}{\overset{\|}{C}}F$$

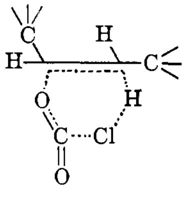
6. Thermal Decomposition of Chloroformates

Aliphatic chloroformates decompose thermally by the two paths shown in the following equation (533, 710) (Table XIX). The temperature required for decomposition varies widely depending on the structure of the aliphatic radical. For example, *t*-butyl chloroformate is unstable at room temperature (133, 464, 465). The most recent studies on the mechanism of this reaction were carried out in the vapor phase at temperatures near 250° (429–432). Path 1 above is thought to proceed through a rather polar transition state of the SNi type (XIV). This mechanism was





XIV



XV

TABLE XIX

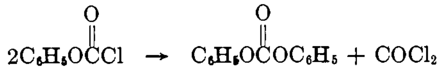
THERMAL DECOMPOSITION OF CHLOROFORMATES, $R(OCOCl)_n$

R	Product(s)	Yield, %	Reference
Cl_3C	$COCl_2$	100	569
$-(CH_2)_2-$	$CH_2{=}CHOCOCl$, $(CH_2Cl)_2$, CH_3CHCl_2		417
$Cl(CH_2)_2$	$ClCH_2CH_2Cl$		360
C_2H_5	C_2H_5Cl, $CH_2{=}CH_2$, HCl, CO_2		131, 132, 429, 513, 546, 592, 710, 718
$CH_3\overset{\vert}{C}HCH_2-$	$CH_3CH{=}CHOCOCl$		417
$(CH_3)_2CH$	$(CH_3)_2CHCl$, CO_2, $CH_2{=}CHCH_3$, HCl		134, 150
$CH_3CH{=}CHCH_2$	$CH_3CH{=}CHCH_2Cl$, $CH_3CH(CH{=}CH_2)Cl$, $(CH_2{=}CH)_2$		533
$CH_3CH(CH{=}CH_2)$	$CH_3CH{=}CHCH_2Cl$, $CH_3CH(CH{=}CH_2)Cl$, $(CH_2{=}CH)_2$		533
$FCOO(CH_2)_2S(CH_2)_2$	$F(CH_2)_2S(CH_2)_2Cl$	22	380
$(CH_3)_2CHCH_2$			428
$(CH_3)_3C$	$(CH_3)_2C{=}CH_2$, HCl, CO_2	>98	133, 464, 465
$C_6H_5CH_2$	$C_6H_5CH_2Cl$		676, 710
$C_6H_5CH(CH_3)$	$C_6H_5CH(CH_3)Cl$		710
$CH_3(CH_2)_5CH(CH_3)$	$CH_3(CH_2)_5CH(CH_3)Cl$		296, 337
$[(CH_3)_3C]_2CH$	$[(CH_3)_3C]_2CHCl$	40	379
	$(CH_3)_3CCH(CH_3)C(CH_3){=}CH_2$	50	80
$(C_6H_5)_2CH$			80
$(C_6H_5)_3C$	$(C_6H_5)_3CCl$	100	80
3-Cholesteryl	3-Cholesteryl chloride		454, 711
Various tertiary alkyl radicals			465
Various alkyl-substituted α-phenetyl radicals	Corresponding chlorides		710
Various long-chain aliphatic radicals			296
Various steroidal radicals	Corresponding chlorides		454, 711

supported by the relative reactivities of the different alkyl chloroformates (3° > 2° > 1° >>> C_6H_5), the large negative entropy of activation, the retention of configuration, and the absence of rearranged alkyl chlorides. The elimination reaction (2) was shown to be a completely stereospecific *cis* elimination and the transition state XV was postulated to be operative. Transition state XV was described as leading to an intermediate of substantial charge separation that can react to give different olefins and rearranged products, but does not dissociate enough to give stereochemically random products. The extent of the importance of ion pairs was also discussed.

Benzyl chloroformates decompose quite readily on heating to yield the respective chlorides (80, 676, 710). Presumably the stabilization of the incipient positive charge by the phenyl group (*i.e.*, a benzyl carbonium ion) facilitates their decomposition (21).

Literature reports that aryl chloroformates can be converted to aryl carbonates and phosgene by simply heating are probably not true (37, 38, 80, 308, 556). Recent research has shown that aryl chloroformates

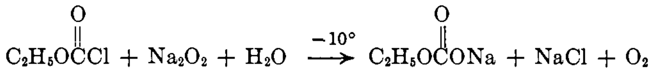


$$2C_6H_5O\overset{\overset{O}{\|}}{C}Cl \rightarrow C_6H_5O\overset{\overset{O}{\|}}{C}OC_6H_5 + COCl_2$$

are very stable thermally when pure (418). Apparently, moisture or other catalysts were present when this reaction was reported to occur.

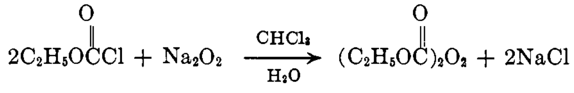
7. *Peroxides*

Metal peroxides or hydrogen peroxide and base react with chloroformates to give peroxy compounds. At low temperatures, the sodium salt of ethyl monoperoxycarbonic acid (450) was not obtainable. Instead, the following reaction occurred. However, the symmetrical



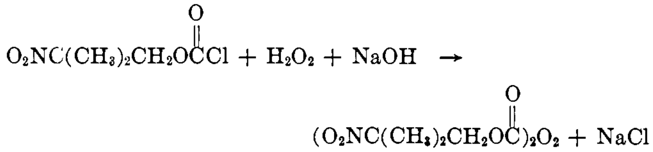
$$C_2H_5O\overset{\overset{O}{\|}}{C}Cl + Na_2O_2 + H_2O \xrightarrow{-10^\circ} C_2H_5O\overset{\overset{O}{\|}}{C}ONa + NaCl + O_2$$

diethyl ester of peroxydicarbonic acid has been prepared by the reaction shown below (656, 660, 712). Many di-



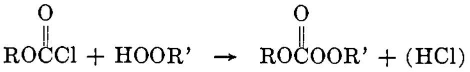
$$2C_2H_5O\overset{\overset{O}{\|}}{C}Cl + Na_2O_2 \xrightarrow[H_2O]{CHCl_3} (C_2H_5O\overset{\overset{O}{\|}}{C})_2O_2 + 2NaCl$$

alkyl peroxides of this type have been reported. Peroxydicarbonates formed *in situ* have been found to be good initiators for vinyl polymerizations (263). An example that used hydrogen peroxide and sodium hydroxide is shown in the following reaction (66).



$$O_2NC(CH_3)_2CH_2O\overset{\overset{O}{\|}}{C}Cl + H_2O_2 + NaOH \rightarrow (O_2NC(CH_3)_2CH_2O\overset{\overset{O}{\|}}{C})_2O_2 + NaCl$$

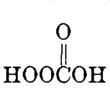
The reaction of hydroperoxides with chloroformates in the presence of acid acceptors has yielded esters of monoperoxycarbonic acid (660). With peroxycar-



$$RO\overset{\overset{O}{\|}}{C}Cl + HOOR' \rightarrow RO\overset{\overset{O}{\|}}{C}OOR' + (HCl)$$

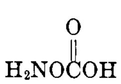
boxylic acids, the mixed anhydrides were prepared (541).

Compounds which can be considered to be amide derivatives of monoperoxycarbonic acid (XVI) have



$$HOO\overset{\overset{O}{\|}}{C}OH$$

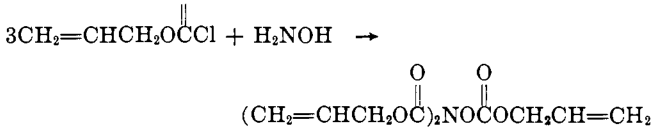
XVI



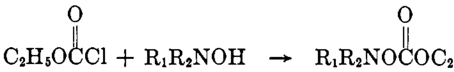
$$H_2NO\overset{\overset{O}{\|}}{C}OH$$

XVII

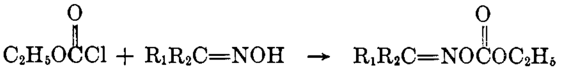
been prepared by the reaction of hydroxylamine, dialkylhydroxylamines, and oximes with chloroformates (85, 749). An example of each type is shown. These



$$3CH_2{=}CHCH_2O\overset{\overset{O}{\|}}{C}Cl + H_2NOH \rightarrow (CH_2{=}CHCH_2O\overset{\overset{O}{\|}}{C})_2NO\overset{\overset{O}{\|}}{C}OCH_2CH{=}CH_2$$



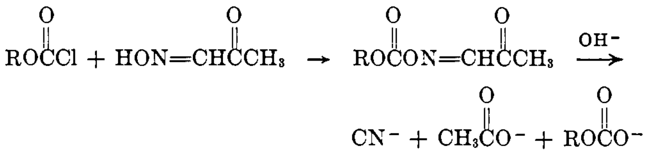
$$C_2H_5O\overset{\overset{O}{\|}}{C}Cl + R_1R_2NOH \rightarrow R_1R_2NO\overset{\overset{O}{\|}}{C}OC_2H_5$$



$$C_2H_5O\overset{\overset{O}{\|}}{C}Cl + R_1R_2C{=}NOH \rightarrow R_1R_2C{=}NO\overset{\overset{O}{\|}}{C}OC_2H_5$$

compounds can be analyzed iodometrically because they yield peroxy structures on hydrolysis.

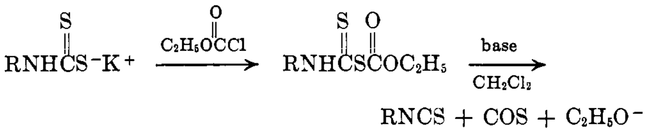
An analytical method for determination of chloroformates is based on their reaction with isonitrosoacetone. Subsequent hydrolysis liberates cyanide ion (603). Quantitative analysis of the cyanide ion is a measure of the chloroformate content.



$$\mathrm{RO\overset{O}{\overset{\|}{C}}Cl + HON{=}CH\overset{O}{\overset{\|}{C}}CH_3 \rightarrow RO\overset{O}{\overset{\|}{C}}ON{=}CH\overset{O}{\overset{\|}{C}}CH_3 \xrightarrow{OH^-} CN^- + CH_3\overset{O}{\overset{\|}{C}}O^- + RO\overset{O}{\overset{\|}{C}}O^-}$$

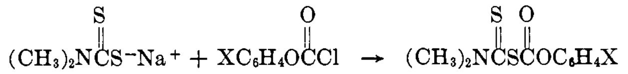
8. *Synthesis of Isothiocyanates*

The synthesis of isothiocyanates based on the early observations of Kaluza is a general method (200–202, 370, 383–386, 709). This route, from which high yields can be obtained, is shown in the following equations. The final step was improved by using triethylamine in methylene chloride (244). The kinetics and mechanism of the decomposition of the intermediate carbethoxy dithiocarbamates have been studied (320, 321).



$$\mathrm{RNH\overset{S}{\overset{\|}{C}}S^-K^+ \xrightarrow{C_2H_5O\overset{O}{\overset{\|}{C}}Cl} RNH\overset{S}{\overset{\|}{C}}S\overset{O}{\overset{\|}{C}}OC_2H_5 \xrightarrow[CH_2Cl_2]{base} RNCS + COS + C_2H_5O^-}$$

An analogous reaction of dithiocarbamates derived from secondary amines with aryl chloroformates yielded the expected products (369). The products decomposed slowly at room temperature over a period of weeks.

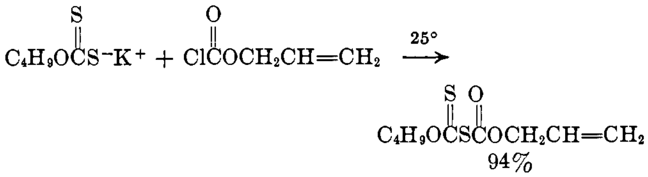


$$\mathrm{(CH_3)_2N\overset{S}{\overset{\|}{C}}S^-Na^+ + XC_6H_4O\overset{O}{\overset{\|}{C}}Cl \rightarrow (CH_3)_2N\overset{S}{\overset{\|}{C}}S\overset{O}{\overset{\|}{C}}OC_6H_4X}$$

$X = \mathrm{H}, p\text{-}\mathrm{CH_3}, m\text{-}\mathrm{Cl}$

9. *Xanthates*

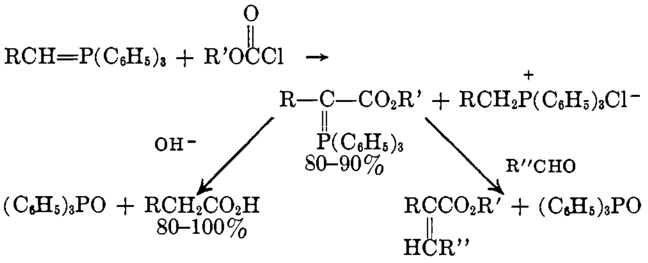
Several patents have described the reaction of chloroformates with alkylxanthates to yield alkyl xanthogen formates (74, 75, 228). These products are claimed to possess utility in the concentration of minerals by flotation processes.



$$\mathrm{C_4H_9O\overset{S}{\overset{\|}{C}}S^-K^+ + Cl\overset{O}{\overset{\|}{C}}OCH_2CH{=}CH_2 \xrightarrow{25^\circ} \underset{94\%}{C_4H_9O\overset{S}{\overset{\|}{C}}S\overset{O}{\overset{\|}{C}}OCH_2CH{=}CH_2}}$$

10. *Phosphoranes (Wittig Reaction)*

The reaction of a chloroformate with phosphoranes led to a new synthesis of substituted acrylates (61).



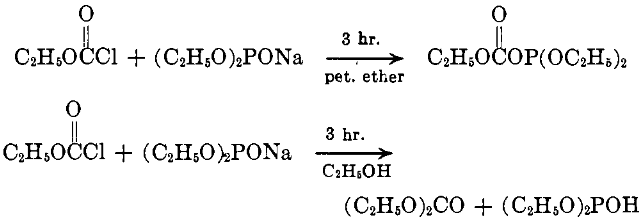
$$\mathrm{RCH{=}P(C_6H_5)_3 + R'O\overset{O}{\overset{\|}{C}}Cl \rightarrow \underset{80\text{–}90\%}{R{-}\underset{P(C_6H_5)_3}{\underset{\|}{C}}{-}CO_2R'} + RCH_2\overset{+}{P}(C_6H_5)_3Cl^-}$$

$$\xrightarrow{OH^-} \mathrm{(C_6H_5)_3PO + \underset{80\text{–}100\%}{RCH_2CO_2H}}$$

$$\xrightarrow{R''CHO} \mathrm{R\underset{HCR''}{\underset{\|}{C}}CO_2R' + (C_6H_5)_3PO}$$

11. *Phosphites and Phosphines*

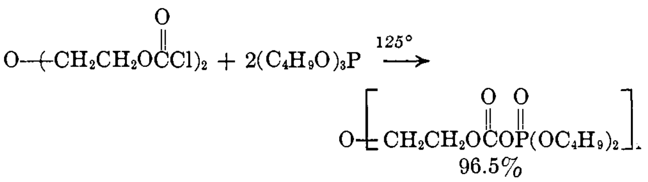
Sodium diethyl phosphite can react with ethyl chloroformate in both of the ways shown in the following equations (12).



$$\mathrm{C_2H_5O\overset{O}{\overset{\|}{C}}Cl + (C_2H_5O)_2PONa \xrightarrow[pet.\ ether]{3\ hr.} C_2H_5O\overset{O}{\overset{\|}{C}}OP(OC_2H_5)_2}$$

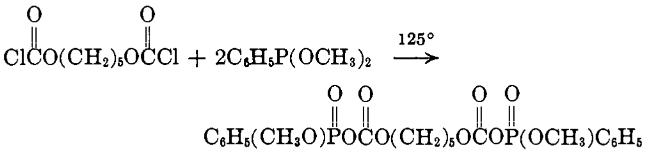
$$\mathrm{C_2H_5O\overset{O}{\overset{\|}{C}}Cl + (C_2H_5O)_2PONa \xrightarrow[C_2H_5OH]{3\ hr.} (C_2H_5O)_2CO + (C_2H_5O)_2POH}$$

Trialkyl phosphites have been treated with bis(chloroformates) to yield products resulting from an Arbuzov-type rearrangement (297).



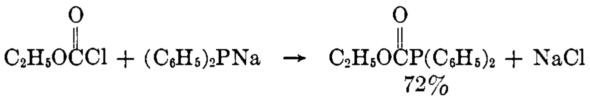
$$\mathrm{O{\left(CH_2CH_2O\overset{O}{\overset{\|}{C}}Cl\right)_2} + 2(C_4H_9O)_3P \xrightarrow{125^\circ} \underset{96.5\%}{O{\left[CH_2CH_2O\overset{O}{\overset{\|}{C}}\overset{O}{\overset{\|}{P}}(OC_4H_9)_2\right]_2}}}$$

Similar results were obtained with phenyl dimethyl phosphonite.



$$\mathrm{Cl\overset{O}{\overset{\|}{C}}O(CH_2)_5O\overset{O}{\overset{\|}{C}}Cl + 2C_6H_5P(OCH_3)_2 \xrightarrow{125^\circ} C_6H_5(CH_3O)\overset{O}{\overset{\|}{P}}O\overset{O}{\overset{\|}{C}}O(CH_2)_5O\overset{O}{\overset{\|}{C}}O\overset{O}{\overset{\|}{P}}(OCH_3)C_6H_5}$$

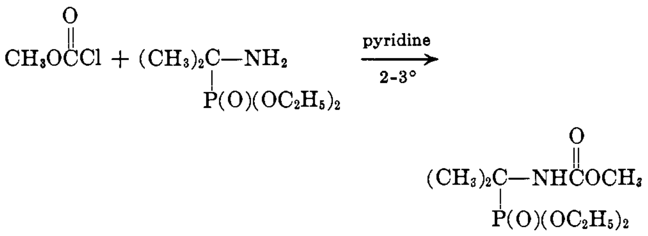
Metal phosphides yielded the expected products on reaction with chloroformates (347).



$$\mathrm{C_2H_5O\overset{O}{\overset{\|}{C}}Cl + (C_6H_5)_2PNa \rightarrow \underset{72\%}{C_2H_5O\overset{O}{\overset{\|}{C}}P(C_6H_5)_2} + NaCl}$$

12. *α-Amino Phosphonates*

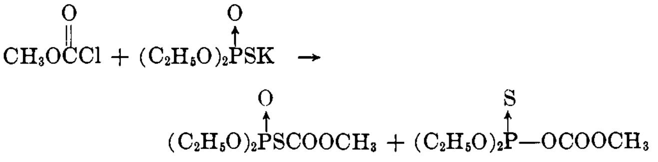
Acylation of the amino group in α-amino phosphonates by chloroformates occurs readily in the presence of a tertiary amine (458).



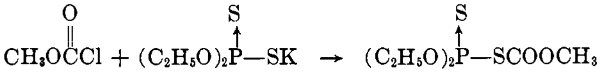
$$\mathrm{CH_3O\overset{O}{\overset{\|}{C}}Cl + (CH_3)_2\underset{P(O)(OC_2H_5)_2}{\underset{|}{C}}{-}NH_2 \xrightarrow[2\text{-}3^\circ]{pyridine} (CH_3)_2\underset{P(O)(OC_2H_5)_2}{\underset{|}{C}}{-}NH\overset{O}{\overset{\|}{C}}OCH_3}$$

13. *Thiophosphates*

The thiophosphates shown in the following equations were acylated in good yield by methyl chloroformate (97).



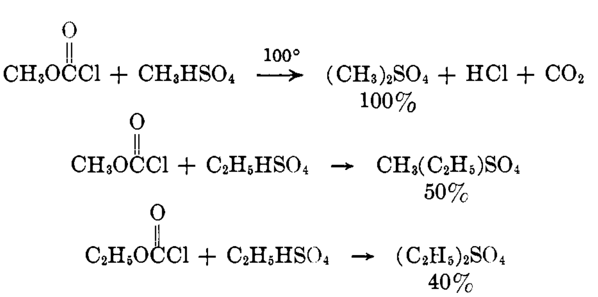
$$CH_3O\overset{O}{\overset{\|}{C}}Cl + (C_2H_5O)_2\overset{O}{\overset{\uparrow}{P}}SK \rightarrow (C_2H_5O)_2\overset{O}{\overset{\uparrow}{P}}SCOOCH_3 + (C_2H_5O)_2\overset{S}{\overset{\uparrow}{P}}{-}OCOOCH_3$$



$$CH_3O\overset{O}{\overset{\|}{C}}Cl + (C_2H_5O)_2\overset{S}{\overset{\uparrow}{P}}{-}SK \rightarrow (C_2H_5O)_2\overset{S}{\overset{\uparrow}{P}}{-}SCOOCH_3$$

14. *Organic Sulfates*

Alkyl chloroformates behave as alkylating agents toward alkyl hydrogen sulfates (408). Some examples are

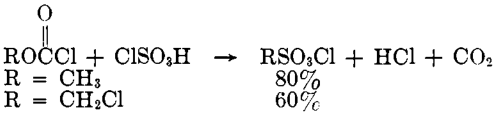


$$CH_3O\overset{O}{\overset{\|}{C}}Cl + CH_3HSO_4 \xrightarrow{100^\circ} \underset{100\%}{(CH_3)_2SO_4} + HCl + CO_2$$

$$CH_3O\overset{O}{\overset{\|}{C}}Cl + C_2H_5HSO_4 \rightarrow \underset{50\%}{CH_3(C_2H_5)SO_4}$$

$$C_2H_5O\overset{O}{\overset{\|}{C}}Cl + C_2H_5HSO_4 \rightarrow \underset{40\%}{(C_2H_5)_2SO_4}$$

Chloromethyl chloroformate behaved differently, yielding methyl chlorosulfonate in 78% yield. The reaction of chlorosulfonic acid with chloroformates yielded alkyl chlorosulfonates (174, 409).



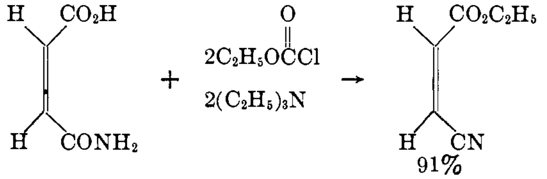
$$RO\overset{O}{\overset{\|}{C}}Cl + ClSO_3H \rightarrow RSO_3Cl + HCl + CO_2$$

$R = CH_3$ 80%

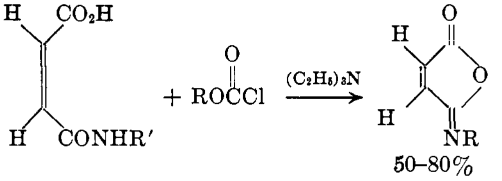
$R = CH_2Cl$ 60%

15. *Amic Acids*

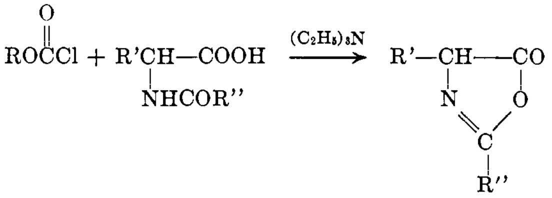
Maleamic acid was simultaneously esterified and dehydrated by chloroformates and triethylamine to yield β-cyanoacrylates in high yields (600).



N-substituted maleamic acids yielded isomaleimides from the same reactants (158, 600, 601).

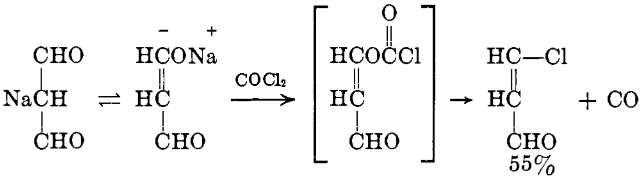


Similarly, dehydration of N-acylamino acids with ethyl chloroformate and triethylamine gave azlactones in 40–70% yields (528).



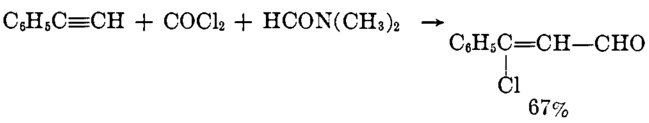
16. *Enols*

Phosgene reacts with enols *via* chloroformates to effect their chlorination (14–19). An example is shown.



$$\begin{array}{c}CHO\\ |\\ NaCH\\ |\\ CHO\end{array} \rightleftharpoons \begin{array}{c}HC\overset{-}{O}\overset{+}{Na}\\ \|\\ HC\\ |\\ CHO\end{array} \xrightarrow{COCl_2} \left[\begin{array}{c}HCO\overset{O}{\overset{\|}{C}}Cl\\ \|\\ HC\\ |\\ CHO\end{array}\right] \rightarrow \begin{array}{c}HC{-}Cl\\ \|\\ HC\\ |\\ CHO\\ 55\%\end{array} + CO_2$$

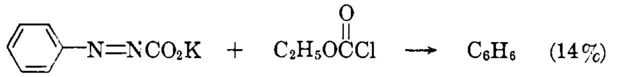
The chloroformylation of phenylacetylene probably proceeds through a similar type of intermediate (747).



$$C_6H_5C{\equiv}CH + COCl_2 + HCON(CH_3)_2 \rightarrow \underset{67\%}{C_6H_5\underset{Cl}{\underset{|}{C}}{=}CH{-}CHO}$$

17. *Phenylazoformates*

Ethyl chloroformate gave a mixture of products on reaction with potassium phenylazoformate (523). A free-radical mechanism was proposed.



$C_6H_5NHCO_2C_2H_5$ (17.5%)

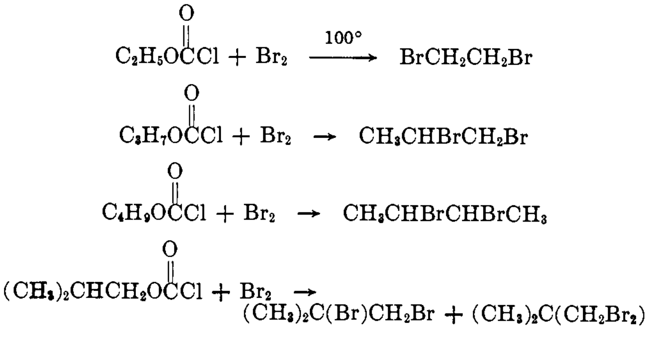
$C_6H_5NHCONHC_6H_5$ (13%)

$C_6H_5CH_2OC_2H_5$

$(C_2H_5O)_2CO$

18. *Bromine*

Alkyl bromides were obtained from the reaction of bromine with alkyl chloroformates (340, 524).



$$C_2H_5O\overset{O}{\overset{\|}{C}}Cl + Br_2 \xrightarrow{100^\circ} BrCH_2CH_2Br$$

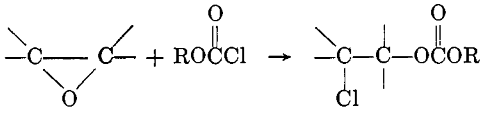
$$C_3H_7O\overset{O}{\overset{\|}{C}}Cl + Br_2 \rightarrow CH_3CHBrCH_2Br$$

$$C_4H_9O\overset{O}{\overset{\|}{C}}Cl + Br_2 \rightarrow CH_3CHBrCHBrCH_3$$

$$(CH_3)_2CHCH_2O\overset{O}{\overset{\|}{C}}Cl + Br_2 \rightarrow (CH_3)_2C(Br)CH_2Br + (CH_3)_2C(CH_2Br_2)$$

19. Epoxides

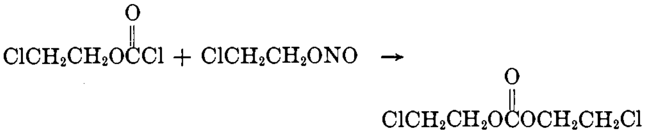
As mentioned later in section V, chloroformates react with epoxides to yield β-chlorocarbonates (360).



Acids or bases catalyze this reaction.

20. Nitrite Esters

The following reaction has been reported (519). Its



$$\mathrm{ClCH_2CH_2O\overset{\overset{O}{\|}}{C}Cl + ClCH_2CH_2ONO \rightarrow ClCH_2CH_2O\overset{\overset{O}{\|}}{C}OCH_2CH_2Cl}$$

generality is unknown.

21. Reducing Agents

Formic acid was obtained in 51% yield by treatment of ethyl chloroformate with sodium amalgam (725). The electrolytic reduction of methyl chloroformate has also been studied (256).

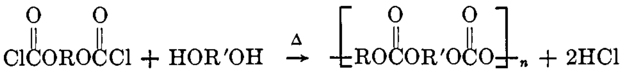
V. POLYMER SYNTHESES FROM CHLOROFORMATES

The utility of chloroformates, especially bis(chloroformates), has been greatly extended recently because of the recent research on interfacial polymerization. They have been used for the preparation of many different classes of polymers through their acid chloride type reactivity. Brief summaries of the available literature on these various types are presented below.

A. POLYCARBONATES

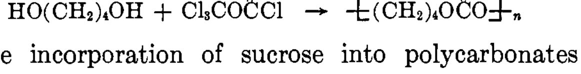
1. Aliphatic Polycarbonates

The condensation of an aliphatic bis(chloroformate) with an aliphatic diol can be effected merely by heating under vacuum (412).



$$\mathrm{Cl\overset{\overset{O}{\|}}{C}OR O\overset{\overset{O}{\|}}{C}Cl + HOR'OH \xrightarrow{\Delta} \left[RO\overset{\overset{O}{\|}}{C}OR'O\overset{\overset{O}{\|}}{C}O \right]_n + 2HCl}$$

A patent has also described the condensation of diols with trichloromethyl chloroformate to yield aliphatic polycarbonates that were described as being wax-like with good oil solubility (716).

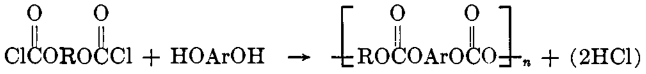


$$\mathrm{HO(CH_2)_4OH + Cl_3CO\overset{\overset{O}{\|}}{C}Cl \rightarrow \left[(CH_2)_4O\overset{\overset{O}{\|}}{C}O \right]_n}$$

The incorporation of sucrose into polycarbonates by direct reaction with phosgene or ester exchange with diphenyl carbonate has also been reported (673–675). Reaction of the hydroxyl groups of polyvinyl alcohol with monochloroformates was described in a recent patent (253).

2. Aliphatic–Aromatic Polycarbonates

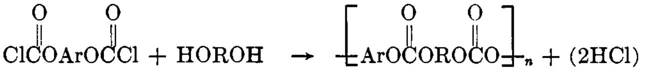
Mixed polycarbonates of this type have been prepared by both possible routes (32, 145, 147, 212, 214, 252, 261, 262, 580, 620). The polycondensation of an aliphatic bis(chloroformate) with a bisphenol has been



$$\mathrm{Cl\overset{\overset{O}{\|}}{C}ORO\overset{\overset{O}{\|}}{C}Cl + HOArOH \rightarrow \left[RO\overset{\overset{O}{\|}}{C}OArO\overset{\overset{O}{\|}}{C}O \right]_n + (2HCl)}$$

effected in interfacial systems as well as by the use of stoichiometric amounts of a tertiary base (*e.g.*, pyridine). The mixed polycarbonate from ethylene glycol and 2,2-bis(4-hydroxyphenyl)propane undergoes an interesting thermal decomposition at 280°. Ethylene carbonate and the polycarbonate of 2,2-bis(4-hydroxyphenyl)propane (665) were obtained in quantitative yield.

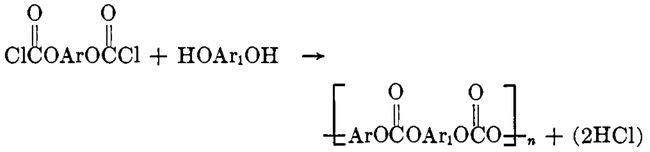
The alternate route using an aromatic bis(chloroformate) proceeds well only when stoichiometric amounts of a tertiary base are employed (619). Attempts at using this route in interfacial systems have yielded the completely aromatic polycarbonate.



$$\mathrm{Cl\overset{\overset{O}{\|}}{C}OArO\overset{\overset{O}{\|}}{C}Cl + HOROH \rightarrow \left[ArO\overset{\overset{O}{\|}}{C}ORO\overset{\overset{O}{\|}}{C}O \right]_n + (2HCl)}$$

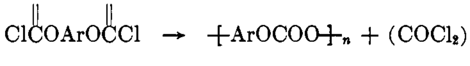
3. Aromatic Polycarbonates

Completely aromatic polycarbonates are prepared most economically by the direct phosgenation of bisphenols. They can also be readily prepared by the reaction of a bisphenol with an aryl bis(chloroformate). This latter route can be used advantageously to prepare polycarbonates containing bisphenols that cannot be phosgenated directly, *i.e.*, the most acidic and hindered ones. This polymerization can be carried out in interfacial systems, by using stoichiometric amounts of a tertiary base, and catalytically in inert solvents using metal-containing catalysts (77, 78, 206–211, 213, 218–220, 222, 579, 614–619). Catalysis of this type of interfacial polymerization with phosphonium, arsonium, and sulfonium salts has been the subject of a recent patent (255).



$$\mathrm{Cl\overset{\overset{O}{\|}}{C}OArO\overset{\overset{O}{\|}}{C}Cl + HOAr_1OH \rightarrow \left[ArO\overset{\overset{O}{\|}}{C}OAr_1O\overset{\overset{O}{\|}}{C}O \right]_n + (2HCl)}$$

The self-polymerization of an aryl bis(chloroformate) to an aromatic polycarbonate by hydrolysis in an interfacial system has also been accomplished. This process lacks practicality because of poor phosgene efficiency.



$$\mathrm{Cl\overset{\overset{O}{\|}}{C}OArO\overset{\overset{O}{\|}}{C}Cl \rightarrow \left[ArOCOO \right]_n + (COCl_2)}$$

Cyclic tetramers of bisphenol-A carbonate have been isolated (21%) from the reaction of bisphenol-A dichloroformate with bisphenol-A under high dilution reaction conditions. Polymerization of these cyclic oligomers to very high molecular weight polymers was also effected (621).

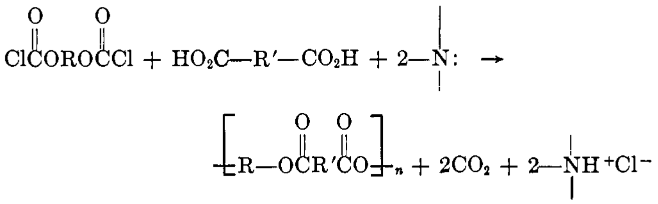
4. *Copolycarbonates*

The interfacial polymerization of hydroxyl-terminated aromatic polycarbonates with polymeric bis(chloroformates) to yield high molecular weight copolymers has been patented. The polymeric bis(chloroformates) that were described were prepared from polyethylene glycols, polytetramethylene glycol, polystyrene glycol, and hydroxyl-terminated poly(ethylene adipate) (398, 468).

Copolymerization of a bisphenol with a bis(chloroformate) and phenyl phosphonyl dichloride was used for the preparation of poly(carbonate–phosphonates) in interfacial systems (254). Phosphonium salts were used as catalysts.

B. POLYESTERS

The reaction of a bis(chloroformate) with a dicarboxylic acid in the presence of excess tertiary amine has been patented as a route to polyesters (247).

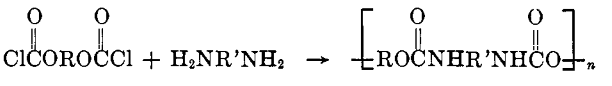


$$Cl\overset{O}{\overset{\|}{C}}ORO\overset{O}{\overset{\|}{C}}Cl + HO_2C—R'—CO_2H + 2—\overset{|}{\underset{|}{N}}: \rightarrow \left[R—O\overset{O}{\overset{\|}{C}}R'\overset{O}{\overset{\|}{C}}O\right]_n + 2CO_2 + 2—\overset{|}{\underset{|}{N}}H^+Cl^-$$

C. POLYURETHANS

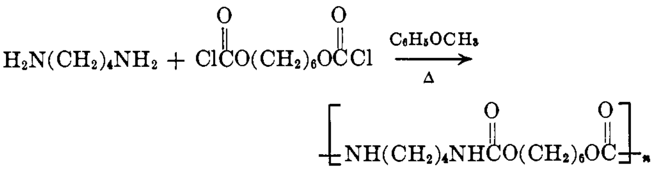
1. *Aliphatic Polyurethans*

Many different aliphatic polyurethans have been prepared in interfacial systems from aliphatic bis(chloroformates) and diamines (67, 115–117, 205, 342, 361, 387, 411, 444, 526, 562, 728, 730). This route, of course, is an alternate to that using diisocyanates and glycols. Low molecular weight aliphatic polyurethans have been prepared in anhydrous systems using calcium hydroxide and other metalliferous hydrogen chloride acceptors (236, 653). Cross-linked, aliphatic polyurethans have been obtained from the above reactions by using reactants with a functionality of greater than two (30, 166).



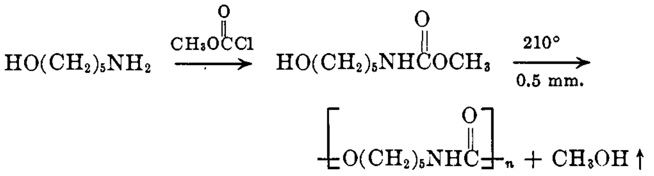
$$Cl\overset{O}{\overset{\|}{C}}ORO\overset{O}{\overset{\|}{C}}Cl + H_2NR'NH_2 \rightarrow \left[RO\overset{O}{\overset{\|}{C}}NHR'NH\overset{O}{\overset{\|}{C}}O\right]_n$$

Polyurethans have been prepared from bis(chloroformates) and diamines by using an excess of the diamine and heating in an inert solvent (332).

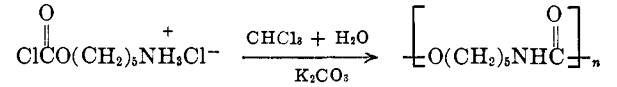


$$H_2N(CH_2)_4NH_2 + Cl\overset{O}{\overset{\|}{C}}O(CH_2)_6O\overset{O}{\overset{\|}{C}}Cl \xrightarrow[\Delta]{C_6H_5OCH_3} \left[NH(CH_2)_4NH\overset{O}{\overset{\|}{C}}O(CH_2)_6O\overset{O}{\overset{\|}{C}}\right]_n$$

The use of a chloroformate in an intermediate step in a melt process for polyurethan synthesis has been described (612). A similar technique, but a variant on an interfacial process, is also shown (27, 344, 402, 605, 638).

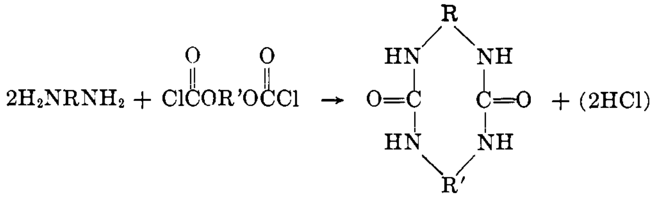


$$HO(CH_2)_5NH_2 \xrightarrow{CH_3O\overset{O}{\overset{\|}{C}}Cl} HO(CH_2)_5NH\overset{O}{\overset{\|}{C}}OCH_3 \xrightarrow[0.5\ mm.]{210°} \left[O(CH_2)_5NH\overset{O}{\overset{\|}{C}}\right]_n + CH_3OH\uparrow$$



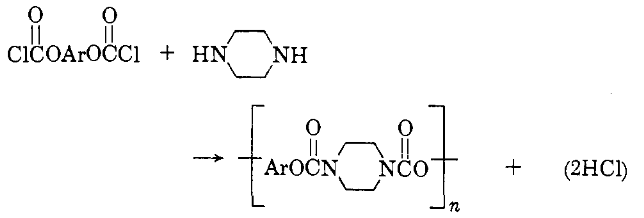
$$Cl\overset{O}{\overset{\|}{C}}O(CH_2)_5\overset{+}{N}H_3Cl^- \xrightarrow[K_2CO_3]{CHCl_3 + H_2O} \left[O(CH_2)_5NH\overset{O}{\overset{\|}{C}}\right]_n$$

Oligomeric urethans were prepared in 30–70% yields by the reaction of excess diamine with bis(chloroformates) in dilute solution (378). Earlier work employed the conversion of hydroxyl-terminated oligomers from the diisocyanate–glycol reaction to chloroformates, followed by reaction with mono(carbobenzoxy)hexamethylenediamine, for their characterization (746).



2. *Aliphatic–Aromatic Polyurethans*

Polyurethans prepared from piperazine and aryl bis(chloroformates) have been prepared interfacially (221, 362, 363, 638, 666, 726–728, 730). The polymers obtained possessed softening temperatures of ≥200°. Polyurethans of this class have also been prepared by the interfacial polymerization of the bis(chloroformate) of neopentyl glycol with a series of aromatic diamines (376).



The polymerization of bis(chloroformates) with diamines to yield polyurethans directly on the surface of fibers has been described as a method of shrink-proofing fabrics (436).

D. COPOLYURETHANS

1. *Poly(urethan carbonates)*

Interfacial polymerization of a bis(chloroformate) with a diamine and a bisphenol yielded the title copolymers (146). Various diamines and bisphenols have been used in varying ratios.

Block poly(urethan carbonates) have been prepared from the polymerization of low molecular weight chloroformate-terminated polycarbonates with aliphatic diamines (467). Polymerization of diisocyanates with low molecular weight hydroxyl-terminated polycarbonates has yielded similar products (488). Using amine–dicarboxylic acid salts with low molecular weight, chloroformate-terminated polycarbonates gave poly(urethane amide carbonates) (488).

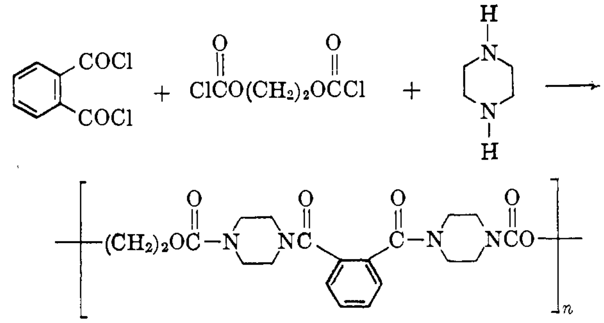
Polymerization of dichloroformates prepared from ester–diols with diamines yielded poly(urethan esters) (733).

2. *Poly(urethan sulfonamides)*

Poly(urethan sulfonamides) have been reportedly prepared by the interfacial reaction of a bis(chloroformate), a bis(sulfonyl chloride), and a diamine (328, 343).

3. *Poly(urethan amides)*

The subject polymers have been prepared by interfacial polymerization of a diacid chloride, a diamine and a bis(chloroformate) (194, 374, 375, 441, 731, 732). An example using piperazine as the diamine is shown.



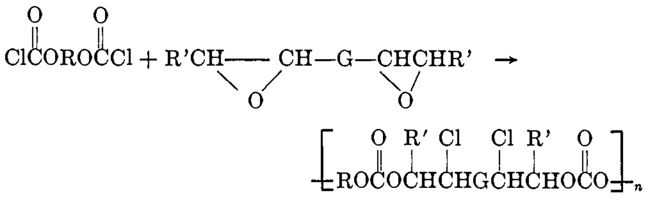
Bis(chloroformates) prepared from phosgene and polyalkylene oxide glycols have also been used in this type of polymerization (142, 143, 235, 260, 375, 401).

4. *Poly(urethan ethers)*

Polymerization of a bis(chloroformate) derived from a glycol polyether with diamines yielded elastomeric polyurethans (264).

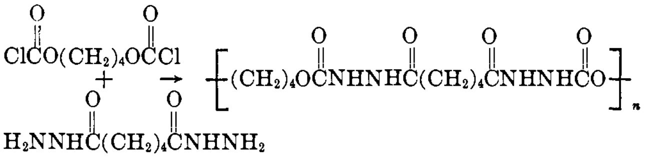
E. POLYMERIZATION OF CHLOROFORMATES WITH DIEPOXIDES

The reaction of a bis(chloroformate) with a diepoxide has led to polymers of the type shown in the following equation (146).



F. POLYMERIZATION OF CHLOROFORMATES WITH BIS(HYDRAZIDES)

Fiber-forming polymers have been prepared by polymerization of bis(chloroformates) with bis(hydrazides) (125, 126, 146, 175).



$$\mathrm{Cl\overset{O}{\overset{\|}{C}}O(CH_2)_4O\overset{O}{\overset{\|}{C}}Cl + H_2NNH\overset{O}{\overset{\|}{C}}(CH_2)_4\overset{O}{\overset{\|}{C}}NHNH_2 \rightarrow \left[(CH_2)_4O\overset{O}{\overset{\|}{C}}NHNH\overset{O}{\overset{\|}{C}}(CH_2)_4\overset{O}{\overset{\|}{C}}NHNH\overset{O}{\overset{\|}{C}}O\right]_n}$$

G. USES OF CHLOROFORMATES IN ADDITION-TYPE POLYMERS

Unsaturated chloroformates have found utility because after reaction of the chloroformate group with other compounds, the resulting monomers can be polymerized through the double bonds (84, 291, 491–505, 548). Saturated and/or unsaturated chloroformates were condensed with various unsaturated and/or saturated hydroxy compounds and the resulting carbonates polymerized through their double bonds.

Similarly, reaction of unsaturated chloroformates with nitrogen compounds (*e.g.*, NH_2OH and NH_2NH_2) led to polymerizable derivatives (85).

A recent patent has claimed the preparation of urethans by reaction of compounds of the general structure $CH_2{=}CH\text{-}S\text{-}Z\text{-}C\ (R_1R_2)NHR$ (Z = any bivalent radical) with chloroformates (596). These materials were then copolymerized with various acrylic-type compounds.

Allyl chloroformate has been found to be a catalyst in the photopolymerization of vinyl monomers, especially acrylates (598). Peroxy compounds prepared from chloroformates and hydroperoxides (637) and peroxycarboxylic acids (541) have been described as initiators for vinyl polymerizations.

H. USES OF CHLOROFORMATES IN THERMOSET POLYMERS

Patents have been issued on the use of alkyl and alkenyl chloroformates for the curing of phenol–formaldehyde resins (419, 549). Ethyl chloroformate is claimed to eliminate shrinkage when it is used to set fluid or semifluid thermosetting resinous mixtures.

The use of bis(chloroformates) or their thio analogs for the tanning of leather has been patented (564). Another patent has described the reaction of chloroformates with proteins to give derivatives which were useful in photographic film manufacture (245).

I. MISCELLANEOUS USES OF CHLOROFORMATES IN POLYMERIC SYSTEMS

Bis(chloroformates) prepared from polyalkylene oxide glycols have found varied uses in preparing polymers (143, 235, 260). For example, condensation of the bis(chloroformate) of poly(tetramethylene ether) glycol with excesses of various diamines gave poly(ether urethans) with terminal NH_2 groups. Further reaction of these prepolymers with aliphatic bis(chloroformates) yielded useful elastomers.

Conversion of low molecular weight, hydroxyl-terminated polyesters to bis(chloroformates), followed by their reaction with diamines and aromatic bis(chloroformates) have yielded poly(ester urethans) (365). Piperazines and the bis(chloroformates) of resorcinol and hydroquinone were used.

Polymers with utility for tanning, dyeing, and textile water repellents have been prepared from chloroformates of alcohols derived from palm oil fatty acids and polyethylenimines (688).

VI. REFERENCES

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(2) Abbott Laboratories, Inc., Belgian Patent 596,083 (1961).
(3) Adam, K., and Trieschmann, H. G., German Patent 890,792; *Chem. Abstr.*, **50**, 12,099*h* (1956).
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