Competitive 1,2- and 1,3-Hydride Shifts and the Possible Role of Protonated and Methylated Cyclopropane Intermediates in Alkyl Group Rearrangements accompanying the Thermal Decomposition of Saturated Alkyl Chloroformates in the Liquid Phase

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Deuterium labelling shows that the thermal decomposition of ethyl chloroformate in the liquid phase yields chloroethane without rearrangement of the ethyl group. Longer chain primary alkyl chloroformates yield rearrangement products which can be rationalised on the basis of two initial competitive pathways, one involving a 1,2-hydride shift and the other the formation of a corner-protonated cyclopropane intermediate. The latter may be captured to yield rearranged primary alkyl chloride (with considerable proton scrambling in the n-propyl case) or give rise to a 1,3-hydride shift in higher alkyl groups (Bu^n, n-pentyl, 3-methylbutyl, n-octyl) where rearrangement to a s- or t-alkyl cation is possible. Successive 1,2-hydride shifts are of minor significance unless the second of these leads to a t-alkyl cation. The 3,3-dimethylbutyl group affords products derived from successive 1,2-shifts of hydrogen and methyl and also a 1,2-t-butyl shift which is thought to involve the intermediacy of a methylated cyclopropane. s-Alkyl cations derived directly from s-alkyl chloroformates show less tendency to rearrangement than those derived by rearrangement from primary alkyl chloroformates. Evidence is presented which suggests that alk-1-enes are formed from primary alkyl chloroformates *via* carbocation intermediates in which rearrangement by 1,2- and/or 1,3-hydride shift has occurred.

PREVIOUS studies have shown that the thermal decomposition of saturated alkyl chloroformates in the liquid phase can be accompanied by high percentages of rearrangement in the alkyl group.[1,2] The results are consistent with an ion-pair mechanism in which transient carbocation intermediates rearrange irreversibly to more stable structures before capture by chloride ion. The route by which unrearranged primary alkyl halides are formed is a matter for further investigation although the present results show that the reaction is not an intermolecular process of the type which occurs in the presence of added chloride ion ($Cl^- \dashrightarrow ROCOCl \longrightarrow ClR + CO_2 + Cl^-$).[3] Thus the relative percentages of rearranged and unrearranged isomers remain essentially unchanged as reactant concentration falls, either in the neat chloroformate [1,2] or in bromobenzene as solvent (Table 1). Product compositions obtained in bromobenzene are in general similar to those obtained by decomposition of the neat liquid, although reaction is faster in the solvent and slightly more rearrangement occurs (Table 2).

TABLE 1

Isomeric composition of chloroalkanes obtained during thermal decomposition of n-pentyl chloroformate (8.4% w/w) in bromobenzene at 150 °C [a]

	Composition (%) [b]		
t/h	1-	2-	3-
2	13	56	31
4	12	57	31
6	12	57	31
17	13	56	31
25	13	56	31

[a] First order; $t_{\frac{1}{2}}$ *ca.* 7.3 h. Overall product composition: RCl (60 mol%), olefin (40 mol%). [b] 1-, 2-, or 3-halogenopentane. No significant variation in composition observed over the temperature range 120—150 °C.

A likely possibility is that an ion-pair is formed by carbon–chlorine heterolysis (Scheme 1) (*cf.* the decomposition of alkyl chloroformates in super-acid media [4] or in the presence of silver ion [5]) and that this ion-pair either collapses with simultaneous expulsion of carbon dioxide to form unrearranged primary halide (route a), or leads further to the formation of a carbocation intermediate in which rearrangement to a more stable structure has occurred (route b). The formation of a

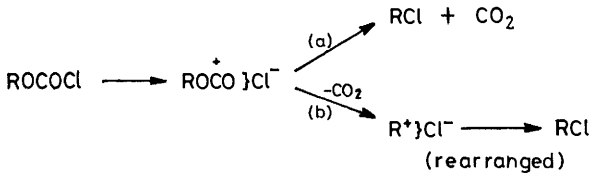
TABLE 2

Thermal decomposition products from alkyl chloroformates, alone and in bromobenzene [a]

ROCOCl		PhBr if present (g)	Product composition (mol. equiv.)			RCl isomers (%) [b]			Hydrocarbon isomers (%) [c]			
R	wt. (g)		ROCOCl	RCl	Hydrocarbon	1-	2-	3-	A	B	C	D
$CH_3CH_2CH_2$	15.0		0.97	0.01	0.02	35	65		77			23
$CH_3CH_2CH_2$	3.2	25.0	0.78	0.05	0.03	36	64		80			20
$CH_3CH_2CH_2CH_2$	16.0		0.90	0.06	0.04	23	77		65	15	20	*d*
$CH_3CH_2CH_2CH_2$	3.8	30.0	0.71	0.14	0.13	14	86		60	17	23	*d*
$CH_3CH_2CH_2CH_2CH_2$	17.0		0.82	0.09	0.08	21	49	30	50	17	32	1 [e]
$CH_3CH_2CH_2CH_2CH_2$	3.5	30.0	0.66	0.17	0.13	14	55	31	55	18	27	*d*
$(CH_3)_2CHCH_2CH_2$	17.0		0.84	0.06	0.05	17	21	(62) [f]	80	(6) [g]	(14) [h]	*d*
$(CH_3)_2CHCH_2CH_2$	3.5	30.0	0.77	0.13	0.09	14	29	(57) [f]	84	(7) [g]	(9) [h]	*d*

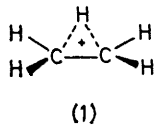
[a] 20 h at 140 °C (n-propyl, no solvent) or 150 °C (all other experiments) (oil-bath temperature). [b] 1-, 2-, or 3-chloroalkane. [c] A = 1-ene; B = *cis*-2-ene; C = *trans*-2-ene; D = cyclopropane or derivative. [d] Not analysed. [e] Three isomers by g.l.c., containing ethylcyclopropane (82%), δ −0.2 to +0.8 (complex m) with maxima at 0.35 and −0.05 (*cf.* W. E. Dupuy, E. A. Goldsmith, and H. R. Hudson, *J.C.S. Perkin II*, 1973, 74). [f] t-Pentyl chloride. [g] 2-Methylbut-1-ene. [h] 2-Methylbut-2-ene.

primary alkyl cation seems less probable but cannot be entirely excluded.[6]



SCHEME 1

We have now used deuterium labelling to study the rearrangements which occur in a number of primary alkyl groups in more detail. No account of possible isotope effects has been taken since the purpose of the investigation at this stage was to establish the pathways by which rearrangement occurs rather than to obtain quantitative rate data. Only in the case of ethyl chloroformate was no rearrangement detectable. Rearrangement by 1,2-shift in the ethyl group has attracted considerable attention in recent years from both the experimental [7] and theoretical [8] points of view and the



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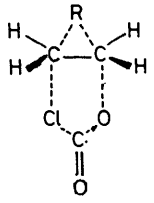
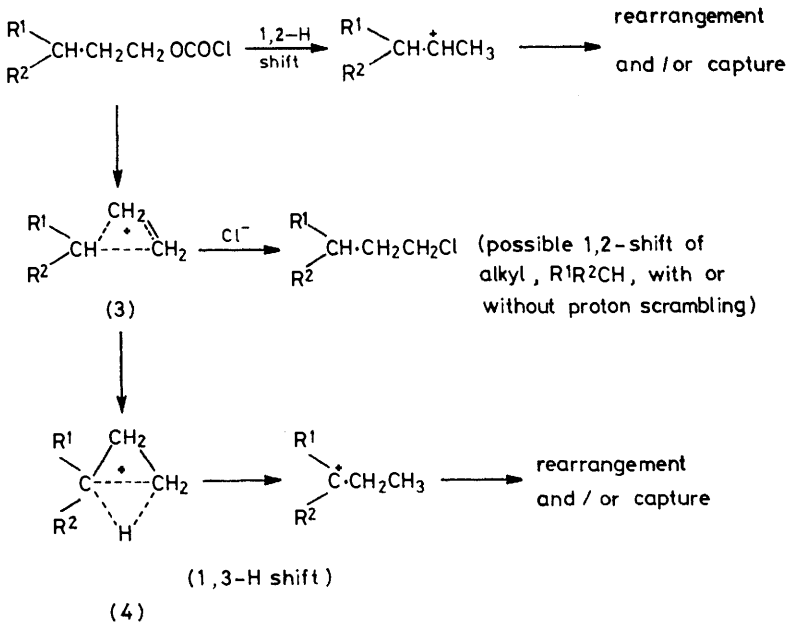


(2)

bridged ethylium ion (1) has been considered to constitute a transition state for rearrangement of the classical ethyl cation. Rearrangement by this route or *via* a concerted cyclic transition state (2; R = H) is however excluded by our result in the chloroformate decomposition.

Results for primary alkyl groups other than ethyl (Pr^n, Bu^n, n-pentyl, isopentyl, n-octyl) were in all cases consistent with a reaction scheme in which rearrangement occurs in the first instance by two competitive pathways, one involving a 1,2-hydride shift and the other involving the formation of a protonated cyclopropane which can either rearrange further to a s- or t-alkyl cation by what is in effect a 1,3-hydride transfer, or undergo capture by chloride ion to yield primary alkyl chloride (Scheme 2). The corner-protonated species (3) is shown as a first intermediate, as this best explains the formation of certain rearranged primary alkyl chlorides discussed below. Theoretical calculations have not so far given any clear indication as to whether the corner- or the edge-protonated cyclopropane is the more energetically favourable,[9] although the latter must presumably be involved either as an intermediate or as a transition state (4) in the 1,3-hydride transfer process. The involvement of protonated cyclopropanes as intermediates in these reactions was suggested by the identification of the corresponding hydrocarbons as reaction by-products.[10]

In the thermal decomposition of n-propyl chloroformate labelled with deuterium at the 1- and/or 2-position, 1-chloropropane was obtained in which extensive scrambling of the label had occurred. The result is qualitatively similar to that obtained in the nitrous acid deamination of n-propylamine [11] although the degree of scrambling is much greater in the case of the chloroformate (Tables 3 and 4). This could be because ring-opening of protonated cyclopropane (3) (Scheme 2; $R^1 = R^2 = H$) cannot yield a s-alkyl cation directly and will probably only occur when the chloride counter-ion is suitably positioned for bimolecular attack (Scheme 3). In aqueous nitrous acid the intermediate is surrounded by nucleophilic water molecules and its life is therefore expected to be shorter under these conditions.



SCHEME 2

To distinguish between edge- and corner-protonated cyclopropanes on the basis of product analysis is in principle not possible unless the rate of capture of the intermediate is comparable to the rate of proton equilibration; and previous experimental results have provided no clear evidence on this point.[10] The ^1H n.m.r. spectra of the 1-chloropropanes obtained from [1,1-$^2H_2$]-n-propyl chloroformate (5) and [2,2-$^2H_2$]-n-propyl chloroformate (6) were complex, as a result of proton–proton and proton–deuteron coupling but both showed identical patterns differing only in the relative intensities of the peaks present. From a knowledge of known deuterium isotope effects and H–D coupling constants (see Experimental section) it was possible to rationalise the spectra in terms of peaks assignable to each of the six possible [$^2H_2$]-n-propyl chlorides [structures (7)—(12), Table 3]. If it is now assumed that *ca.* 16% of 1-chloropropane is formed directly, without rearrangement, by a route not involving a cyclopropane intermediate (*e.g.* route a, Scheme 1), then the isomer distributions in the remaining 84% are virtually identical for the products derived from each of the two chloroformates. This result is only compatible with the formation of a common first intermediate, *viz.* the corner-protonated species (13). The overall product compositions are thus consistent with *ca.* 28% of 1-chloropropane being formed by capture of this first intermediate, a further 16% by capture of the second intermediates (14) and (15) and the remaining 40% by further extensive scrambling before capture. (For simplicity, we have calculated the composition of this final 40% on the basis of statistical distribution of the deuterium amongst the six isomers, *i.e.* on the assumption of complete equilibration. Although this is an approximation, it yields figures which are not grossly different from those which would be obtained by considering a further series of possible successive intermediates.)

TABLE 3

Deuterium scrambling in 1-chloropropane [a] obtained by thermal decomposition of [1,1-$^2H_2$]-n-propyl (5) and [2,2-$^2H_2$]-n-propyl (6) chloroformate in bromobenzene [b]

1-Chloropropane isomer	Composition (%) [c]		Calculated composition (%) [d]					
	from (5)	from (6)	*via* direct route [e]	*via* (13)	*via* (14)	*via* (15)	*via* further scrambling [f]	Total
$CH_3CH_2CD_2Cl$ (7) [g]	38	22	16 (or 0)	14		4	2	36 (or 20)
$CH_3CD_2CH_2Cl$ (8) [h]	18	34	16 (or 0)	14		4	2	20 (or 36)
$CHD_2CH_2CH_2Cl$ (9) [j]	14	14			8		6	14
$CH_2DCHDCH_2Cl$ (10) [k]	10	10					11	11
$CH_3CHDCHDCl$ (11) [l]	10	10					8	8
CH_2DCH_2CHDCl (12) [m]	10	10					11	11

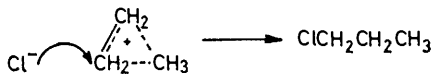
[a] 31—33% of total RCl. [b] 20% w/w solutions (10 g); 168 h at 150 °C (oil-bath). [c] From ^1H n.m.r. (see Experimental section). [d] From Scheme 4 as indicated. [e] 16% is the difference between the percentages of (7) or of (8) obtained from (5) and from (6). [f] Based on statistical distribution of deuterium amongst the six possible structures, *i.e.* in the ratios 1 : 1 : 3 : 6 : 4 : 6 for structures (7)—(12) respectively. [g] δ 1.0 (t, CH_3, J_{HCCH} 6.7 Hz) and 1.75 (m, CH_2). [h] δ 0.97 (quintet, CH_3, J_{HCCD} 1.0 Hz) and 3.43 (quintet, CH_2, J_{HCCD} 1.0 Hz). [j] δ 3.46 (t, α-CH_2, J_{HCCH} 6.3 Hz). [k] δ 3.45 (2t, α-CH_2, J_{HCCH} 7.0, J_{HCCD} 1.0 Hz). [l] δ 0.99 (2t, CH_3 J_{HCCH} 7.0, J_{HCCD} 1.0 Hz). [m] δ 3.43 (3t, CHD, J_{HCCH} 7.0, J_{HCD} 2.0 Hz).

TABLE 4

Proton distribution in the 1-chloropropane [a] obtained by thermal decomposition of [1,1,2,2-$^2H_4$]-n-propyl chloroformate in bromobenzene [b]

Proton position	Found (%)	Predicted (%) [d]
1	17	17
2	16	17
3	67	66

[a] 32% of total RCl. [b] 20% w/w solution (10 g); 168 h at 150 °C (oil-bath). [c] From ^1H n.m.r. integration: δ 0.9—1.1 (methyl), 1.7—1.8 (β-methylene), and 3.4—3.6 (α-methylene). [d] From routes analogous to those in Scheme 4, with 40% *via* statistical distribution of H and D amongst the eight possible [$^2H_4$]-n-propyl chlorides.



SCHEME 3

The ^1H n.m.r. spectrum of the 1-chloropropane obtained from [1,1,2,2-$^2H_4$]-n-propyl chloroformate was also complex and consisted of broad bands in the regions δ 0.9—1.1 (methyl), 1.7—1.8 (β-methylene), and 3.4—3.6 (α-methylene). Integration of the ^1H signal in each of these regions nevertheless gave values which agreed closely with those predicted from Scheme 4 (Table 4).

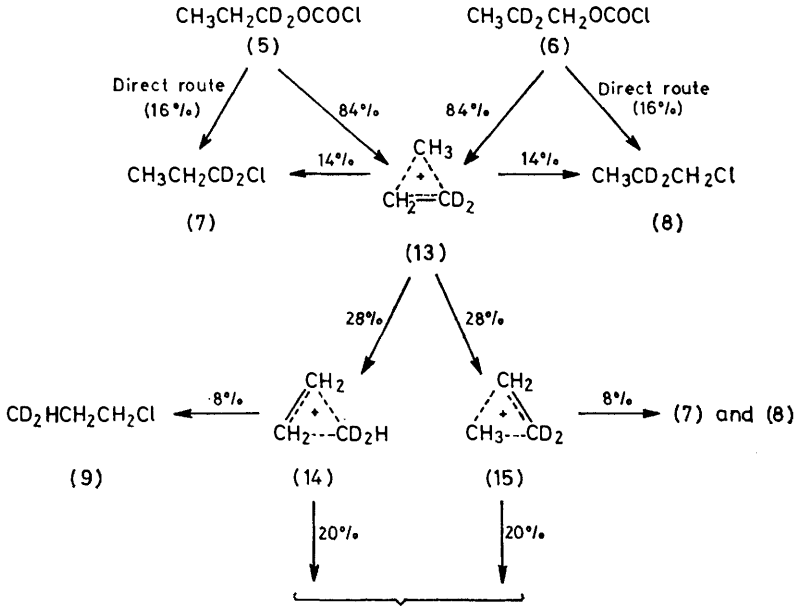
The 2-chloropropane obtained from each of the deuteriated propyl chloroformates revealed no proton–deuteron scrambling and was presumably formed only by irreversible 1,2-hydride shift.

In the higher n-alkyl systems (Bu^n, n-pentyl), rearrangement by 1,3-hydride shift was a significant reaction pathway [12] and accounted for a major proportion of those products which were previously thought to be formed by successive 1,2-hydride shifts.[1] Results obtained by ' proton-labelling ' at position 3 of otherwise fully deuteriated n-butyl chloroformate are shown in Table 5. The ^1H n.m.r. spectrum of the product obtained in this way was relatively simple to interpret and showed that s-butyl chloride was formed by at least four routes, an initial 1,3-hydride shift accounting for *ca.* 28% of the total substitution products. Similarly, the thermal decomposition of [3,3-$^2H_2$]-n-pentyl chloroformate gave rearranged alkyl halides which had arisen mainly by parallel 1,2- and 1,3-hydride shifts (Table 5), successive 1,2-hydride shifts being of minor importance in the formation of 3-chloropentane.

In addition, the thermal decomposition of [1,1,4,4,4-

$^2H_5$]-n-butyl chloroformate showed that a 1,2-shift of ethyl had occurred during the formation of *ca.* 2% of 1-chlorobutane (Table 6), suggesting direct capture of intermediate (3) (Scheme 2; $R^1 = H$, $R^2 = Me$) by chloride ion. Earlier studies on the nitrous acid deamination of n-butylamine failed to provide evidence for a 1,2-shift of ethyl [13] and although a trace of methylcyclopropane (0.6%) was detected in a later investigation, protonated cyclopropane intermediates were excluded on the grounds that no scrambling was observed in the butan-1-ol produced.[14] Some isotopic scrambling was, however, detected in the trifluoroacetolysis of [1-^{14}C]-n-butyl tosylate and [1-^{14}C]-n-butylmercury perchlorate.[15]

It is just conceivable that the minor products attributed to successive 1,2-hydride shifts in both the butyl and pentyl systems could have been formed in alternative ways, *e.g. via* proton–deuteron scrambling in the protonated cyclopropane intermediate (3) (Scheme 2; $R^1 = H$, $R^2 = Me$ or Et) before ring opening. It seems unlikely, however, that the necessary degree of scrambling would occur in an intermediate which can rearrange directly *via* (4) to a more stable secondary carbocation. A further possibility that cannot be dis-



Further scrambling to yield all six [$^2H_2$]-n-propyl chlorides (7)—(12) (see Table 3)

SCHEME 4

TABLE 5

Competitive 1,2- and 1,3-hydride shifts in the thermal decomposition of n-butyl, n-pentyl, and 3-methylbutyl chloroformates [a]

R in ROCOCl	RCl Composition [b] Isomer	%	H Shift
$CD_3CH_2CD_2CD_2$	$CD_3CH_2CD_2CD_2Cl$ [c]	22	
	$CD_3CH_2CDClCD_3$ [d]	43	1,2
	$CD_3CHClCHDCD_3$ [d]	7	2 × 1,2
	$CD_3CHClCD_2CD_2H$ [d]	27	1,3
	$CD_3CHDCDClCD_2H$ [d]	1	1,3 + 1,2
$CH_3CH_2CD_2CH_2CH_2$	$CH_3CH_2CD_2CH_2CH_2Cl$ [e]	36	
	$CH_3CH_2CD_2CHClCH_3$ [f]	48	1,2
	$CH_3CH_2CDClCHDCH_3$ [g]	2	2 × 1,2
	$CH_3CH_2CDClCH_2CH_2D$ [g]	14	1,3
$(CD_3)_2CDCH_2CH_2$	$(CD_3)_2CDCH_2CH_2Cl$ [h]	16	
	$(CD_3)_2CDCHClCH_3$ [j]	25	1,2
	$(CD_3)_2CClCHDCH_3$ [k]	34	2 × 1,2
	$(CD_3)_2CClCH_2CH_2D$ [k]	25	1,3

[a] Neat liquids; 150—160 °C (oil-bath). [b] By g.l.c. and n.m.r. integration (see Experimental section). [c] δ 1.41 (m, CH_2). [d] δ 0.97 (β-CD_2H), 1.43 (α-CD_2H), 1.68 (CH_2 and CHD), and 3.88 (CHCl). [e] δ 0.89 (3 H, t, CH_3, J_{HCCH} 6.3 Hz), 1.27br (2 H, t, δ-CH_2, J_{HCCH} 6.3 Hz), 1.73br (2 H, t, β-CH_2, J_{HCCH} 6.3 Hz), and 3.44 (2 H, t, α-CH_2, J_{HCCH} 6.3 Hz); δ_C 13.84 (s, CH_3), 21.90 (s, δ-CH_2), 28.40 (quintet, CD_2, J_{CD} 1.91 Hz), 32.37 (s, β-CH_2), and 45.04 (s, CH_2Cl). [f] δ 0.89 (3 H, t, δ-CH_3, J_{HCCH} 6.7 Hz), 1.39 (2 H, t, γ-CH_2, J_{HCCH} 6.7 Hz), 1.45 (3 H, d, β-CH_3, J_{HCCH} 6.7 Hz), and 3.92br (1 H, q, α-CH, J_{HCCH} 6.7 Hz). [g] δ 0.7—1.2 (m, CH_3), 1.2—1.8 (m, CH_2 and CHD); δ_D −3.5br (CDCl), −5.6br (CHD), and −6.2br (CH_2D); δ_C 10.64 (t, CH_2D, J_{CD} 19.5 Hz), 10.92 (s, CH_3), 30.94, and 30.99 (s, CH_2), CHD not detectable. [h] δ 1.63 (2 H, 3t, β-CH_2, J_{HCCH} 7.0, J_{HCCD} 0.8 Hz) and 3.52 (2 H, t, α-CH_2, J_{HCCH} 7.0 Hz); δ_C 22.71 [septet, $(CD_3)_2$, J_{CD} 18 Hz], 41.33 (s, β-CH_2), and 43.35 (s, α-CH_2). [j] δ 1.43 (3 H, d, CH_3, J_{HCCH} 6.7 Hz), 3.92br (1 H, q, CHCl, J_{HCCH} 6.7 Hz); δ_C 22.16 (s, CH_3) and 64.73 (s, CHCl). [k] 0.7—1.2 (m, CH_3 and CH_2D) and 1.3—2.0 (m, β-CH_2); δ_C 9.10 (t, CH_2D, J_{CD} 1.9 Hz), 9.28 (s, CH_3), 31.82 and 32.08 (sextets, CD_3, J_{CD} 1.9 Hz), 38.22 (t, CHD, J_{CD} 1.9 Hz), 38.44 (s, CH_3), 70.70br (s, CCl).

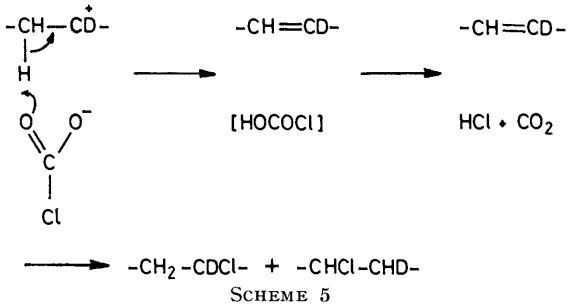
TABLE 6

1,2-Alkyl shifts between primary carbon centres in the thermal decomposition of alkyl chloroformates [a]

R in ROCOCl	Primary RCl composition [b] Isomer	%	Alkyl shift
$CD_3CH_2CH_2CD_2$	$CD_3CH_2CH_2CD_2Cl$ [c]	98	
	$CD_3CH_2CD_2CH_2Cl$ [c]	2	Et
$(CH_3)_2CHCH_2CD_2$	$(CH_3)_2CHCH_2CD_2Cl$ [d]	99	
	$(CH_3)_2CHCD_2CH_2Cl$ [d]	1	Pr^i
$(CH_3)_3CCH_2CD_2$	$(CH_3)_3CCH_2CD_2Cl$ [e]	90	
	$(CH_3)_3CCD_2CH_2Cl$ [e]	10	Bu^t

[a] Neat liquids; 150 °C (oil-bath). [b] From n.m.r. integration. [c] δ 1.43 (γ-CH_2), 1.71 (β-CH_2), and 3.48 (quintet, α-CH_2). δ_D −6.35 (CD_3), −5.54 (β-CD_2), and −3.79 (α-CD_2). [d] δ 0.90 (d, Me_2C, J_{HCCH} 6.3 Hz), 1.25—2.25 (CH_2 and CH), and 3.48br (s, α-CH_2); δ_C 22.10 (s, Me_2), 25.61 (s, CH), and 41.33 (s, β-CH_2). [e] δ 0.91 (s, Me_3C), 1.70 (quintet, β-CH_2, J_{DCCH} 1.1 Hz), and 3.45 (quintet, α-CH_2, J_{DCCH} 1.1 Hz).

tinguished from the second 1,2-hydride shift is that of elimination and re-addition of hydrogen (or deuterium) chloride within a solvent cage (Scheme 5); although it



SCHEME 5

was shown that no significant reaction occurred between free hydrogen chloride formed in the reaction medium and another added olefin.[1] Additional rearrangements not shown in Tables 5 and 6 might also have occurred to a small extent but were below the limits of reliable detectability.

The main findings are thus different from those obtained in the nitrous acid deamination of n-butylamine [14] or n-pentylamine.[16] In these reactions it was shown that the products could be accounted for exclusively on the basis of successive 1,2-hydride shifts in intermediate carbocations, 1,3-shifts and protonated cyclopropanes being of negligible importance.

A 1,3-hydride shift will largely account for the observation that n-pentyl and n-octyl chloroformates give appreciably higher percentages of 3-chloroalkane than are obtained from the 1-methylbutyl and 1-methylheptyl esters. The extent to which s-alkyl cations derived from straight-chain s-alkyl chloroformates rearrange before capture by chloride ion is in general small.[1,12] Results for the various octyl isomers are shown in Table 7. In each case, trace amounts of

TABLE 7

Thermal decomposition of straight-chain octyl chloroformates [a]

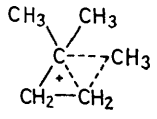
R in ROCOCl	RCl Yield (mol. equiv.)	RCl Composition (%) [b] 1-	2-	3-	4-
$CH_3(CH_2)_6CH_2$	0.20 [c]	44	36	18	2
$CH_3(CH_2)_5CHCH_3$	0.68 [d]	0	97.8	1.7	0.5
$CH_3(CH_2)_4CHEt$	0.65 [d]	0	0.6	98.6	0.8
$CH_3(CH_2)_3CHCH_2Et$	0.67 [d]	0	0.1	0.9	99.0

[a] Neat liquids (15.0 g, 1 mol. equiv.); 150 °C (oil-bath), 250 h. [b] 1-, 2-, 3-, or 4-halogeno-octane. [c] ROCOCl (0.62 mol. equiv. remained); product composition constant (±1%) at reaction times 50, 100, 150, 200, 250, and 300 h; olefin (0.18 mol. equiv.) (82% oct-1-ene) also formed, containing n-pentylcyclopropane (1%) (g.l.c.), δ +0.6 to −0.2 (complex m) with maxima at +0.4 and −0.1. [d] Olefins (0.32—0.35 mol. equiv.) also formed, containing in each case *ca.* 4—5% cyclopropane derivatives (g.l.c.), with characteristic ^{1}H n.m.r. in region δ +0.2 to −0.5 (complex m); maxima at +0.3, +0.2, and −0.3 (from 1-methylheptyl); +0.3, −0.03, −0.1, and −0.14 (from 1-ethylhexyl); +0.04, −0.05, and −0.08 (from 1-propylpentyl).

cyclopropane by-products were detectable and suggest that protonated cyclopropane intermediates could also be involved to a small extent in the rearrangements of these s-alkyl groups. The sequence and types of shift leading from n-octyl chloroformate to 4-chloro-octane has not been determined but several routes involving 1,2- and/or 1,3-hydride shifts are possible. The ion-pairs involved in these rearrangements appear to be longer lived and presumably therefore less tightly bound than those derived directly from the s-alkyl chloroformates since a higher percentage of 4-chloro-octane is found in the product derived from n-octyl chloroformate than is the case when either 1-methylheptyl or 1-ethylhexyl chloroformate is the starting material.

Rearrangement by successive 1,2-hydride shifts assumed greater importance in the thermal decomposition of 3-methylbutyl chloroformate, the second shift leading in this case from a s- to a t-alkyl cation. Two rearranged substitution products are formed, *viz.* 2-chloro-3-methyl- and 2-chloro-2-methyl-butane;[1] and by use of the heptadeuterio derivative shown (Table 5) the ^{1}H n.m.r. spectrum was simplified and it was shown that the 2-chloro-2-methylbutane was formed to approximately equal extents by a 1,3-hydride shift and (apparently) successive 1,2-hydride shifts. The alternative routes referred to above must be borne in mind, although it seems even less likely in this case that proton–deuteron scrambling in the protonated cyclopropane (3) (Scheme 2; $R^1 = R^2 = Me$) could account for the presence of deuterium at the 2-position of 2-chloro-2-methylbutane. This intermediate would be expected to rearrange readily to the t-pentyl cation and to have a shorter life than that of the corresponding intermediates in the n-butyl and n-pentyl rearrangements, yet significantly more label is found at the 2-position of the product derived from 3-methylbutyl chloroformate than is the case with the n-alkyl compounds. A 1,2-shift of isopropyl was also found to have occurred in *ca.* 1% of 1-chloro-3-methylbutane formed (Table 6), presumably *via* capture of intermediate (3) (Scheme 2; $R^1 = R^2 =$ Me) by chloride ion; and traces of 2-chloropropane and ethylene were formed by fragmentation. A possible mechanism is discussed below.

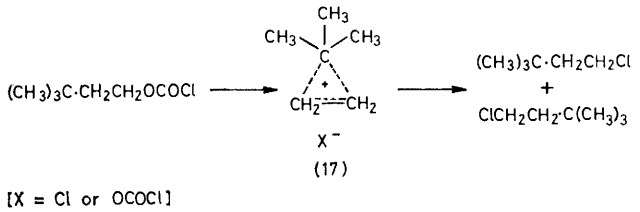
In the case of 3,3-dimethylbutyl chloroformate there is no possibility of rearrangement by 1,3-hydride shift, and we could not find evidence for the occurrence of a 1,3-methyl shift which would have given products derived from the 1,1-dimethylbutyl cation ($Me_2\overset{+}{C}CH_2$-CH_2CH_3) (*cf.* ref. 18). An edge-methylated cyclopropane (16) is thus excluded, either as an intermediate or as a



(16)

transition state in this system. Products derived from a 1,2-hydride shift and from two successive 1,2-shifts (hydrogen followed by methyl) were however formed in substantial quantities, together with small amounts of t-butyl chloride and ethylene (Table 8). Deuterium

labelling of 3,3-dimethylbutyl chloroformate at position 1 showed also that a 1,2-shift of t-butyl had occurred during formation of *ca.* 10% of the apparently unrearranged 1-chloro-3,3-dimethylbutane (Table 6). This represents 4% of the total substitution products and contrasts with earlier results obtained in the nitrous acid deamination of [1-^{14}C]-3,3-dimethylbutylamine, in which no t-butyl shift was detected.[17] 1,2-Shifts of t-butyl have previously been reported only in certain examples of rearrangement from one t-alkyl cation to another.[18] In view of the instability of primary alkyl cations it is thought that the t-butyl shift now observed in the 3,3-dimethylbutyl group most probably occurs *via* (17) (Scheme 6), which could be regarded as a corner-



SCHEME 6

methylated cyclopropane, formed analogously to the corner-protonated species postulated in Scheme 2 above.

The alternative of a single cyclic transition state (2; R = Bu^t) is thought less likely in view of our results with other primary alkyl systems for which the evidence points to a cationic species. G.l.c. showed the products to contain neither chloromethane nor 1,1-dimethylcyclopropane, which would be the anticipated products of demethylation of (17) (*cf.* deprotonation of protonated cyclopropanes for which ample evidence exists).[10] t-Butyl chloride and ethylene were, however, obtained and it is suggested that these might have been formed by fragmentation of (17); such a mechanism would constitute the exact reverse of that by which t-butyl chloride is thought to add to ethylene in the presence of aluminium trichloride;[19] and a similar scheme could apply to the fragmentation of 3-methylbutyl chloroformate referred to above. Fragmentation of the 3,3-dimethylbutyl group has previously been reported in the anodic oxidation of potassium 4,4-dimethylpentanoate [20] and in the deoxidation of 3,3-dimethylbutan-1-ol; [20] but not in the nitrous acid deamination of 3,3-dimethylbutylamine which also showed no evidence for a 1,2-t-butyl shift.[17]

It is interesting to note that both 3-methylbutyl and 3,3-dimethylbutyl chloroformate gave significantly higher yields of products derived from the t-alkyl cation than were obtained from the corresponding s-alkyl esters (Table 8 and ref. 1). As with the straight-chain examples above, it appears that s-alkyl cations derived from s-alkyl chloroformates have a shorter life within more tightly bound ion-pairs than those derived by rearrangement from t-alkyl chloroformates.

Alkenes obtained during the thermal decompositions of alkyl chloroformates can less easily be identified with specific rearrangement processes, as the same product can often be formed from alternative carbocation intermediates. However, alk-1-enes were found to be the principal, and sometimes exclusive, elimination products of primary alkyl chloroformates and were thought to be formed *via* concerted *cis*-elimination.[1] Elimination from a carbocation–chloroformate ion-pair has also been suggested.[21] Our results with deuterium-labelled n-butyl, 3-methylbutyl, and 3,3-dimethylbutyl compounds now show that a 1,2-shift of hydrogen accompanies the formation of alk-1-ene (Table 9) with the clear implication that the same intermediate is involved as occurs in the formation of rearranged alkyl chloride (Scheme 7). Preferential formation of the terminal

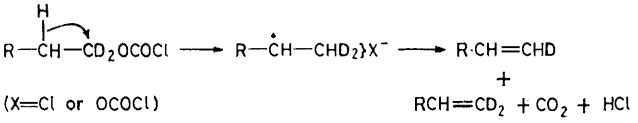
TABLE 8

Thermal decomposition of 3,3-dimethylbutyl and 1,2,2-trimethylpropyl chloroformates [a]

ROCOCl			Product composition [b] (mol. equiv.)			RCl composition [c] (mol. %)				Hydrocarbon composition (mol. %)			
R	g	*t*/h	ROCOCl	RCl	Hydrocarbon	A	B	C	D	E	F	G	H
$Me_3CCH_2CH_2$	3.3	100	0.57	0.34	0.09	40	9	49	2	75	17	9	
Me_3CCHMe	11.2	75	0.04	0.81	0.15		59	41		67	22	7	4

[a] Neat liquids; 150 °C (oil-bath); no significant difference in product compositions at 25 h intervals. [b] By analysis of the liquid reaction mixture. The evolved gas was also analysed and shown to contain (a) from $Me_3CCH_2CH_2OCOCl$: ethylene (0.02 mol. equiv.) but neither CH_3Cl nor 1,1-dimethylcyclopropane; (b) from $Me_3CCH(Me)OCOCl$: ethylene (0.01 mol. equiv.), C_2H_5Cl (0.07 mol. equiv.), and isobutene (trace). [c] A = $Me_3CCH_2CH_2Cl$; B = $Me_3CCHClMe$; C = Me_2CClCH_2Me; D = Me_3CCl. [d] E = $Me_3CCH{=}CH_2$; F = $Me_2C{=}CMe_2$; G = $CH_2{=}CMeCHMe_2$; H = 1,1,2-trimethylcyclopropane.

olefin from a secondary carbocation is unusual and must be attributable in this case to the relative positioning



SCHEME 7

of the groups in the ion-pair intermediate. We have also shown that a 1,3-shift of hydrogen occurs during the formation of *ca.* 11% of the olefins obtained from [1,1,2,2,4,4,4-$^2H_7$]butyl chloroformate (Table 9). Earlier studies on the thermal decomposition of *N*-methyl-*N*-n-propyl-3-methylbutylamine oxide showed the unexpected formation of 2-methylbut-1-ene (*ca.* 1%).[22] This is consistent with the occurrence of two successive 1,2-shifts and/or a 1,3-hydride shift, although the main olefinic products were considered to be formed by con-

certed *cis*-elimination. The possibility should now be considered that pyrolytic eliminations from primary alkyl esters in the liquid phase might in general proceed *via* the formation of ion-pair intermediates in which rearrangement by 1,2- and/or 1,3-hydride shift has occurred.

TABLE 9

Alkenes derived from deuterium labelled alkyl chloroformates

R in ROCOCl	Alkene composition (%) [a]	
$Me_3CCH_2CD_2$	$Me_3CCH{=}CD_2$ [b]	19
	$Me_3CCH{=}CHD$ [b]	31
	$CH_2{=}CMeCH(Me)CHD_2$ [b]	20
	$Me_2C{=}C(Me)CHD_2$ [b]	30
$Me_2CHCH_2CD_2$	$Me_2CHCH{=}CD_2$ [c]	31
	$Me_2CHCH{=}CHD$ [c]	47
	$CH_2{=}C(Me)CH_2CHD_2$	7
	$Me_2C{=}CHCHD_2$	15
$CD_3CH_2CH_2CD_2$	*d*	
$CD_3CH_2CD_2CD_2$	*e*	

[a] By g.l.c. and ^1H n.m.r. (see Experimental section). [b] Combined alkenes integrated in the regions δ 5.61—6.07 (–CH=) and 4.61—5.01 (=CDH, $=CH_2$). [c] 3-Methylbut-1-ene separated by preparative g.l.c. and integrated in the regions δ 5.4—6.1 (–CH=) and 4.70—5.0 (=CHD). [d] Complex mixture of but-1-ene (60%) and but-2-ene (40%) isomers containing CD_3CH_2-CH=CHD (*ca.* 32%) [δ 4.83 (*cis*-CHD, d, J_{HCCH} 10 Hz; t, J_{HCD} 1.0 Hz); 4.89 (*trans*-CHD, d, J_{HCCH} 17 Hz; t, J_{HCD} 1.5 Hz); *cf.* L. K. Montgomery and J. W. Matt, *J. Amer. Chem. Soc.*, 1967, **89**, 6556]. [e] Complex mixture of but-1-ene (63%) and but-2-ene (37%) isomers containing $CD_2{=}CHCD_2CD_2H$ (*ca.* 8%), δ 0.9 (m, CD_2H) and 5.85 (m, =CH–).

EXPERIMENTAL

Starting materials were obtained commercially unless otherwise specified and were checked for purity by g.l.c. and/or ^1H n.m.r. Bromobenzene was dried (P_2O_5) and redistilled, b.p. 155—156 °C. Di-n-butyl carbonate, b.p. 52.5—53 °C at 0.25 mmHg, was prepared from the chloroformate and excess butan-1-ol in the absence of base.[23]

G.l.c.—Analytical separations were carried out on a Perkin–Elmer F11 chromatograph with nitrogen carrier gas and flame ionisation detection. A no. 18 stream splitter was used with capillary or support-coated open tubular (SCOT) columns. The following columns were used: (a) 2 m × 1/8 in o.d. stainless steel packed with polyethylene glycol adipate (PEGA) (8%) and silicone fluid MS 200 (3%), or with PEGA (10%), on 85—100 mesh Celite, for the analysis of alcohols and for following changes in the overall hydrocarbon, alkyl chloride, and alkyl chloroformate content of reaction mixtures; (b) 50 m × 0.25 mm i.d. stainless steel capillary columns containing squalane or silicone oil MS550 [24] for the analysis of isomeric alkyl halides and alkenes [products from 3,3-dimethylbutyl and 1,1,2-trimethylpropyl chloroformates were analysed on the silicone oil column (20 °C; N_2 inlet pressure 10 lb in^{-2}) as follows (t_R/min): 3,3-dimethylbut-1-ene (7.1), 2-chloro-2-methylpropane (7.4), 1,1,2-trimethylcyclopropane (8.5), 2,3-dimethylbut-1-ene (8.8), 2,3-dimethylbut-2-ene (13.2), 2-chloro-3,3-dimethylbutane (32.9), 2-chloro-2,3-dimethylbutane (and 2-chloro-2-methylpentane) (34.0), 1-chloro-3,3-dimethylbutane (40.5)]; (c) 50 ft × 0.02 in i.d. SCOT column containing PEGA (21 °C; N_2 inlet pressure 0.5 lb in^{-2}) for the separation of chloro-octane isomers (t_R/min): 4-(42.6), 3-(45.6), 2-(50.0), 1-(83.3); (d) 15 ft × 9 mm o.d. glass column containing 15% squalane on 60—80 mesh Phaseprep A (21 °C; N_2 inlet pressure 4 lb in^{-2}) for analysis of gaseous products (t_R/min): ethylene (3.0), propene (4.6), chloromethane (5.8), 2-methylpropene (9.8), and chloroethane (13.0).

Preparative g.l.c. was carried out on Varian-Aerograph Autoprep and Pye 105 chromatographs with N_2 as carrier gas and columns as specified.

N.m.r. Spectroscopy.—^1H N.m.r. spectra were run at 60 MHz on a Perkin-Elmer R12B and in certain cases at 220 MHz on a Varian H220 instrument. ^{13}C Spectra were obtained on Brüker HX 90E and HX 90FT spectrometers, the latter also being used for recording ^2H spectra. ^1H and ^{13}C chemical shifts are quoted relative to tetramethylsilane and ^2H chemical shifts relative to $CDCl_3$.

Microanalytical Data.—Standard methods were used for the determination of C, H, and Cl. In the case of deuterium containing compounds, the figures given for hydrogen (H*) are ' apparent ' values, obtained by assuming the total water produced on combustion to be H_2O.

Preparation of Alkyl Chlorides.—(a) 2-*Chloro*-2,3-*dimethylbutane*. 2,3-Dimethylbutan-2-ol (5.0 g) was converted by the use of thionyl chloride and pyridine [25] into the corresponding chloride (1.9 g, 30%), b.p. 116—118 °C, n_D^{20} 1.420 2 (98% pure by g.l.c.), δ 0.99 (6 H, d, Me_2C, J_{HCCH} 6.0 Hz), 1.5 (6 H, s, Me_2CCl), and 1.73 (1 H, septet, CH, J_{HCCH} 6.0 Hz).

(b) 2-*Chloro*-2-*methylpentane*. 2-Methylpentan-2-ol (5.1 g) similarly [25] gave the chloride (2.2 g, 34%), b.p. 110—112 °C, n_D^{20} 1.412 9 (98% pure by g.l.c.), δ 2.5 (6 H, s, Me_2CCl) and 1.3—2.9 (7 H, complex m, $CH_3CH_2CH_2$).

(c) 2-*Chloro*-3,3-*dimethylbutane*. 3,3-Dimethylbutan-2-ol (10.2 g, 0.1 mol) was added to chloromethylenedimethylammonium chloride (15.5 g, 0.12 mol) in hexamethylphosphoramide (71.6 g) and the mixture was heated under reflux for 18 h.[26] Distilled water (150 cm^3) was added and the organic layer which separated was washed and then dried (K_2CO_3) to yield a product (4.8 g) containing (g.l.c.) the required chloride (61%), 2-chloro-2,3-dimethylbutane (0.6%), and hydrocarbons (38.4%). Separation by preparative g.l.c. on silicone oil SE30 at 80 °C afforded 2-chloro-3,3-dimethylbutane (0.5 g, 99.5% pure), n_D^{20} 1.418 2, δ 0.98 (9 H, s, Me_3C), 1.41 (3 H, d, Me, J_{HCCH} 6.7 Hz), and 3.84 (1 H, q, CHCl, J_{HCCH} 6.7 Hz).

(d) 1-*Chloro*-3,3-*dimethylbutane*. A described method [27] starting from t-butyl chloride (100 g), aluminium trichloride (5.0 g), and ethylene in excess, gave (i) 66.7 g, b.p. 110—120 °C (88% 1-chloro-3,3-dimethylbutane); (ii) 20.2 g, b.p. 120—150 °C (52% 1-chloro-3,3-dimethylbutane). Fraction (ii) (1.5 g) was purified by preparative g.l.c. on PEGA at 110 °C to yield 1-chloro-3,3-dimethylbutane (0.3 g), n_D^{20} 1.415 9, δ 0.91 (9 H, s, Me_3C), 1.7 (2 H, t, β-CH_2, J_{HCCH} 7.7 Hz), and 3.47 (2 H, t, α-CH_2, J_{HCCH} 7.7 Hz).

Preparation of 3,3-*Dimethylbutan*-1-*ol.*—Crude 1-chloro-3,3-dimethylbutane (30.0 g) [fraction (i) above] was converted as described [27] to the alcohol (10.4 g), b.p. 140—145 °C (83% pure) which was purified by preparative g.l.c. on PEGA at 140 °C to yield 3,3-dimethylpropan-1-ol (6.45 g), n_D^{20} 1.419 2 (99% pure by g.l.c.), δ 0.92 (9 H, s, Me_3C), 1.5 (2 H, t, β-CH_2, J_{HCCH} 9.5 Hz), 3.58 (2 H, t, α-CH_2, J_{HCCH} 9.5 Hz), and 4.82 (1 H, s, OH). Reduction of 3,3-dimethylbutanoic acid (12.7 g) by $LiAlH_4$ [28] also gave the alcohol (4.8 g, 43%), b.p. 58 °C at 15 mm, n_D^{20} 1.419 2.

Preparation of Cyclopropane Derivatives.—1,1-Dimethylcyclopropane, δ 1.06 (6 H, s, Me), 0.21 (4 H, s, ring protons),

was prepared from 1,3-dibromo-2,2-dimethylpropane as described.[29] Another procedure,[30] starting from methylene iodide and 2-methylbut-2-ene, gave 1,1,2-trimethylcyclopropane, b.p. 56—58 °C, δ 0.8 to −0.2 (complex m, ring protons) with sharp maxima at 0.42 and −0.12. Similarly, methylene iodide (26.8 g, 100 mmol) and hept-1-ene (19.6 g, 200 mmol), in the presence of a zinc–copper couple prepared from zinc (16.4 g, 250 mmol), gave *n-pentylcyclopropane* (1.3 g, 5.2%), b.p. 35—38 °C at 20 mmHg, M^+ 112, δ 0.6 to −0.2 (complex multiplet, ring protons) with sharp maxima at 0.36 and −0.08.

Deuterium Labelling.—(a) *Carboxylic acids.* [$^2H_4$]-Ethanoic acid (99.5 atom% D) was obtained from Prochem. [2,2-$^2H_2$]Propanoic acid, b.p. 138—140 °C, n_D^{20} 1.387 3, δ 0.6 (m, CH_3), was prepared as described.[31] Butanoic acid derivatives were prepared from [2,2,2-$^2H_3$]ethanol (53.6 g) (see below) which was treated with hydrobromic and sulphuric acids [32] to yield [2,2,2-$^2H_3$]-1-bromoethane (82.0 g, 67.5%), b.p. 37—38 °C, n_D^{20} 1.423 4. The bromide was added to sodiodiethyl malonate [33] to give diethyl [2,2,2-$^2H_3$]ethylmalonate (124.7 g, 90%), b.p. 56.8—57 °C at 0.2 mmHg, n_D^{20} 1.416 9, which on hydrolysis yielded [2,2,2-$^2H_3$]ethylmalonic acid (96.5%), m.p. 109—112 °C, δ(CD_3CN) 1.82br (2 H, d, CH_2, J_{HCCH} 7.3 Hz), and 3.29 (1 H, t, CH, J_{HCCH} 7.3 Hz). The latter compound (50.0 g) was treated with eight successive quantities of D_2O (total 200 g) as described [34] to give [2,2,2-$^2H_3$]ethyl[$^2H_3$]malonic acid (46.8 g, 91.6%), m.p. 110—112 °C, δ(CD_3CN) 1.82br (s, CH_2). Decarboxylation at 130—170 °C then yielded [2,2,4,4,4-$^2H_5$]*butanoic* [^2H]*acid* (31.6 g, 99%), b.p. 61—64 °C at 18—20 mmHg, n_D^{20} 1.397 3 (Found: C, 51.0; H*, 9.1. $C_4H_2D_6O_2$ requires C, 51.0; H*, 9.3%), δ 1.61br (m, β-CH_2) (>98% by integration). A further quantity of [2,2,2-$^2H_3$]ethylmalonic acid (19.0 g) was decarboxylated directly to yield [4,4,4-$^2H_3$]butanoic acid (12.7 g, 99.2%), b.p. 60—61 °C at 18 mmHg, n_D^{20} 1.402 5 (Found: C, 52.5; H*, 9.1. Calc. for $C_4H_5D_3O_2$: C, 52.7; H*, 9.2%), δ 1.61br (2 H, t, β-CH_2, J_{HCCH} 7.3 Hz), 2.29br (2 H, t, α-CH_2, J_{HCCH} 7.3 Hz).

(b) *Preparations of alcohols from carboxylic acids.* Reduction of the corresponding acids by $LiAlH_4$ or $LiAlD_4$ as appropriate was carried out in diglyme [35] to yield [2,2,2-$^2H_3$]ethanol (87%); b.p. 78—80 °C, n_D^{20} 1.360 9; δ 3.58br (2 H, m, CH_2) and 2.7 (1 H, s, OH); [1,1-$^2H_2$]propan-1-ol (56%),[36] b.p. 97 °C, n_D^{23} 1.381 3, δ 0.62 (3 H, t, CH_3, J_{HCCH} 7.0 Hz), 1.25br (2 H, q, CH_2, J_{HCCH} 6.7 Hz), and 4.82br (1 H, s, OH); [2,2-$^2H_2$]propan-1-ol (61%),[36] b.p. 96—97 °C, n_D^{20} 1.384 3; [1,1,2,2-$^2H_4$]*propan-1-ol* (64%), b.p. 96 °C, n_D^{20} 1.383 9 (Found: C, 56.4; H*, 13.4. $C_3H_4D_4O$ requires C, 56.3; H*, 13.2%), δ 0.6br (m, CH_3); or in anhydrous ether [28] to yield [1,1,4,4,4-$^2H_5$]*butan-1-ol* (68%), b.p. 64—67 °C at 80—92 mmHg, n_D^{20} 1.399 2 (Found: C, 59.4; H*, 13.1. $C_4H_5D_5O$ requires C, 60.7; H*, 13.5%), δ 1.39br (4 H, m, CH_2CH_2) and 4.15 (1 H, s, OH); [1,1,2,2,4,4,4-$^2H_7$]*butan-1-ol* (73%), b.p. 72 °C at 115 mmHg, n_D^{20} 1.399 2 (Found: C, 57.2; H*, 12.6. $C_4H_3D_7O$ requires C, 59.2; H*, 13.4%), δ 1.32br (2 H, m, CH_2) and 3.22 (1 H, s, OH); [1,1-$^2H_2$]-3-*methylbutan-1-ol* (67%), b.p. 131—133 °C, n_D^{20} 1.407 3 (Found: C, 66.6; H*, 13.4. $C_5H_{10}D_2O$ requires C, 66.7; H*, 13.6%), δ 0.65 (6 H, d, Me_2, J_{HCCH} 6.0 Hz), 0.8—2.1 (3 H, complex m, $CHCH_2$), and 4.64 (1 H, s, OH); [1,1-$^2H_2$]-3,3-*dimethylbutan-1-ol* (45%), b.p. 49 °C at 12 mmHg, n_D^{20} 1.4192 (Found: C, 68.5; H*, 13.8. $C_6H_{12}D_2O$ requires C, 69.2; H*, 13.8%), δ 0.9 (9 H, s, Me_3C), 1.48 (2 H, quintet, CH_2, J_{HCCD} 1.2 Hz), and 3.0 (1 H, s, OH).

(c) [3,3-$^2H_2$]*Pentan-1-ol.* By a described procedure,[36] [1,1-$^2H_2$]propan-1-ol (8.0 g) was converted into the bromide (10.8 g) and thence *via* the Grignard reagent and reaction with ethylene oxide (10.0 g) to [3,3-$^2H_2$]pentan-1-ol (2.0 g, 17%), b.p. 138 °C, n_D^{20} 1.410 6, δ 0.89 (3 H, t, CH_3, J_{HCCH} 6.7 Hz), 1.1—1.7 (4 H, complex m, β- and δ-CH_2), 3.2—3.7 (2 H, m, α-CH_2), and 5.08 (1 H, t, OH, J_{HOCH} 4.8 Hz).

(d) 3-[$^2H_3$]*Methyl*[3,4,4,4-$^2H_4$]*butan-1-ol.* [$^2H_6$]Acetone (25.0 g) was reduced by $LiAlD_4$ in diglyme [35] to yield [$^2H_7$]propan-2-ol (24.9 g, 95%), b.p. 82 °C, n_D^{20} 1.377 1, which was heated under reflux (2 h) with concentrated hydrochloric acid (89.7 cm^3) and anhydrous $ZnCl_2$ (152.5 g) [37] to yield [$^2H_7$]-2-chloropropane (16.5 g, 52%), b.p. 34—36 °C, n_D^{20} 1.379 1. The latter compound was added (2 h) to a stirred suspension under argon of an intimate mixture of finely divided lithium (2 g) and sodium (0.06 g) in anhydrous ether (250 cm^3) at −30 °C.[38] After a further 2 h, ethylene was passed in excess (4 h) followed by CO_2-free air (2 h), whilst the temperature was allowed to rise to 20 °C. After reintroduction of the argon atmosphere, saturated aqueous ammonium chloride was added in excess. Extraction with ether, followed by drying ($MgSO_4$) and distillation yielded 3-[$^2H_3$]*methyl*[3,4,4,4-$^2H_4$]*butan-1-ol* (4.5 g, 25%), b.p. 132 °C, n_D^{20} 1.407 1 (Found: C, 37.9; H*, 13.5. $C_5H_7D_5O$ requires C, 37.9; H*, 13.5%), δ 1.15br (2 H, t, α-CH_2, J_{HCCH} 6.7 Hz), 3.3 (2 H, t, β-CH_2, J_{HCCH}), and 4.8 (1 H, s, OH).

Preparation of Alkyl Chloroformates.—n-Propyl, n-butyl, n-pentyl, 3-methylbutyl, n-octyl, and 1-methylheptyl chloroformate were prepared as described.[1] By similar procedures, the following were obtained: [2,2,2-$^2H_3$]*ethyl chloroformate* (73%), b.p. 46—48 °C at 140—145 mmHg, n_D^{20} 1.395 2 (Found: Cl, 31.4. $C_3H_2D_3ClO_2$ requires Cl, 31.8%), δ 4.3 (septet, CH_2, J_{HCCD} 1.1 Hz); [1,1-$^2H_2$]-*n-propyl chloroformate* (59%), b.p. 28—30 °C at 30 mmHg, n_D^{20} 1.405 0 (Found: C, 38.7; H*, 5.9. $C_4H_5D_2ClO_2$ requires C, 38.6; H*, 5.8%), δ 0.99 (3 H, t, CH_3, J_{HCCH} 7.0 Hz) and 1.76br (2 H, q, CH_2, J_{HCCH} 6.7 Hz); [2,2-$^2H_2$]-*n-propyl chloroformate* (59%), b.p. 28—30 °C at 30 mmHg, n_D^{20} 1.405 1 (Found: C, 38.6; H*, 5.8. $C_4H_5D_2ClO_2$ requires C, 38.6; H*, 5.8%), δ 0.99br (3 H, m, CH_3) and 4.28br (2 H, m, α-CH_2); [1,1,2,2-$^2H_4$]-*n-propyl chloroformate* (65%), b.p. 29—31 °C at 30 mmHg, n_D^{20} 1.404 6 (Found: C, 38.3; H*, 6.0. $C_4H_3D_4ClO_2$ requires C, 38.0; H*, 5.9%), δ 0.99br (s, CH_3); [1,1,4,4,4-$^2H_5$]-*n-butyl chloroformate* (91%), b.p. 42 °C at 20 mmHg, n_D^{20} 1.412 2 (Found: C, 42.3; H*, 6.4; Cl, 25.2. $C_5H_4D_5ClO_2$ requires C, 42.4; H*, 6.7; Cl, 25.0%), δ 1.36br (2 H, t, γ-CH_2, J_{HCCH} 6.0 Hz) and 1.67br (2 H, t, β-CH_2, J_{HCCH} 6.0 Hz); [1,1,2,2,-4,4,4-$^2H_7$]-*n-butyl chloroformate* (81%), b.p. 57 °C at 35 mmHg, n_D^{20} 1.412 2 (Found: C, 39.1; H*, 6.7; Cl, 24.3. $C_5H_2D_7ClO_2$ requires C, 41.8; H*, 6.9; Cl, 24.7%), δ 1.36br (s, CH_2); [3,3-$^2H_2$]-*n-pentyl chloroformate* (91%), b.p. 56 °C at 18 mmHg, n_D^{20} 1.419 0 (Found: C, 47.1; H*, 7.4. $C_6H_9D_2ClO_2$ requires C, 47.2; H*, 7.4%), δ 0.9 (3 H, t, CH_3, J_{HCCH} 6.7 Hz), 1.36br (2 H, q, δ-CH_2, J_{HCCH} 6.3 Hz), 1.71br (2 H, t, β-CH_2, J_{HCCH} 6.7 Hz), and 4.27 (2 H, t, α-CH_2, J_{HCCH} 6.7 Hz); [1,1-$^2H_2$]-3-*methylbutyl chloroformate* (87%), b.p. 55—57 °C at 22 mmHg, n_D^{20} 1.417 8 (Found: C, 47.3; H*, 7.4. $C_6H_9D_2ClO_2$ requires C, 47.2; H*, 7.4%), δ 0.93 (6 H, d, Me_2, J_{HCCH} 5.3 Hz) and 1.2—2.2 (3 H, complex m, $CHCH_2$); 3-[$^2H_3$]*methyl*[3,4,4,4-$^2H_4$]*butyl chloroformate* (88%), b.p. 55—56 °C at 22 mmHg, n_D^{20} 1.417 5 (Found: C, 46.0; H*, 7.2. $C_6H_4D_7ClO_2$ requires C, 45.7; H*, 7.5%), δ 1.60br (2 H, t, β-CH_2, J_{HCCH} 6.7 Hz) and 4.31

(2 H, t, α-CH_2, J_{HCCH} 7.0 Hz); 3,3-*dimethylbutyl chloroformate* (75%), b.p. 53 °C at 15 mmHg, n_D^{20} 1.420 2 (Found: C, 50.7; H, 8.2; Cl, 21.7. $C_7H_{13}ClO_2$ requires C, 51.1; H, 8.0; Cl, 21.5%), δ 0.93 (9 H, s, Me_3), 1.61 (2 H, t, β-CH_2, J_{HCCH} 7.3 Hz), and 4.29 (2 H, t, α-CH_2, J_{HCCH} 7.3 Hz); [3,3-$^2H_2$]-3,3-*dimethylbutyl chloroformate* (93%), b.p. 53 °C at 15 mmHg, n_D^{20} 1.420 2 (Found: C, 50.1; H*, 8.0; Cl, 21.4. $C_7H_{11}D_2ClO_2$ requires C, 50.5; H*, 8.0; Cl, 21.3%), δ 0.93 (9 H, s, Me_3) and 1.62br (2 H, s, CH_2); 1,2,2-*trimethylpropyl chloroformate* (78%), b.p. 44 °C at 12 mmHg, n_D^{20} 1.418 2 (Found: C, 50.4; H, 8.2; Cl, 21.8. $C_7H_{13}ClO_2$ requires C, 51.1; H, 8.0; Cl, 21.5%), δ 0.93 (9 H, s, Me_3), 1.26 (3 H, d, CH_3, J_{HCCH} 6.7 Hz), and 4.68 (1 H, q, CH, J_{HCCH} 6.7 Hz); 1-*ethylhexyl chloroformate* (75%), b.p. 91.5 °C at 15 mmHg, n_D^{22} 1.427 3 (Found: C, 56.3; H, 8.9; Cl, 18.4. $C_9H_{17}ClO_2$ requires C, 56.1; H, 8.8; Cl, 18.4%), δ 0.6—1.8 (16 H, complex m, Et, n-C_5H_{11}) and 4.3—4.9 (1 H, complex m, CH); 1-*propylpentyl chloroformate* (77%), b.p. 90 °C at 15 mmHg, n_D^{22} 1.426 3 (Found: C, 56.2; H, 8.9; Cl, 18.4. $C_9H_{17}ClO_2$ requires C, 56.1; H, 8.8; Cl, 18.4%), δ 0.5—1.7 (16 H, complex m, n-C_4H_9, n-C_3H_7) and 4.4—4.9 (1 H, complex m, CH).

Thermal Decompositions of Alkyl Chloroformates.—(a) *Unlabelled chloroformates.* Experiments reported in Tables 1, 2, 7, and 8 were carried out under reflux and with a cold trap (−80 °C) attached to avoid losses. Gaseous products (Tables 2 and 8) were collected over water. The total products were analysed by g.l.c.

(b) [2,2,2-$^2H_3$]*Ethyl chloroformate.* The compound (2.2 g, 20 mmol) in di-n-butyl carbonate (22.4 g) was heated (150 °C for 30 h). Products were allowed to distil directly into an n.m.r. tube (−80 °C) which collected [2,2,2-$^2H_3$]-chloroethane (0.18 g, 2.7 mmol), δ 6.48 (septet, CH_2, J_{DCCH} 0.9 Hz), only. In a similar experiment, the total products from the chloroformate (1.1 g, 10 mmol) were collected over water as a gaseous mixture of chloroethane (1.0 mmol) and ethylene (0.65 mmol); the residual chloroformate remained unchanged.

(c) [1,1-$^2H_2$]-, [2,2-$^2H_2$]-, *and* [1,1,2,2-$^2H_4$]-*n-Propyl chloroformates.* In each case the chloroformate (2 g) in bromobenzene (10 g) was heated (150 °C for 168 h). Volatile products were distilled directly as formed to a receiver (−80 °C) and were subsequently separated by preparative g.l.c. on squalane at 21 °C to yield 1- and 2-chloropropane. The 1-chloropropane fractions obtained from both the [$^2H_2$]propyl chloroformates had similar complex ^1H n.m.r. spectra, differing only in the relative intensities of the peaks present. On the basis of known deuterium isotope shifts and deuterium–proton coupling constants,[38] assignments were made as shown (Table 3). [1,1-$^2H_2$]-n-Propyl chloroformate also yielded [1,1-$^2H_2$]-2-chloropropane, δ 1.44 (1 H, d of quintets, CD_2H, J_{HCCH} 6.5, J_{HCD} 2.0 Hz), 1.47 (3 H, d, CH_3, J_{HCCH} 6.5 Hz), and 4.12 (1 H, quintet of quintets, CHCl, J_{HCCH} 6.5, J_{HCCD} 1.0 Hz); δ_C 26.71 (quintet, CD_2H, J_{CD} 20 Hz), 27.17 (s, CH_3), and 53.81 (s, CHCl). The [2,2-$^2H_2$]-n-propyl ester similarly gave [1,2-$^2H_2$]-2-chloropropane, δ 1.35—1.55 (2 H, m, CH_2D) and 1.47 (3 H, t, CH_3, J_{HCCD} 1.0 Hz); δ_C 28.64 (t, CDH_2, J_{CD} 19 Hz), 27.10 (s, CH_3), and 53.49 (t, CDCl, J_{CD} 24 Hz).

The [$^2H_4$]-n-propyl chloroformate yielded a mixture of 1-chloropropane isomers with a proton distribution as shown (Table 4) and [1,1,2,2-$^2H_4$]-2-chloropropane, δ 1.46 (t, CH_3, J_{HCCD} 1.0 Hz); δ_C 26.32 (septet, CD_3, J_{CD} 19 Hz), 27.0 (s, CH_3), and 53.42 (t, CDCl, J_{CD} 24 Hz).

(d) *Deuterium labelled n-butyl, n-pentyl, 3-methylbutyl, and 3,3-dimethylbutyl chloroformates.* The chloroformates were heated at the temperatures and for the times specified below. In each case the products were allowed to distil as formed, alkyl chlorides being collected in a flask held at 20 to −80 °C and alkenes in a further trap at −80 °C. The alkyl chloride isomers were then separated by preparative g.l.c. (C_4 and C_5 products on squalane at 50 °C; C_6 products on dinonyl phthalate at 60 °C). Thus, [1,1,2,2,4,4,4-$^2H_7$]-n-butyl chloroformate (6.0 g) (150 °C for 720 h) gave chlorobutanes (1.2 g) which were separated into 1-chlorobutane (99.5% pure) and 2-chlorobutane (99.5% pure) (Table 5). Alkenes (0.2 g) were redistilled directly into an n.m.r. tube (Table 9). [1,1,4,4,4-$^2H_5$]-n-Butyl chloroformate (5.0 g) (150 °C for 160 h) gave chlorobutanes (1.6 g) which were separated into 1-chlorobutane (>99% pure) (Table 6) and 2-chlorobutane (>99% pure) consisting of CD_3CH_2-$CHClCHD_2$ (53%) (*via* 1,2-H shift) and $CD_3CHClCH_2CHD_2$ (47%) (*via* 1,3- and/or 2 × 1,2-H shift), δ 0.7—1.2 (γ-CHD_2), 1.2—1.5 (β-CHD_2), 1.5—1.9 (CH_2), and 3.6—4.1 (CHCl). Alkenes (0.4 g) were redistilled directly into an n.m.r. tube (Table 9). [3,3-$^2H_2$]-n-Pentyl chloroformate (11.2 g) (160 °C for 168 h) gave chloropentanes (4.8 g) which were separated into 1-chloropentane (*ca.* 100% pure), 2-chloropentane (98% pure), and 3-chloropentane (94% pure) (Table 5).

3-[$^2H_3$]Methyl[3,4,4,4-$^2H_4$]butyl chloroformate (14.1 g) (150 °C for 168 h) gave alkyl chlorides (6.3 g) which were separated into 1-chloro-3-methylbutane, 2-chloro-3-methylbutane, and 2-chloro-2-methylbutane (each *ca.* 100% pure) (Table 5).

[1,1-$^2H_2$]-3-Methylbutyl chloroformate (7.1 g) (150 °C for 168 h) similarly gave alkyl chlorides (3 g) and alkenes (0.6 g). The chlorides were separated as above to give 1-chloro-3-methylbutane isomers (Table 6), [1,1-$^2H_2$]-2-chloro-3-methylbutane, δ 0.98 (6 H, d, Me_2C, J_{HCCH} 6.7 Hz), 1.2—2.3 (2 H, complex m, CD_2H and β-CH), and 3.6—4.1 (1 H, complex m, CHCl), and [4,4-$^2H_2$]-2-chloro-2-methylbutane, δ 1.0br (1 H, t, CD_2H, J_{HCCH} 6.7 Hz) and 1.25—2.4 (8 H, complex m, Me_2CClCH_2). The alkenes contained 3-methylbut-1-ene (78%), 2-methylbut-1-ene (7%), and 2-methylbut-2-ene (15%). The 3-methylbut-1-ene was separated by preparative g.l.c. on squalane at 20 °C and was analysed by ^1H n.m.r. (Table 9).

[1,1-$^2H_2$]-3,3-Dimethylbutyl chloroformate (6.0 g) (150 °C for 870 h) gave alkyl chlorides (0.9 g) which were separated to yield 1-chloro-3,3-dimethylbutane isomers (Table 6). Alkenes (0.2 g) which were collected were shown by g.l.c. to contain 3,3-dimethylbut-1-ene (50%), 2,3-dimethylbut-1-ene (20%), and 2,3-dimethylbut-2-ene (30%). ^1H N.m.r. integration showed the relative proportions of $Me_3CCH{=}CD_2$ and $Me_3CCH{=}CHD$ to be 38 to 62 (Table 9).

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