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COMPETITIVE 1,2- AND 1,3-HYDRIDE SHIFTS IN THE THERMAL DECOMPOSITION OF N-ALKYL CHLOROFORMATES

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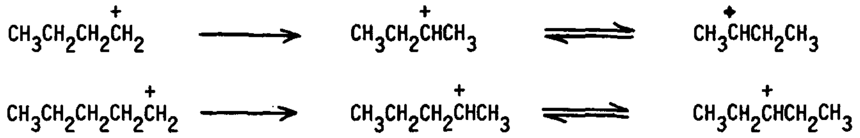
Many examples of rearrangement which occur in straight-chain alkyl groups during kinetically controlled substitutions can be formally represented as proceeding _via_ successive 1,2- shifts in intermediate carbonium ions.[1] In certain cases, this mechanism has been confirmed. Thus, in the nitrous acid deamination of n-butylamine,[2] or n-pentylamine,[3] reversible 1,2-hydride shifts between isomeric secondary cations were shown to account for the rearranged products obtained (Scheme I). 1,3-Shifts and protonated cyclopropanes were found to be of little importance in the rearrangements of open-chain alkyl groups.[4]



$$CH_3CH_2CH_2\overset{+}{C}H_2 \longrightarrow CH_3CH_2\overset{+}{C}HCH_3 \rightleftharpoons CH_3\overset{+}{C}HCH_2CH_3$$

$$CH_3CH_2CH_2CH_2\overset{+}{C}H_2 \longrightarrow CH_3CH_2CH_2\overset{+}{C}HCH_3 \rightleftharpoons CH_3CH_2\overset{+}{C}HCH_2CH_3$$

SCHEME I

In contrast, it is now reported that a significant proportion of the alkyl chloride which is formed in the thermal decomposition of an n-alkyl chloroformate arises by 1,3-hydride shift and that successive 1,2-shifts are of minor importance. Previous studies have revealed a close similarity in the rearrangements observed in nitrous acid deaminations and chloroformate thermolyses.[5] The results obtained by "proton-labelling" of otherwise fully deuterated n-butyl chloroformate, and by deuterium-labelling of n-pentyl chloroformate, are shown in Table 1.

Two main pathways for rearrangement are thus involved (Scheme II). One proceeds _via_ 1,2-hydride shift and accounts for _ca_. 50% of the substitution products (route a). There is little tendency for further rearrangement to another s-alkyl structure before capture (route b), although the detection of a small amount of product arising from the second 1,2-shift provides evidence in favour of the ion-pair mechanism shown, as opposed to the fully concerted rearrangement which has also been recognized as a possibility.[5] (Concerted attack by chloride at C-3 seems improbable and could only occur by intermolecular reaction).

TABLE 1

R in ROCOCl	Temp. (°C)	RCl (Composition %) [a]
$CD_3CH_2CD_2CD_2$-	150	$CD_3CH_2CD_2CD_2Cl$ (22)
		$CD_3CH_2CDClCD_3$ (48)[b]
		$CD_3CHClCD_2CD_2H$ (28)[b]
		$CD_3CHClCHDCD_3$ (2)[b]
$CH_3CH_2CD_2CH_2CH_2$-	160	$CH_3CH_2CD_2CH_2CH_2Cl$ (36)
		$CH_3CH_2CD_2CHClCH_3$ (48)
		$CH_3CH_2CDClCH_2CH_2D$ (14)[c]
		$CH_3CH_2CDClCHDCH_3$ (2)[d]

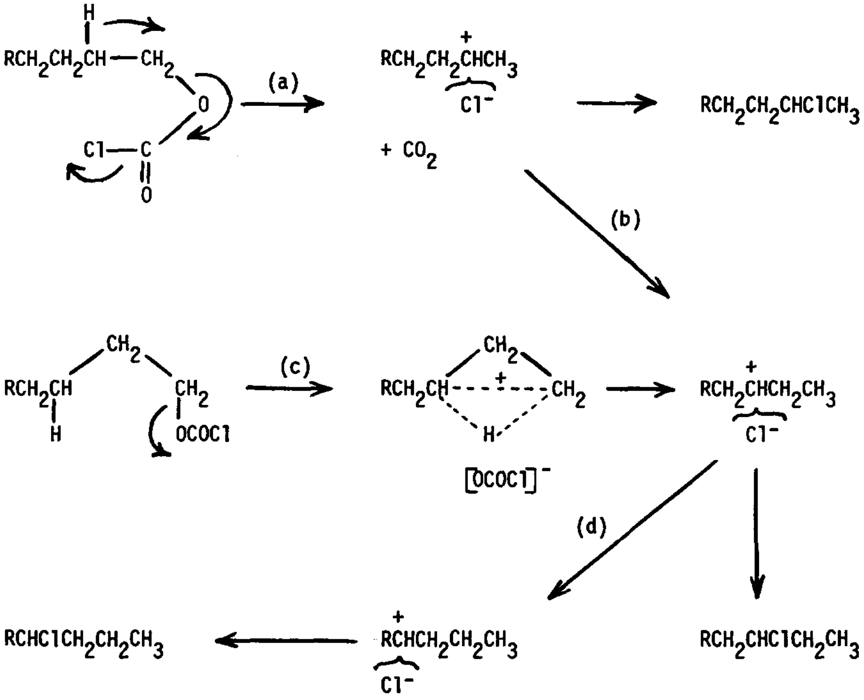
[a] 1-,2-, and 3-chloroalkanes were separated by prep. g.l.c. and analysed by n.m.r.

[b] From integration of the 'H n.m.r. peaks at τ 6.12 ($CHCl$), 8.32 (CH_2 and CHD), 9.03 (CD_2H).

[c] The only 3-chloropentane isomer detectable by proton-decoupled ^{13}C n.m.r. [δ (ppm from TMS) ($CDCl_3$): 10.64 (CH_2D, t, J_{C-D} 19.5 Hz), 10.92 (CH_3, s), 30.94 and 30.99 (CH_2 groups, singlets)].

[d] Relative proportions of the two 3-chloropentane isomers were calculated from estimated areas of the broad ^2H n.m.r. peaks centered at δ (ppm upfield from $CDCl_3$): 3.5 ($CDCl$), 5.6 (CHD), 6.2 (CH_2D).

The alternative pathway involves a 1,3-hydride shift and accounts for 15-30% of the substitution products. The identification of methylcyclopropane, ethylcyclopropane, and n-pentylcyclopropane, as minor by-products in the n-butyl, n-pentyl, and n-octyl systems respectively, suggests that protonated cyclopropane intermediates[6] are involved (route c). A 1,3-hydride shift will also explain the observation that in the thermal decomposition of n-pentyl or n-octyl chloroformate, the percentage of 3-chloroalkane formed is significantly greater than that obtained from the corresponding 1-methylbutyl and 1-methylheptyl esters. The extent to which rearrangement occurs in the secondary alkyl carbonium-ion intermediates derived from straight-chain s-alkyl chloroformates is in general very small. Results obtained for the octyl isomers are given in Table 2. It is however interesting to note that cyclopropane derivatives were in all cases detected amongst the hydrocarbon by-products and it seems likely that 1,3-hydride shifts also occur to some extent in the s-alkyl systems. The formation of 4-chloro-octane (2%) from n-octyl chloroformate appears to be best explained by the occurrence of a limited amount of further rearrangement by 1,2-shift (route d) after the initial formation of the 3-octyl cation by 1,3- shift of hydrogen. The extent to which addition between hydrogen chloride and olefin occurs in the reaction medium is negligible.



SCHEME II

TABLE 2

R in ROCOCl [a]	Chloro-octane composition obtained (%)			
	1-	2-	3-	4-
$CH_3(CH_2)_6CH_2$-	44	37	17	2
$CH_3(CH_2)_5CHCH_3$	0	97.8	1.7	0.5
$CH_3(CH_2)_4CHCH_2CH_3$	0	0.8	98.6	0.6
$CH_3(CH_2)_3CH(CH_2)_2CH_3$	0	0.1	0.9	99.0

[a] All heated at 150°C.

There has been considerable interest in recent years in the role of 1,3-shifts and protonated cyclopropane intermediates in isomerization processes, particularly under conditions of thermodynamic control in super-acid media.[7] The present results now indicate that 1,3-shifts can compete more favourably with 1,2-shifts in certain types of kinetically controlled substitution than has previously been supposed. In solvolytic rearrangements they occur to only a very small extent.[8]

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