Formation of 2-Chloro-3-methylbutane in the Thermal Decomposition of 2-Methylbutyl Chloroformate: Evidence for a 1,3-Shift involving a Protonated Cyclopropane Intermediate in a Kinetically Controlled Substitution

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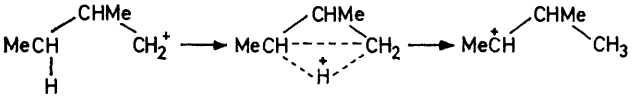
In the thermal decomposition of 2-methylbutyl chloroformate in the liquid phase, a minimum of 3% of the reaction proceeds *via* a 1,3-hydride shift which gives rise to the formation of 2-chloro-3-methylbutane together with some 3-methylbut-1-ene. The identification of *trans*-1,2-dimethylcyclopropane amongst the hydrocarbon products suggests that a protonated cyclopropane intermediate is involved.

A STUDY of the alkyl group rearrangements which occur during the thermal decomposition of the isomeric propyl, butyl, and pentyl chloroformates has shown that in all cases but one (2-methylbutyl), the substitution products can be rationalized in terms of 1,2-hydride or -alkyl shifts which occur between carbonium ions of similar stability, or which lead irreversibly to more stable structures.[1] This is considered to be typical of the behaviour of transient carbonium intermediates which are captured irreversibly by nucleophile. However, 2-methylbutyl chloroformate afforded 2-chloro-3-methylbutane (3% of the substitution products) and some accompanying 3-methylbut-1-ene in addition. These could not have been formed as a result of two successive 1,2-shifts (Scheme 1), since the t-pentyl cation

$$\mathrm{EtMeCHCH_2^+ \longrightarrow EtMe\overset{+}{C}CH_3 \xrightarrow{\times} Me\overset{+}{C}HCHMe_2}$$

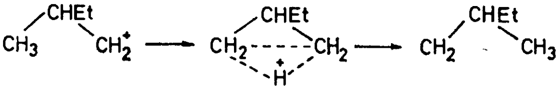
SCHEME 1

does not afford rearranged products under the conditions of this reaction. The detection of *trans*-1,2-dimethylcyclopropane amongst the products now confirms our earlier suggestion [1] that rearrangement occurs *via* a protonated cyclopropane intermediate (Scheme 2).



SCHEME 2

This is the only 1,3-shift in a carbonium ion derived from any of the lower alkyl groups (C_3, C_4, or C_5) which gives a structurally different rearrangement product from any which could be alternatively explained on the basis of successive 1,2-shifts. A similar 1,3-hydride shift accounts for the formation of 3-methylbut-1-ene in the deoxidation of 2-methylbutan-1-ol.[2] In the present work (as in the deoxidation reaction [2]) ethylcyclopropane was also detected. A 1,3-hydride shift involving the corresponding protonated species (Scheme 3) would, in this case, however, give the identical 2-methylbutyl cation, distinguishable only by isotopic labelling. This possibility has not been investigated, although small contributions from degenerate 1,3-shifts have been reported in isotopically labelled n-propyl [3] and isobutyl [4] cations and it is likely that a similar rearrangement occurs in this system also.



SCHEME 3

The extent to which protonated cyclopropanes occur as intermediates in substitution and elimination reactions has given rise to some interest in recent years.[2-6] Work on the nitrous acid-deamination of primary alkylamines has indicated that the total contribution of edge-protonated cyclopropanes to the reaction path is usually small, being *ca.* 6% for n-propylamine but less than 1% if alkyl substituents are present in the 2- or 3-position.[7,8] Our results for the thermal decomposition of 2-methylbutyl chloroformate indicate that at least 3% of the reaction products arise from an intermediate of this type and that the total contribution is almost certainly higher. Thus, this minimum value takes no account of 2-methylbut-2-ene which would presumably be the major olefinic product from the 1,2-dimethylpropyl cation (but which is also formed from the 1,1-dimethylpropyl cation) and includes no contribution from 1,3-shifts involving protonated ethylcyclopropane. It is also possible that the straight-chain chloropentanes and pentenes which are formed in this decomposition [1] arise to some extent from ring opening of the above protonated species after further

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rapid rearrangement to other edge-protonated structures. We have also observed that at least 10% of the reaction path in the thermal decomposition of cyclohexylmethyl chloroformate and in the nitrous-acid deamination of cyclohexylmethylamine appears to proceed *via* a cyclopropane intermediate, there being little significant difference in this respect between the chloroformate and amine systems.[6] A possible explanation for the greater involvement of 1,3-shifts in the 2-methylbutyl and cycloalkylmethyl systems, as compared to isobutyl and neopentyl,[7] is that the rearrangement in each of the first two examples proceeds to a more stable secondary carbonium ion. 1,3-Hydride shifts in isobutyl and neopentyl would give only the identical primary cations.

EXPERIMENTAL

Preparation of Reference Samples of Cyclopropane Derivatives.—*cis*- and *trans*-1,2-Dimethylcyclopropane were prepared by a modification [9] of a described procedure.[10] Reactions were carried out by condensing an excess of the olefin into the reaction mixture in dioxan (−10 °C), followed by stirring at room temperature (20 h). The cyclopropanes, which distilled together with unchanged olefin on mild warming were condensed (−80 °C), and characterized by g.l.c.–mass spectrometry and ^{1}H n.m.r. analysis. *cis*-But-2-ene afforded *cis*-1,2-dimethylcyclopropane (*m/e* 70) [τ 9·4, 10·4 (ring protons, broad singlets)].[11] *trans*-But-2-ene afforded *trans*-1,2-dimethylcyclopropane (*m/e* 70) [τ 9·35—10·1 (ring protons, complex multiplet) with a sharp maximum at 9·8].[11,12] Ethylcyclopropane, n_D^{20} 1·3784, (*m/e* 70) [τ 9·2—10·2 (ring protons, complex multiplet) with sharp maxima at 9·65 and 10·0] was prepared by Wolff–Kishner reduction of cyclopropyl methyl ketone.[13]

Pyrolysis of 2-Methylbutyl Chloroformate.—The chloroformate was prepared and decomposed as described.[1] Hydrocarbon products were analysed by g.l.c. on 4 m × $\frac{1}{8}$ in o.d. stainless-steel columns containing (*a*) saturated silver nitrate–ethylene glycol (30%) on 85—100 mesh Silocel at 40°: [14] this confirmed the presence of cyclopropane derivatives (3%), which were eluted before the olefins but which were not resolved from one another: (*b*) di-n-butyl D-tartrate (10%) on 85—100 mesh Celite at 20°, which gave the results in the Table. High sensitivity ^{1}H n.m.r. analysis of the combined hydrocarbons, in the region τ 9—10·5, confirmed the presence of cyclopropane derivatives, as indicated.

Hydrocarbon	Relative retention time [a]	Composition (%)
3-Methylbut-1-ene	1·00	2
trans-1,2-Dimethylcyclopropane [b]	1·18	1
Pent-1-ene	1·25	18
2-Methylbut-1-ene	1·41	3
trans-Pent-2-ene	1·52	42
Ethylcyclopropane [c]	1·64	22
cis-Pent-2-ene	1·64	
cis-1,2-Dimethylcyclopropane [d]	1·65	
2-Methylbut-2-ene	1·77	12

[a] Elution is in order of increasing b.p. [b] τ 9·6, 10·0. [c] τ 9·8. The relative intensities of the ring proton n.m.r. peaks for this compound and for *trans*-1,2-dimethylcyclopropane indicated that ethylcyclopropane (1—2%) was present. [d] The broader n.m.r. peaks for this compound were not distinguishable in this complex mixture.

We thank the University of London Central Research Fund for a grant (to H. R. H.) for the purchase of a Perkin-Elmer F.11 chromatograph.

[2/1967 *Received*, 17*th August* 1972]

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