

Rearrangements and the Intervention of Protonated Cyclopropanes in the Thermal Decompositions of Cycloalkyl Chloroformates

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The thermal decompositions of cycloalkyl chloroformates in the liquid phase are accompanied in most cases by the formation of rearrangement products. The cycloalkyl chlorides and cycloalkenes formed are largely accounted for in terms of carbonium ion rearrangements which proceed irreversibly to more stable structures. In addition, 5–10% of the products obtained by the thermal decomposition of cyclopentylmethyl, cyclohexylmethyl, and cycloheptyl chloroformate are considered to be formed *via* protonated cyclopropane intermediates; supporting evidence comes from the identification of bicyclo[3,1,0]hexane and bicyclo[4,1,0]heptane as products in the six- and seven-carbon systems respectively. Preponderant retention of configuration in the unrearranged decomposition products from *cis*- or *trans*-2-methylcycloalkyl chloroformates is indicative of a mechanism involving collapse of an intermediate ion-pair. The decompositions are accelerated by catalytic quantities of pyridinium chloride or aluminium trichloride; the former almost entirely eliminates the formation of rearrangement products and olefins in the primary alkyl systems, whilst the latter causes increased rearrangement and isomerization of the products.

THE thermal decompositions of saturated alkyl chloroformates in the liquid phase have been shown to have considerable carbonium-ion character. Extensive rearrangement occurs and follows patterns similar to those observed in nitrous acid deaminations of primary amines.^{1,2} An extension of the investigation to a series of cycloalkyl chloroformates has now given the results presented in Tables 1–3. The first striking observation

is that the product composition (illustrated for the decomposition of cyclohexylmethyl chloroformate in Table 1) showed little variation throughout the course of the decomposition, even though the temperature was falling and the composition of the reaction medium was changing as the reaction proceeded. The decompositions of cyclopentyl, cyclohexyl, and cycloheptyl chloroformates at *ca.* 150 °C also gave results very similar to

¹ P. W. Clinch and H. R. Hudson, *Chem. Comm.*, 1968, 925; *J. Chem. Soc. (B)*, 1971, 747.

² P. Beak, R. J. Trancik, and D. A. Simpson, *J. Amer. Chem. Soc.*, 1969, **91**, 5073.

TABLE 1

Variation of product composition with time during the thermal decomposition of cyclohexylmethyl chloroformate^a

t/h	T/°C ^c	Composition of reaction mixture ^b (mol. equiv.)				Volatile product composition (mol %)									
		ROCOCl	(RO) ₂ CO	RCl	Hydrocarbon	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)
10	145	0.88	0.03	0.05	0.01	2.2	0.3	5.0	8.6	2.7	26.3	1.4	0.4	23.6	29.5
20	145	0.83	0.03	0.09	0.02	2.1	0.1	4.8	8.0	2.9	30.1	1.4	0.6	23.3	26.6
30	145	0.82	0.03	0.10	0.02	2.1	0.1	5.4	7.5	3.5	27.2	1.8	0.8	27.0	24.5
40	145	0.77	0.05	0.11	0.02	2.6	0.3	3.6	5.3	3.2	31.8	2.1	0.8	26.6	23.6
50	145	0.71	0.06	0.14	0.03	2.4	0.3	4.5	7.0	2.7	30.1	2.3	0.7	23.5	26.5
60	144	0.64	0.07	0.18	0.04	2.1	0.3	5.3	6.6	2.2	29.2	2.0	0.7	24.3	27.2
70	143	0.61	0.08	0.19	0.04	2.5	0.3	6.9	7.2	1.9	28.1	2.5	1.1	23.4	26.0
80	142	0.57	0.08	0.22	0.05	2.8	0.3	5.9	7.3	1.8	28.0	2.5	0.8	24.3	26.2
94	142	0.51	0.09	0.26	0.05	2.6	0.1	4.7	8.3	1.7	28.5	2.7	0.8	24.3	26.3
100	142	0.48	0.09	0.28	0.06	2.6	0.1	4.5	7.8	1.6	28.8	2.4	0.8	25.3	26.0
110	140	0.45	0.11	0.27	0.06	2.8	0.1	6.4	7.7	1.4	28.3	2.7	1.1	24.5	24.9
120	140	0.40	0.11	0.31	0.07	2.6	0.1	6.2	7.4	1.3	28.3	2.8	1.1	25.6	24.5
130	140	0.38	0.11	0.33	0.06	2.6	0.3	5.5	7.0	1.2	28.2	2.8	0.9	26.7	24.7
140	140	0.36	0.13	0.32	0.06	2.6	0.3	5.7	6.7	1.2	28.6	2.7	1.0	25.0	26.2
150	140	0.33	0.13	0.34	0.07	2.2	0.3	6.8	7.0	0.9	27.7	2.9	1.0	25.1	26.0
160	139	0.30	0.14	0.35	0.07	2.8	0.2	6.3	7.5	0.9	28.3	3.0	0.9	25.1	24.9
170	139	0.27	0.15	0.36	0.07	2.9	0.3	4.8	6.6	0.8	29.3	2.9	1.1	25.6	25.7
180	138	0.25	0.15	0.37	0.08	3.0	0.1	6.6	7.0	0.8	25.9	3.0	1.0	26.8	25.7
190	138	0.23	0.15	0.38	0.08	3.3	0.1	6.8	7.2	0.8	27.0	3.1	1.1	26.0	24.5
200	137	0.21	0.16	0.38	0.09	3.5	0.1	7.3	7.6	0.7	25.3	3.0	1.2	26.6	24.6

^a 20.0 g (1 mol. equiv.). ^b R = C₆H₁₁·CH₂. ^c Of reaction mixture; oil-bath 150 °C.

TABLE 2

Thermal decomposition of the C₆ cycloalkyl chloroformates

R in ROCOCl	T/°C ^a	t/h	Catalyst ^b	Composition of reaction mixtures (mol. equiv.)				Volatile product composition (mol %)											
				RO·COCl	(RO) ₂ CO	RCl	Hydrocarbon	(11)	(12)	(13)	(14)	(15)	(16)	(17)	(18)	(19)	(20)	(21)	
Cyclopentylmethyl	145 ^e	100		0.20	0.01	0.48	0.31	4.0	1.0		1.3	30.3	3.5	4.3		1.2	3.9	15.2	35.3
Cyclohexyl	145—118 ^e	30		0.00	0.00	0.65	0.35	Trace	Trace			34.8	0.3		Trace	Trace			64.6
Cyclohexyl	98—95 ^d	97		0.00	0.00	0.69	0.31					31.3							68.6
<i>cis</i> -2-Methylcyclopentyl	140—110 ^e	30		0.00	0.00	0.32	0.68	59.3	8.8		Trace				15.3	14.8	1.6		
Cyclopentylmethyl	145 ^e	10	C ₅ H ₅ NHCl	0.00	Trace ^e	0.99	Trace	Trace				Trace						99.5	Trace
Cyclohexyl	145—110 ^e	10	C ₅ H ₅ NHCl	0.00	0.01 ^e	0.60	0.39	Trace				38.9	Trace						60.8
Cyclohexyl	98—95 ^d	54	C ₅ H ₅ NHCl	0.00	0.01 ^e	0.57	0.42					42.2							57.7
<i>cis</i> -2-Methylcyclopentyl	140—110 ^e	13	C ₅ H ₅ NHCl	0.00	0.00	0.66	0.34	57.2	8.3		Trace				17.2	8.9	8.4		
1-Methylcyclopentyl	20	4		0.00	0.00	0.65	0.35								65.0				

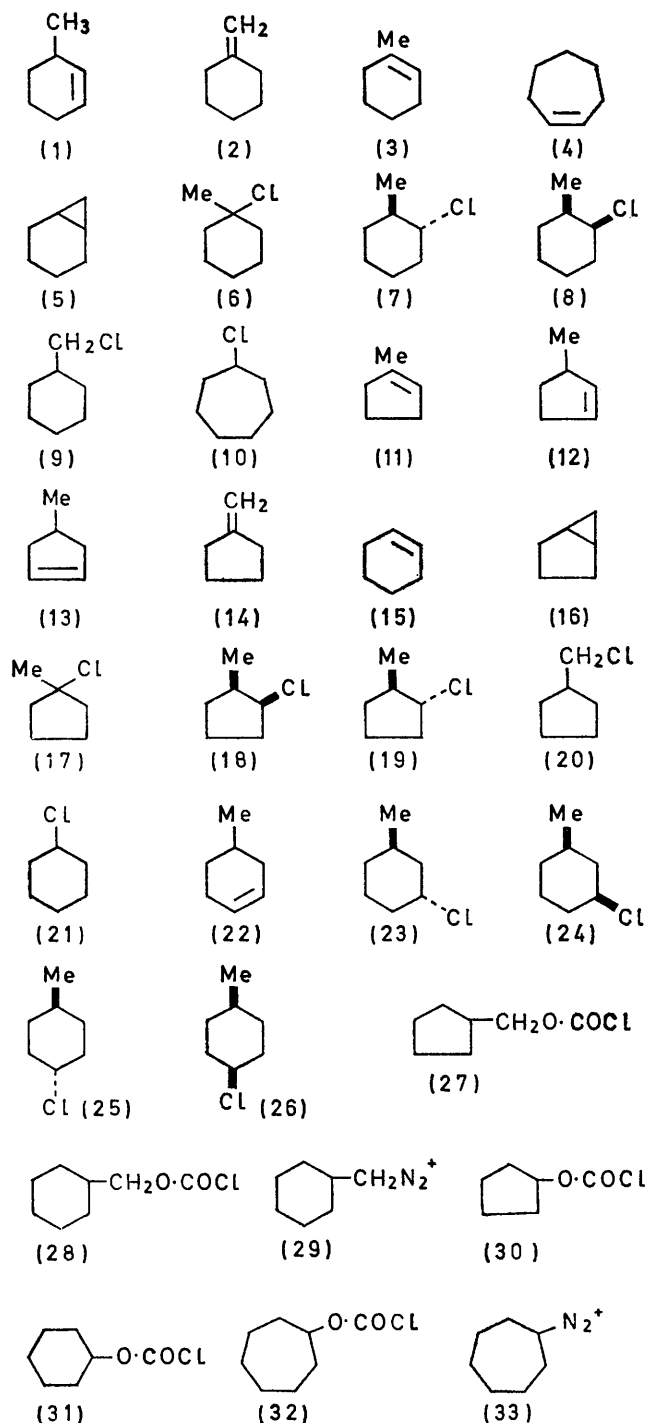
^a Of reaction mixture. ^b 0.05 mol. equiv. ^c Oil-bath 150 °C. ^d Oil-bath 100 °C. ^e Carbonate formation in the catalysed decompositions might be due to traces of moisture in the pyridinium chloride used.

TABLE 3

Thermal decomposition of the C₇ cycloalkyl chloroformates

R in ROCOCl	T/°C ^a	t/h	Catalyst ^b	Composition of reaction mixture (mol. equiv.)				Volatile product composition (mol %)														
				ROCOCl	(RO) ₂ CO	RCl	Hydrocarbon	(3)	(1)	(22)	(2)	(4)	(5)	(6)	(7)	(8)	(23)	(24)	(25)	(26)	(9)	(10)
Cyclohexylmethyl	145—200			0.21	0.16	0.38	0.09	7.3	3.5		0.1	7.6	0.7	25.3	3.0	1.2				26.6	24.6	
Cycloheptyl	145—137 ^{e,d}	30		0.00	0.00	0.60	0.40	Trace	0.2			38.4	1.1	0.4	1.2	0.3				1.2	57.0	
Cycloheptyl	100 ^e	90		0.00	0.00	0.61	0.39					2.6										
<i>cis</i> -2-Methylcyclohexyl	145—130 ^e	18		0.00	0.00	0.28	0.72	54.8	16.0		1.7	35.5	1.2	0.6	1.2	0.3				1.3	57.2	
<i>trans</i> -2-Methylcyclohexyl	145—130 ^e	20		0.00	0.00	0.69	0.31	18.4	11.4		1.3			8.9	52.0	8.0						
3-Methylcyclohexyl	145—140 ^e	28		0.00	0.00	0.57	0.43	1.7	12.8	28.4	0.6								26.9	(29.6) ^f		
4-Methylcyclohexyl	145—140 ^e	32		0.00	0.00	0.53	0.47		Trace	46.4									Trace	(33.4) ^f	19.7	
Cyclohexylmethyl	145 ^e	16	C ₆ H ₅ NHCl	0.00	0.01 ^e	0.98	Trace	0.1	Trace		Trace	Trace	Trace	0.5	Trace	Trace				99.2	0.1	
Cycloheptyl	145—140 ^e	10	C ₆ H ₅ NHCl	0.00	0.01 ^e	0.60	0.39				Trace	Trace	Trace	0.2	1.5	0.2				1.2	57.4	
Cycloheptyl	100 ^e	50	C ₆ H ₅ NHCl	0.00	0.01 ^e	0.60	0.39					36.3	1.2	0.5	1.9	0.3				1.3	56.2	
<i>cis</i> -2-Methylcyclohexyl	145—130 ^e	13	C ₆ H ₅ NHCl	0.00	0.00	0.32	0.68	50.5	16.2		1.1			12.1	4.5	15.5						
<i>trans</i> -2-Methylcyclohexyl	145—130 ^e	9	C ₆ H ₅ NHCl	0.00	0.00	0.76	0.24	8.9	14.3		1.3			4.1	51.3	20.1						
3-Methylcyclohexyl	145—140 ^e	13	C ₆ H ₅ NHCl	0.00	0.00	0.55	0.45	1.2	16.7	26.0	0.6								25.9	(29.6) ^f		
4-Methylcyclohexyl	145—140 ^e	10	C ₆ H ₅ NHCl	0.00	0.01 ^e	0.51	0.48		Trace	48.3									Trace	(30.2) ^f	21.0	
Cyclohexylmethyl	23	40	AlCl ₃	0.00	0.00	0.96	0.04							25.3	8.4	4.0	5.6		(16.4) ^f	4.2	32.0	1.1
1-Methylcyclohexyl	20	4		0.00	0.00	0.67	0.33	32.9			0.6			66.5								

^a Of reaction mixture. ^b 0.05 mol. ^c Oil-bath 150 °C. ^d Underwent 0.1% decomposition during 100 h at 100 °C. ^e Oil-bath 100 °C. ^f *cis*-3- and *trans*-4-chloro-1-methylcyclohexane not separable by g.l.c. ^g Carbonate formation in the catalysed decompositions might be due to traces of moisture in the pyridinium chloride used.



those obtained at 100 °C (Tables 2 and 3). No systematic examination of solvent and temperature effects on product composition was therefore made in the present work but it is expected that they will be small. The isomer distributions in the products from cyclohexylmethyl and cycloheptyl chloroformates were also similar to those obtained by the nitrous acid deamination of the

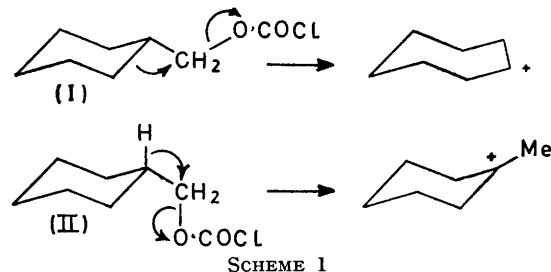
³ W. E. Dupuy, H. R. Hudson, and P. A. Karam, *Tetrahedron Letters*, 1971, 3193.

⁴ R. Kotani, *J. Chem. and Eng. Data*, 1966 **11**, 248.

corresponding amines,^{3,4} although the conditions in the two types of reaction are very different. A common type of carbonium ion intermediate is implied.

Under the conditions used for the thermal decompositions of the chloroformates (usually *ca.* 140–150 °C), most of the reaction products were shown to be stable. There was however some interconversion of the tertiary chlorides (1-chloro-1-methylcycloalkanes), the 1-methylcycloalkenes, and the methylenecycloalkanes on prolonged heating.

Cyclohexylmethyl chloroformate and cyclopentylmethyl chloroformate gave rise to rearrangement products resulting in both cases from ring expansion and from 1,2-hydride shift. In the cyclohexylmethyl system, the extent of rearrangement by ring expansion to the cycloheptyl (secondary) cation was as great as that by 1,2-hydride shift (Table 3), although the latter gives the considerably more stable tertiary cation and the seven-membered ring is slightly less stable than the six.⁵ It is probable that stereoelectronic factors are involved. Thus, conformation (I) will favour ring expansion, whereas hydride shift will be favoured only in the less likely conformation (II) (Scheme 1). Ring expansion is favoured to a still greater extent, by relief of steric strain, in the decomposition of cyclopentylmethyl chloroformate (Table 2).

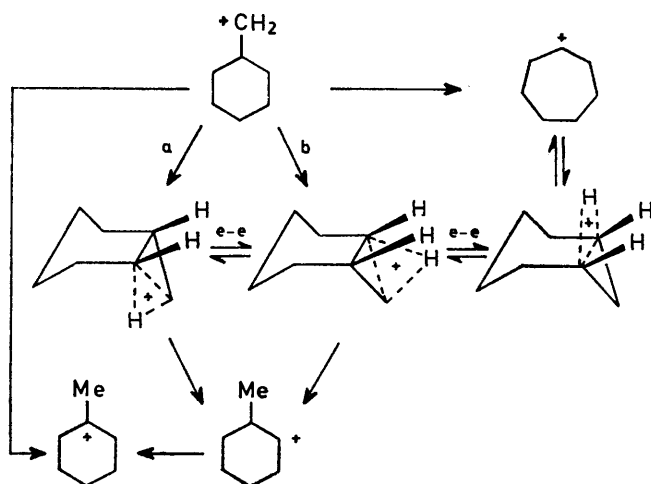


In both systems, small but significant amounts of substitution and elimination products were apparently derived from the corresponding 2-methylcycloalkyl cations. It was shown that these did not arise from 1,2-hydride shifts in the tertiary cations since decomposition of 1-methylcyclopentyl and 1-methylcyclohexyl chloroformates yielded only the corresponding tertiary halides, together with 1-methylcycloalkenes and methylenecycloalkanes, none of which afforded 2-chloro-1-methylcycloalkanes or 3-methylcycloalkenes when heated under reaction conditions. The detection of bicyclo[3,1,0]hexane and bicyclo[4,1,0]heptane in the six- and seven-carbon systems respectively is significant and strongly suggests the intervention of protonated cyclopropane intermediates.⁶ Ring contraction in the thermal decomposition of cycloheptyl chloroformate (and to a small but detectable extent in the thermal decomposition of cyclohexyl chloroformate) was similarly accompanied by the formation of bicyclic hydrocarbons; again, protonated cyclopropanes are implicated. The

⁵ G. H. Whitham, 'Alicyclic Chemistry,' Oldbourne Press, London, 1963, p. 4.

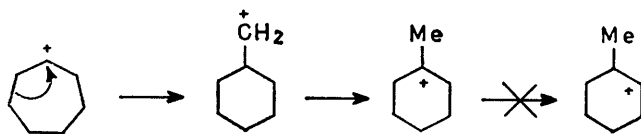
⁶ C. J. Collins, *Chem. Rev.*, 1969, **69**, 543.

overall range of possible reaction paths for the seven-carbon system is thought to be as shown in Scheme 2.



SCHEME 2 a, Insertion of equatorial CH_2^+ into axial C-H. b, Insertion of axial CH_2^+ into equatorial C-H (of low probability). e-e, Edge-edge proton equilibration

Analogous routes are available in the six-carbon system. The deamination of cyclohexylamine⁷ and cycloheptylamine^{3,8} has also been shown to be accompanied by the formation of bicyclo[3,1,0]hexane and bicyclo[4,1,0]heptane respectively. It is much more plausible that these and other similar kinetically controlled ring contractions should proceed *via* protonated cyclopropanes than by classical 1,2-shifts which necessarily involve the initial unfavourable rearrangement to a primary cation (Scheme 3). Further rearrangement



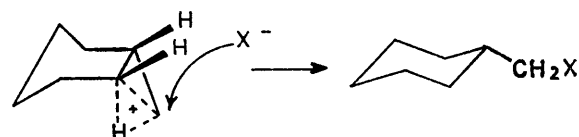
SCHEME 3

of the latter (if formed) would be expected to give the tertiary halides or alcohols as major rearranged substitution products, although the 2-methylcycloalkyl compounds were found to be present in greatest amount in the present work. Methylene cyclohexane was also completely absent from the products. The formation of traces of primary alkyl substitution products in ring-contraction processes could possibly be accounted for by a concerted attack by nucleophile on, and ring opening of, the protonated cyclopropane, *e.g.*, as shown in Scheme 4.

The extent to which ring expansion might proceed *via* a protonated cyclopropane intermediate, rather than by a direct 1,2-shift (Scheme 2), is unknown. It is worth noting, however, that protonated cyclopropane inter-

mediates are thought to account for rapid isomerization and proton equivalence in the cyclopentylmethyl cation in $\text{SbF}_5\text{-SO}_2\text{ClF}$ solution.⁹

The percentage of each product which must necessarily have been formed *via* a protonated cyclopropane intermediate (*i.e.*, excluding any that could alternatively be



SCHEME 4

accounted for by successive 1,2-shifts), in the present and related work,³ is given in Table 4. The cyclo-

TABLE 4

Minimum percentages of products arising *via* protonated cyclopropanes in the thermal decompositions of cycloalkyl chloroformates and the nitrous acid deaminations of cycloalkylamines^a

Reactant	Substitution products	Bicyclic hydrocarbon	Olefins	Total
(27) ^b	5.1	3.5	1.0	9.6
(28) ^b	4.2	0.7	3.5	8.4
(29) ^c	1.1	1.3	7.8	10.2
(30) ^b	0	0	0	0
(31) ^b	Trace	0.3	Trace	<i>ca.</i> 0.3
(32) ^b	3.1	1.1	0.2	4.4
(33) ^c	0.8	4.0	0.8	5.6

^a *I.e.* excluding products which are explicable on the basis of successive 1,2-shifts. The total percentages arising *via* protonated cyclopropanes could be higher. ^b Decomposition at 150° (oil-bath temperature). ^c Previous work.³

pentylmethyl and cyclohexylmethyl derivatives gave significantly higher proportions of products *via* this route than was reported for the deamination of isobutylamine (0.6%), which is substituted at the β -position to a similar extent.¹⁰ (It was however pointed out that results in the isobutyl system should not necessarily be extrapolated to the analogous cyclic systems.¹⁰) The alicyclic chloroformates gave rather more substitution product and correspondingly less elimination product by the protonated cyclopropane route than did the corresponding amines. No figure for the olefin yield arising from protonated cyclopropanes in the acyclic systems is available for comparison.

Three 2-methylcycloalkyl chloroformates were studied: *cis*-2-methylcyclopentyl chloroformate, *cis*-2-methylcyclohexyl chloroformate, and *trans*-2-methylcyclohexyl chloroformate. Thermal decomposition yielded in each case the unrearranged halide of predominantly retained configuration (Tables 2 and 3), as would be expected if internal return in an ion-pair intermediate was the main route involved.¹ (Preponderant retention has generally been observed when substituted cyclohexyl chloroform-

⁷ O. E. Edwards and M. Lesage, *Canad. J. Chem.*, 1963, **41**, 1592.

⁸ A. T. Jurewicz, Ph.D. Thesis, Case Institute of Technology, June, 1967. Referred to by L. Friedman, in 'Carbonium Ions,' eds. G. A. Olah and P. von R. Schleyer, Wiley, New York, 1970, ch. 16, p. 673.

⁹ M. Saunders and J. Rosenfeld, *J. Amer. Chem. Soc.*, 1969, **91**, 7756.

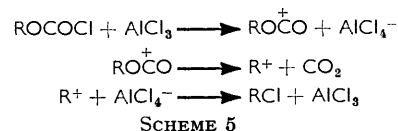
¹⁰ G. J. Karabatsos, C. E. Orzech, jun., J. L. Fry, and S. Meyerson, *J. Amer. Chem. Soc.*, 1970, **92**, 606; G. J. Karabatsos, Nelson Hsi, and S. Meyerson, *ibid.*, p. 621.

ates are thermally decomposed, alone or in hexane; in pyridine the products are of largely inverted configuration.¹¹⁻¹³) In addition, 1,2-hydride shifts gave products derived from the more stable tertiary cations but no rearrangement to the isomeric secondary cations, or ring contraction, was detectable. From 3-methylcyclohexyl and 4-methylcyclohexyl chloroformate, only traces of olefins and/or halides which could have been derived from rearranged carbonium ions were detected. Thermoneutral 1,2-hydride shift between isomeric secondary cations occurs to a much smaller extent in chloroformate decompositions¹ than in nitrous acid deaminations.¹⁴

The elimination products obtained from all the cycloalkyl chloroformates studied are explicable on the basis of carbonium-ion intermediates, whereas in the acyclic systems certain olefins were more probably formed by concerted *cis*-eliminations.¹ Whilst the latter type of process is not necessarily excluded in alicyclic systems,¹⁵ it is in most cases less likely. A planar six-membered transition state is possible only when the O·COCl group is attached to an exocyclic carbon atom, as for example in cyclopentylmethyl or cyclohexylmethyl chloroformate, or (if the O·COCl group is attached to a ring carbon) when the ring is in the boat conformation. The cycloalkylmethyl chloroformates gave only small yields (1% or less) of the methylenecycloalkanes which would be the products of such *cis*-elimination. In addition to the main products of decomposition, small percentages of carbonate were formed by redistribution reactions of the primary, but not the secondary, cycloalkyl chloroformates. Bis(cycloalkyl) carbonates have been reported as by-products of cycloalkyl chloroformate decompositions in pyridine, whilst from fluoroformates they are the exclusive products.¹²

The effect of pyridinium chloride was similar to that reported for the acyclic chloroformate decompositions.¹ Traces (0.05 mol. equiv.) had a marked catalytic effect, especially on the primary cycloalkyl systems, in which the extent of rearrangement was reduced to less than 1% and olefin formation was almost eliminated. As described previously, the added chloride ion is thought to initiate a chain of S_N2 displacements (Cl⁻ → RO·COCl → ClR + CO₂ + Cl⁻). Whilst the secondary cycloalkyl chloroformates also decomposed more rapidly in the presence of pyridinium chloride, both S_N2 and carbonium-ion mechanisms appear to be enhanced since the product ratio was not altered appreciably. Aluminium trichloride was also found to catalyse the decomposition of cyclohexylmethyl chloroformate. It is considered to act as a Lewis acid, *e.g.*, as shown in Scheme 5.

The products underwent further isomerization after their initial formation to give a mixture of isomeric halides (Table 3) which was similar to that obtained during the



thermal decomposition of cyclohexylmethyl dichloroborinate.¹⁶ Olefins were not detectable in the products from the aluminium trichloride-catalysed decomposition, although some methylcyclohexane (which has also been found in the products from other aluminium trichloride-catalysed isomerizations¹⁷) was produced.

EXPERIMENTAL

Starting Materials.—The alcohols were obtained commercially and checked for purity by g.l.c. on polyethylene glycol 400. Impurities present in cyclopentylmethanol, 1-methylcyclopentanol, and 1-methylcyclohexanol were removed by preparative g.l.c. on polyethylene glycol 400. The identities of the alcohols were confirmed by i.r. and/or ¹H n.m.r. spectroscopy, the latter distinguishing clearly between the *cis*- and *trans*-2-methylcycloalkanol.¹⁸ Carbonyl chloride was from a cylinder (B.D.H.).

Chloroformate Preparations.—The primary or secondary alcohol (40–50 g), in an equal volume of sodium-dried ether, was added dropwise (30 min) to freshly-distilled carbonyl chloride (*ca.* 1.5 mol. equiv.) at –80 °C. After removal of hydrogen chloride and excess of carbonyl chloride at room temperature, the residue was in each case distilled to afford the chloroformate as follows (R in RO·COCl, % yield, b.p. °C/mmHg, *n*_D²⁰, Cl % found, Cl % calc.): cyclopentyl, 75, 26–27/0.2, 1.4494, 23.9, 23.9; cyclohexyl, 82, 33–34/0.25, 1.4584, 21.9, 21.8; cycloheptyl, 90, 44/0.3, 1.4681, 20.1, 20.1; cyclohexylmethyl, 90, 50/0.4, 1.4591, 20.1, 20.1. Esters not previously characterized were similarly prepared, thus: cyclopentylmethanol (15.5 g) gave *cyclopentylmethyl chloroformate* (15.7 g, 0.60 mol. equiv.), b.p. 28 °C/0.25 mmHg, *n*_D²⁰ 1.4522 (Found: C, 51.4; H, 6.5; Cl, 21.8. C₇H₁₁ClO₂ requires C, 51.7; H, 6.8; Cl, 21.8%); *cis*-2-methylcyclopentanol (8.9 g) gave *cis*-2-methylcyclopentyl chloroformate (11.0 g, 0.78 mol. equiv.), b.p. 25–26 °C/0.20 mmHg, *n*_D²⁰ 1.4480 (Found: C, 51.9; H, 6.6; Cl, 21.6%); *cis*-2-methylcyclohexanol (9.5 g) gave *cis*-2-methylcyclohexyl chloroformate (11.1 g, 0.75 mol. equiv.), b.p. 37 °C/0.6 mmHg, *n*_D²⁰ 1.4550 (Found: C, 54.6; H, 7.6; Cl, 20.1. C₈H₁₃ClO₂ requires C, 54.4; H, 7.4; Cl, 20.1%); *trans*-2-methylcyclohexanol (9.1 g) gave *trans*-2-methylcyclohexyl chloroformate (11.9 g, 0.88 mol. equiv.), b.p. 36 °C/0.4 mmHg, *n*_D²⁰ 1.4542 (Found: C, 54.3; H, 7.45; Cl, 20.1%); 3-methylcyclohexanol (24.7 g) (*cis*, 67; *trans*, 33%) gave 3-methylcyclohexyl chloroformate (31.2 g, 0.82 mol. equiv.) b.p. 40 °C/0.5 mmHg, *n*_D²⁰ 1.4542 (Found: C, 54.6; H, 7.5; Cl,

¹¹ K. W. Buck and A. B. Foster, *J. Chem. Soc.*, 1963, 2217.

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20.2%); 4-methylcyclohexanol (26.7 g) (*cis*, 37; *trans*, 63%) gave 4-methylcyclohexyl chloroformate (36.6 g, 0.91 mol. equiv.), b.p. 46 °C/0.55 mmHg, n_D^{20} 1.4545 (Found: C, 54.7; H, 7.5; Cl, 20.1%).

Preparations of Bis(cycloalkyl) Carbonates.—Bis(cyclohexyl)carbonate, m.p. 41–43 °C (Found: C, 69.1; H, 9.9. Calc. for $C_{18}H_{22}O_3$: C, 69.0; H, 9.7%), and bis(cyclohexylmethyl)carbonate, b.p. 134 °C/0.35 mmHg, n_D^{20} 1.4713 (Found: C, 70.6; H, 10.4. Calc. for $C_{15}H_{26}O_3$: C, 70.9; H, 10.2%), were prepared from carbonyl chloride, pyridine, and the corresponding alcohols, in anhydrous ether as described.¹² By an analogous experimental procedure, cyclopentyl chloroformate (9.0 g), cyclopentanol (5.2 g), and pyridine (5.0 g) in ether (15 ml) yielded *bis(cyclopentyl) carbonate* (8.0 g, 0.68 mol. equiv.), b.p. 73–74 °C/0.3 mmHg, n_D^{20} 1.4628 (Found: C, 67.3; H, 9.5. $C_{11}H_{18}O_3$ requires C, 66.7; H, 9.1%); cyclopentylmethyl chloroformate (3.3 g), cyclopentylmethanol (2.0 g), and pyridine (2.0 g) in ether (15 ml) yielded *bis(cyclopentylmethyl) carbonate* (2.5 g, 0.55 mol. equiv.), b.p. 96–98 °C/0.1 mmHg, n_D^{20} 1.4650 (Found: C, 68.9; H, 10.0%); cycloheptyl chloroformate (10.1 g), cycloheptanol (6.5 g), and pyridine (5.5 g) in ether (20 ml) yielded *bis(cycloheptyl) carbonate* (9.2 g, 0.63 mol. equiv.) b.p. 137 °C/0.5 mmHg, n_D^{20} 1.4818 (Found: C, 71.1; H, 10.5%).

Thermal Decompositions of Chloroformates.—The chloroformates (5–20 g) were heated under reflux as described.¹ No condensable product was collected in a trap (–80 °C) attached to the exit of the condenser. Cyclopentyl chloroformate (17.1 g) underwent 100% decomposition at 150 °C (30 h) to yield a product consisting of cyclopentene (22%) and cyclopentyl chloride (78%). In the presence of pyridinium chloride (0.26 g, 0.05 mol. equiv.) the chloroformate (6.7 g) decomposed completely at 150 °C (10 h) to give a mixture of cyclopentene (26%) and cyclopentyl chloride (74%). No other product was detectable in either case.

Analytical Methods.—Products were analysed for cycloalkyl chlorides, elimination products, unchanged chloroformate, and carbonate by a combination of g.l.c. (below) and chemical analysis.¹

Gas Chromatography.—Analytical separations were on a Perkin-Elmer F11 chromatograph with flame ionization detector. Complete analysis of the hydrocarbon and cycloalkyl chloride products was achieved in most cases on a 50 m × 0.25 mm stainless steel capillary column coated with silicone oil MS 550.¹⁹ A 4 m × $\frac{1}{8}$ in o.d. stainless steel column containing saturated silver nitrate–ethylene glycol (30%) on 85–100 mesh Silocel (70%) afforded separations of 3- and 4-methylcycloalkenes (the only hydrocarbons not separable on silicone oil) and gave additional confirmatory evidence for the bicyclohydrocarbons, which had shorter retention times than had the isomeric olefins on this column.¹⁹

¹⁹ W. E. Dupuy, H. R. Hudson, and P. A. Karam, *J. Chromatography*, 1972, **71**, 347.

²⁰ W. G. Dauben and W. Todd Wipke, *Canad. J. Chem.*, 1967, **32**, 2976.

Preparative g.l.c. (Autoprep) on polyethylene glycol 400 or polyethyleneglycol adipate and/or distillation afforded fractions whose identities were further confirmed by i.r., n.m.r., and mass spectral analysis. High sensitivity or accumulated (CAT) ¹H n.m.r. spectra of combined hydrocarbon fractions showed peaks in the τ 9–10 region when cyclopropane derivatives were present,²⁰ and were identical with those of authentic specimens of bicyclo[3,1,0]hexane or bicyclo[4,1,0]heptane, prepared by a described method.²¹

Preparation and Decomposition of Tertiary Cycloalkyl Chloroformates.—(a) 1-Methylcyclohexyl chloroformate was prepared by a described method for t-alkyl esters,²² from carbonyl chloride (66.0 g, 0.66 mol) and the alkoxide derived from 1-methylcyclohexanol (22.8 g, 0.22 mol). The unstable chloroformate was characterized by i.r. spectroscopy ($\nu_{C=O}$ 1770 cm^{-1}) and allowed to decompose at 20 °C (4 h) when it gave 1-methylcyclohexyl chloride (11.7 g, 0.088 mol), 1-methylcyclohexene (4.2 g, 0.044 mol), and methylenecyclohexane (0.1 g, 0.001 mol) only.

(b) 1-Methylcyclopentyl chloroformate was similarly prepared from carbonyl chloride (50.0 g, 0.50 mol) and the alkoxide from 1-methylcyclopentanol (17.1 g, 0.17 mol). Decomposition at 20 °C (4 h) gave 1-methylcyclopentyl chloride (11.7 g, 0.99 mol) and 1-methylcyclopentene (4.3 g, 0.052 mol) only.

Investigation of Product Stability.—Separate batches (*ca.* 3 g) of cyclohexyl chloroformate were decomposed at 150–155 °C (35 h) in the presence of quantities (*ca.* 0.5 g) of each of the following: (a) 1-methylcyclohexene, (b) 3-methylcyclohexene, (c) methylenecyclohexane, (d) cycloheptene, (e) bicyclo[4,1,0]heptane, (f) 1-methylcyclohexyl chloride, (g) *trans*-2-methylcyclohexyl chloride, (h) cyclohexylmethyl chloride, (i) cycloheptyl chloride, and (j) bis(cyclohexylmethyl) carbonate. Compounds (b), (d), (e), (g), (h), (i), and (j) were unchanged. Compounds (a), (c), and (f) underwent varying degrees of interconversion as shown in Table 5. Bicyclo[4,1,0]heptane was not formed.

TABLE 5

Starting material	Product composition (%)		
	(a)	(c)	(f)
(a)	97.0	0.4	2.5
(c)	54.7	29.4	15.8
(f)	42.1	2.4	55.5

Similar conclusions with respect to the C_6 products were made by studying the variation in the relative amounts of the various products with time, during the decomposition of the C_6 chloroformates.

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